Creep and Damping Properties of Polystyrene*

J. A. SAUER, J. MARIN, AND C. C. HSIAO
Department of Engineering Mechanics, School of Engineering, The Pennsylvania State College, State College, Pennsylvania

The anelastic behavior of polystyrene has been studied by means of creep tests under long-time load application and by means of damping capacity tests under rapidly varying repeated loading. Tensile creep data taken at various stress amplitudes reveal that the log of the creep rate (at 1000 hours) varies linearly with the log of the stress amplitude. A similar type of variation is obtained when damping capacity or energy absorbed per cycle is plotted against stress amplitude. From these two sets of data, the creep rate is found to be proportional to the square of the damping capacity. It would thus appear possible, for polystyrene at least, to predict 1000-hour creep rates from short-time measurements of absorbed energy under dynamic loading conditions.

The data obtained from the creep and damping tests, together with additional data from short-time tension and compression tests, seem to be consistent with an internal structure in which the linear polymer chains and groups of chains are in ordered or partially extended positions, but in which, in the absence of stress, no preference is shown for any particular direction. Under the action of stress—particularly if the stress is maintained for a long period of time—a tendency exists for the ordered regions to orient in the direction of the applied stress. The so-called "crazing" condition which has been observed to occur in the creep specimens is probably a manifestation of this orientation. X-ray evidence appears to support this point of view.

INTRODUCTION

INVESTIGATIONS of anelastic properties of materials are of considerable interest, both because they supply data which are useful for design purposes and also because they shed considerable light on the internal or molecular structure of matter. For metals, this latter aspect has been stressed by Zener,[1] while the former aspect, in particular the importance of high values of damping capacity in reducing stress amplitude for materials subject to resonant vibrations, has been discussed by Foppl[2] and many others. The significance of dynamic modulus and damping capacity values of plastic materials from the engineering point of view has been pointed out by Lazan and Yorgiadis,[3] while many investigators (see Alfrey[4]) have considered the problem of creep, cold flow, or stress relaxation from both points of view.

In the present investigation, measurements are made of the creep and damping properties of stress-free specimens of a thermoplastic material. The measurements are made on fairly large-sized specimens cut directly from molded sheets and are carried out over a broad stress range with maximum stress values as close as possible to static yield strength. The design implications of the data are mentioned, but are considered more fully elsewhere.[5,6] The significance of the test data from the viewpoint of molecular structure is discussed at some length, and an attempt is made to correlate the results with evidence obtained from x-ray diffraction studies of the stressed and non-stressed specimens.

MATERIAL AND TEST SPECIMENS

The material used in this investigation, a grade of polystyrene known commercially as Lustrex, was selected because it could be produced without significant directional properties and because any residual stresses present after molding could be easily detected. The material was molded in the form of flat sheets 12 in. × 12 in., with a thickness dimension of $\frac{1}{2}$ in., $\frac{3}{4}$ in., or 1 in. All of the material was examined under polarized light before use, and sheets showing noticeable internal strains were discarded. The average molecular weight lay between 67,600 and 68,700.**

All test specimens were machined from the flat sheets and kept for at least 72 hours prior to testing in a controlled humidity and temperature room where the relative humidity was held at 50 percent ±2 percent and the temperature maintained at 77°F ± 2°F. The dimensions of the creep test specimens, the damping test specimens, and the specimens used for obtaining the tensile and compressive behavior under so-called static loading conditions, are shown in Fig. 1.

STRESS-STRAIN PROPERTIES IN TENSION AND COMPRESSION

In order to have available rather complete information on the mechanical properties of the par-

* Presented at the sixth meeting of the Division of High-Polymer Physics, American Physical Society, New York City, January 27–29, 1949.

[1] C. Zener, Tech. Pap. 1992, Metals Tech. (August 1946).

[2] O. Foppl, J. Iron and Steel Inst. **134**, 393 (1936).

[3] B. J. Lazan and A. Yorgiadis, Symposium on Plastics, ASTM (1944).

[4] T. Alfrey, Jr., *Mechanical Behavior of High Polymers* (Interscience Publishers, Inc., New York, 1948).

[5] J. Marin, Tech. Report No. 1, Cont. No. N6onr-269, Task Order 6, for Mechanics and Materials Branch, ONR (August 1948).

[6] J. A. Sauer, Tech. Report No. 2, Cont. No. N6onr-269, Task Order 6, for Mechanics and Materials Branch, ONR (January 1949).

** Data supplied by the Plastics Laboratory, Monsanto Chemical Company, Springfield, Mass.

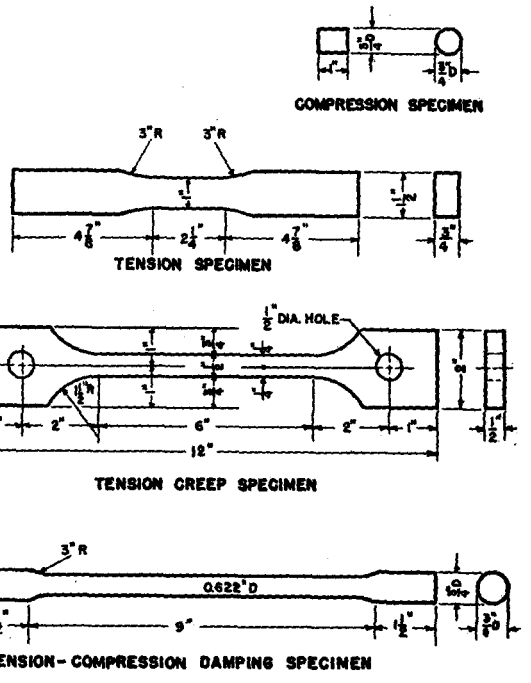


FIG. 1. Types of polystyrene specimens used for tension and compression control tests, tension creep tests, and tension-compression damping tests.

ticular grade of polystyrene selected for the creep and damping tests, it was decided to run rather complete control tests under single load application and at more or less normal testing speeds. At least five separate specimens were tested for each type of loading condition. The stress-strain curves for simple tensile loading are shown in Fig. 2 and for simple compressive loading in Fig. 3. The open circles represent test points and the crossed circles represent fracture.

The tension tests were run on samples proportioned in accordance with ASTM standards for their Type I specimen. Both the tension and compression tests were run on a 60,000-lb. capacity Baldwin Southwark Tate-Emergy hydraulic testing machine.*** Strains were recorded by attaching to the center of the specimen a Type A-1, SR-4 electrical strain gauge connected, in turn, to a standard SR-4 Type K portable strain indicator. In the compression tests, the strain gauge was not attached directly to the specimen, but to a specially designed π-gauge of $\frac{1}{4}$-in. gauge length. The rate of straining was controlled and kept constant throughout the duration of each compressive test, but in the tensile tests only the rate of head separation was kept constant, as it was not thought necessary to accurately control the strain in view of the nearly perfect elastic response of polystyrene to tensile loading.

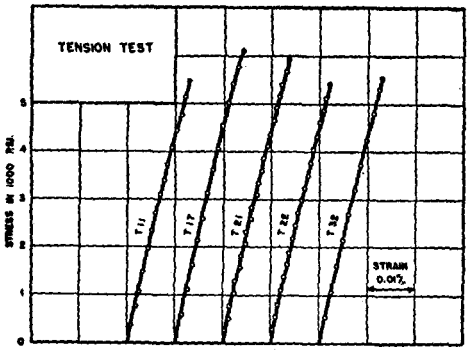


FIG. 2. Tensile stress-strain curves for five samples of polystyrene.

The average values of the significant mechanical properties are summarized in Table I.

It may be noted from this table and from the stress-strain curves of Figs. 2 and 3 that the response of polystyrene to compressive loading is considerably different from its response to tensile loading. Although the elastic modulus is the same, the elastic limit stress or yield strength is much higher in compression; and a comparison of the energy absorptions to yield shows that the material is very much tougher in compression.

It was not found possible to produce fracture under compressive stress. Continued increase of load simply further flattened the specimen until finally longitudinal cracks were produced in the center of the cylinder as a result of development of circumferential tensile stresses. In the specimens subject to tension, the fractured surfaces were amorphous in nature and always perpendicular to the longitudinal axis. The crack or start of failure appeared to originate in a small but visible circular region which usually adjoined the surface, which exhibited concentric circumferential rings, and which showed higher reflectivity than the remainder of the surface.

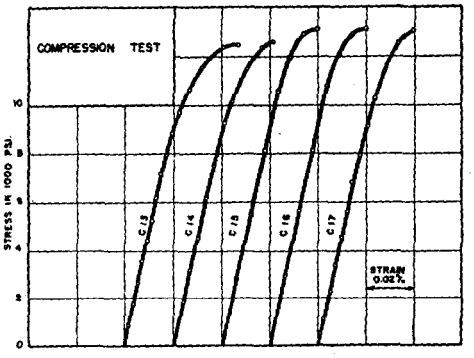


FIG. 3. Compression stress-strain curves for five samples of polystyrene.

*** One tension test and two compression tests were run on a 5000-lb. Dillon Testing Machine. The results were comparable to those obtained by use of the Baldwin Southwark Machine.

CREEP BEHAVIOR OF POLYSTYRENE

The creep tests were carried out on an apparatus (Fig. 4) which permitted nine specimens, all of which were subject to axial tension only, to be tested simultaneously. The entire apparatus was kept in a laboratory whose relative humidity was maintained at 50 percent±2 percent, and whose temperature was kept at 77°F±2°F. The details of the construction and operation of the creep tensile unit has been previously discussed by Marin.[5] The creep strains were measured to 0.00005 in. over a 5-in. gage length by means of a micrometer microscope stand shown in Fig. 4(b).

Each of the specimens was subject to a different stress value ranging from 1760 p.s.i. for the lowest, to 4060 p.s.i. for the highest. Strain readings were taken daily and the test continued for 1000 hours duration, or until the specimen fractured. The total deformation (elastic plus creep) is plotted as a function of time in Fig. 5. The diagram shows that the rate of increase of deformation with time gradually diminishes and appears to become approximately constant even before the 1000-hour period is reached. The values of these constant creep rates C_r are given in Table II for all specimens except those subject to the three highest stresses.

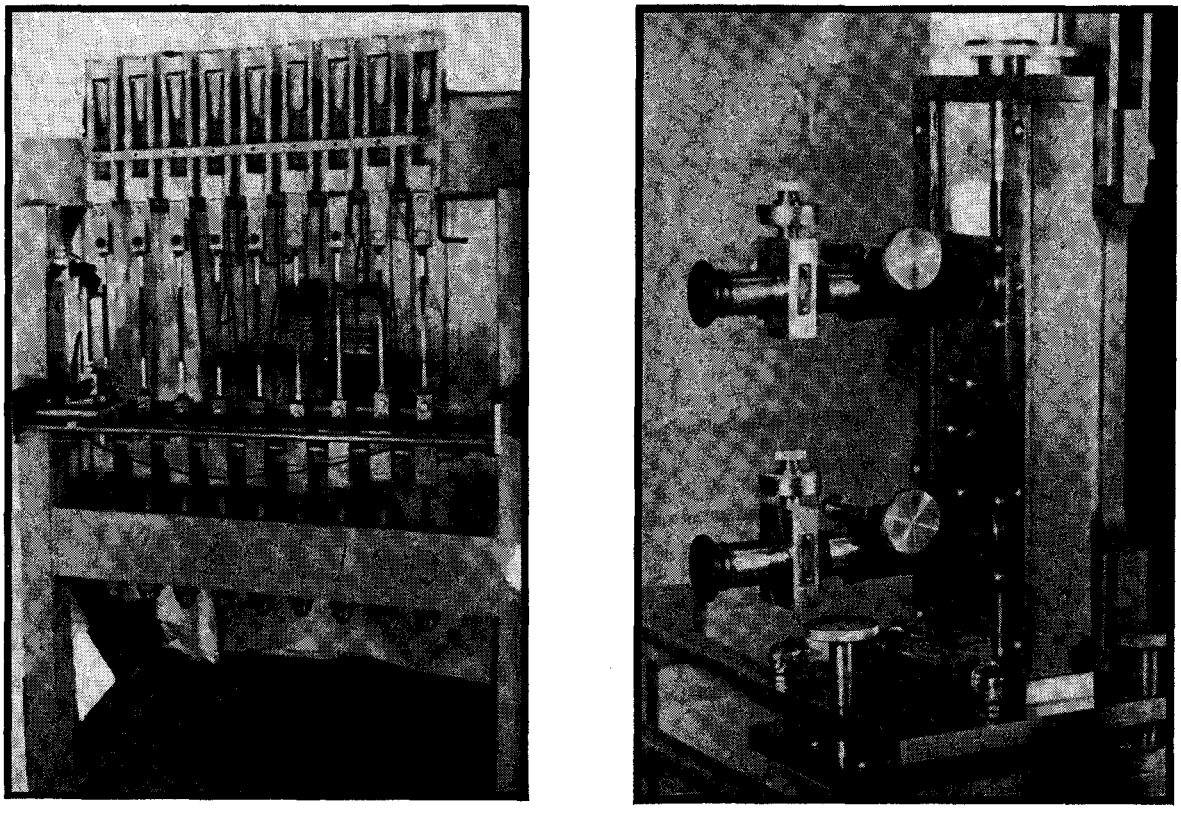
TABLE I. Mechanical properties of polystyrene (Lustrex).

Specific mechanical property	Value obtained from tension test	Value obtained from compression test
Modulus of elasticity (p.s.i.)	4.5×10^5	4.5×10^5
Yield strength (p.s.i.) (0.005 offset)	—	12,400
Fracture strength (p.s.i.)	5700	—
Ductility at fracture (%)	1.35	
Energy to yield (in. lb./cu. in.)	—	171
Energy to fracture (in. lb./cu. in.)	37.1	—

These were omitted as they fractured too early to obtain an accurate creep rate estimate.

The data of Table II show that both the creep and the creep rate increase with increasing stress. It is difficult to find an empirical relation to accurately fit these data, but it is found that the creep rate varies approximately linearly with the stress when the data are plotted on log-log paper (Fig. 6). The creep-rate stress relation may thus be written $C_r = Bs^n$, where B and n are experimental constants which take the values $B = 6.66\times10^{-22}$ and $n = 4.53$, and s is the applied tensile stress.

Discussion of the nature of the fracture under creep conditions and the phenomena of crazing that is associated with long duration of load application will be withheld until the results of the damping capacity tests have been summarized.



(a) (b)

FIG. 4. (a) Apparatus for obtaining tension creep data. (b) Micrometer microscope unit for measuring creep deformation.

TABLE II. Static tension creep test data for polystyrene (Lustrex).

Spec. No.	Area sq. in.	Load lb.	Stress p.s.i.	Creep rate in./in./hr. units of 10^{-7}	Creep at 1000 hr. in./in. units of 10^{-3}
1	0.250	857	3420	66	—
2	0.220	715	3250	60	—
3	0.264	830	3140	40	—
4	0.213	550	2580	22	9.3
5	0.390	988	2525	20	8.9
6	0.362	808	2240	10	7.2
7	0.363	629	1760	3	4.9

DAMPING BEHAVIOR OF POLYSTYRENE

The method used in the present investigation to measure damping capacity, i.e., the energy absorbed under cyclic stress, per cycle, per unit volume, is a resonant-vibration method originally developed by Lazan[7] and used later by Robertson and Yorgiadis.[8] It consists essentially of measuring the energy input of a centrifugal force mechanical oscillator rigidly attached to a single-degree-of-freedom spring-mass system. The experimental set-up is diagrammatically shown in Fig. 7. The specimen whose internal friction is desired acts as the spring, and the masses M_1 and M_2 are varied by addition or removal of the small masses m until the natural frequency of the longitudinal vibrations of the specimen-mass system is identical with the frequency of the oscillator.

The entire apparatus is mounted on hardened, smooth rollers so as to minimize the energy loss to the supports. The specimen is held in place by means of collet chucks attached to the two large masses M_1 and M_2. The condition of resonance is obtained by adding or subtracting small weights until there exists a 90° phase lag between the oscillator force and the longitudinal displacement. The actual phase lag is observed by stopping the vibratory motion at zero displacement and simultaneously observing, under the action of stroboscopic light of twice the oscillator frequency, the angle of the applied force.

The numerical value of the damping capacity is obtained from the measured value of the total displacement $(2a)$ and the amplitude of the oscillator force (F) by the use of the formula for the energy absorbed by a single-degree-of-freedom system operating at resonance, *viz.*,

$$\Delta W = \pi F a / AL.$$

Here ΔW is actually the energy input, but since

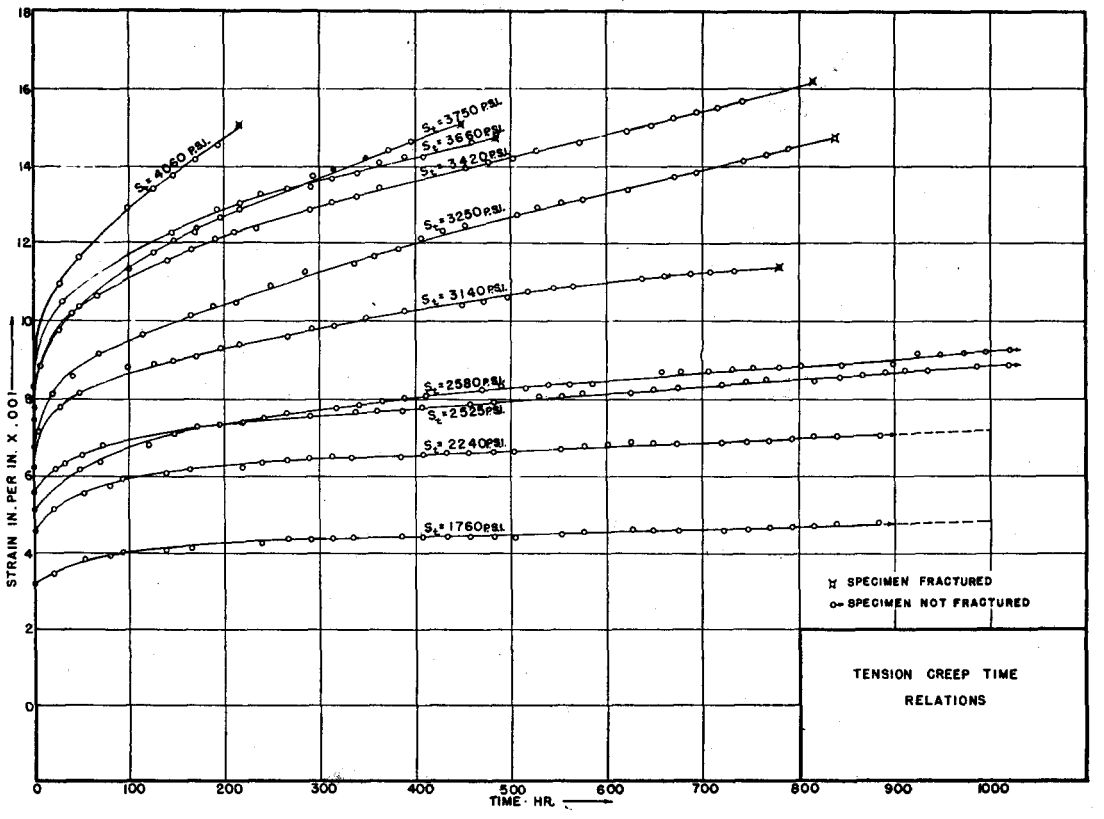


FIG. 5. Tensile creep curves at various stress levels.

[7] B. J. Lazan, Trans. A.S.M.E. 65, 87 (1943).
[8] J. M. Robertson and A. Yorgiadis, J. App. Mech., Trans. A.S.M.E. 68, A173 (1946).

heat losses to surroundings have been kept small, it may also be taken as the energy absorbed.[8] A is the cross-sectional area of the specimen, and L the length of the specimen. The magnitude of the maximum stress (σ) produced in the specimen by the oscillating force is

$$\sigma = M_2\omega^2 a/A,$$

where M_2 is the total mass on the right-hand side of the specimen in Fig. 7 and ω is the circular frequency of the oscillator.

For each specimen, readings of a and F were taken at a number of progressively increasing stress levels varying from 329 p.s.i. to 2105 p.s.i. Measurements at higher stresses were not made because of the danger of fatigue failure. Even at low stresses it is difficult to keep the specimen at constant temperature, since the absorbed energy appears as heat. Fortunately, however, the test data can be taken rather rapidly, and whenever the surface temperature rises more than two or three degrees the test can be discontinued until the specimen cools down.

The results of a typical test are shown in Table III. The damping capacity values from the last column, as well as for two other test specimens, are plotted as a function of stress amplitude in Fig. 8. The test points clearly follow a straight line trend on this plot, indicating that the relation between absorbed energy due to internal friction and stress amplitude is given by an equation of the form

$$\Delta W = C\sigma^n,$$

where C and n are constants which can be readily found from the data. The constant n is simply the slope of the damping capacity-stress amplitude curve on the log-log plot, and takes the value 2.3 for the data of Fig. 8.

Figure 9 indicates the good agreement obtained with previous results when additional measurements are made on the same specimen after completion of the tests at high stress amplitudes. This agreement would appear to indicate that no noticeable change in specimen properties has occurred. Whether the specimens stand one hour or twenty hours before being retested apparently makes little difference.

COMPARATIVE DAMPING QUALITIES OF POLYSTYRENE AND OTHER HIGH POLYMERS

In order to correlate experimental values of damping capacity with internal molecular structure, it seemed appropriate to determine values of internal friction for some other plastic materials. Additional tests were therefore made on several other thermoplastic materials and several thermosetting ones. The complete results, together with a more precise description of the different materials, is given elsewhere by Sauer.[6] For our purposes, it is sufficient to show the results for two other thermoplastic materials and four thermosetting phenolic laminates.

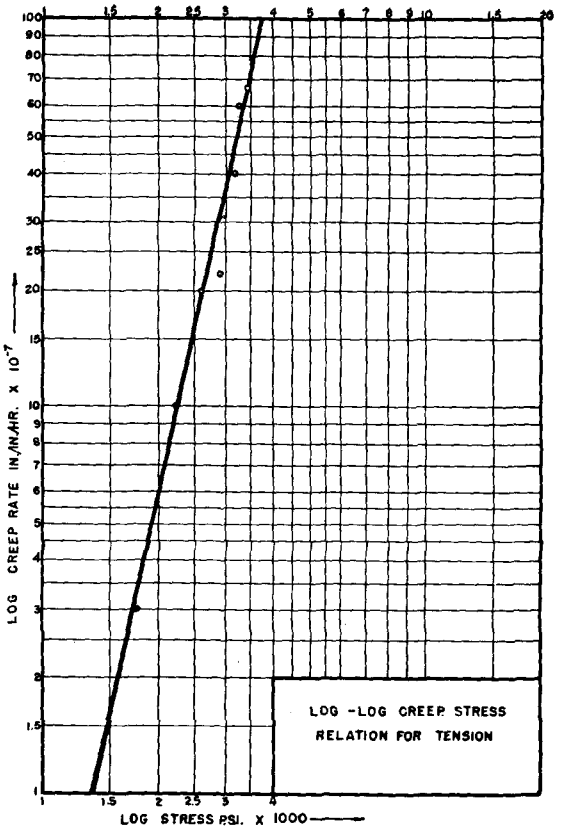


FIG. 6. Relation between tension creep rate and stress amplitude.

Table IV gives values of the experimentally determined dynamic modulus together with dimensional data, and Table V gives comparative values of the damping capacity at two different stress loads for both the Lustrex and the six other high polymers. The data illustrate the increase in damping capacity with increase of stress amplitude, and show also that the damping capacity of polystyrene is considerably below that of cellulose

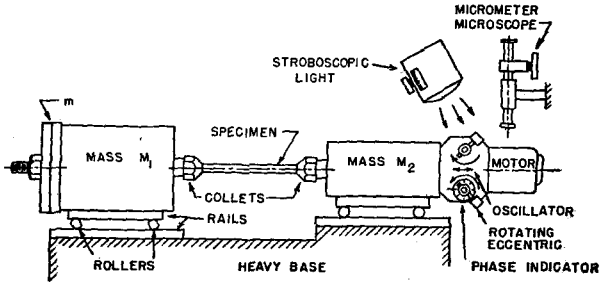


FIG. 7. Diagrammatic sketch of apparatus for measuring damping capacity.

TABLE III. Results of damping capacity measurements on polystyrene (Lustrex). (Specimen No. 10.)

Run No.	Amplitude of oscillator force (lb.)	Weights $W_1=M_1g$ (lb.)	Weights $W_2=M_2g$ (lb.)	W^* (lb.)	Amplitude a (in.)	Stress σ (p.s.i.)	Dynamic modulus E^{**} (p.s.i.)	Damping capacity ΔW in. lb. per cu. in.
1	1.63	660	390	245.2	0.00354	329	5.35×10^5	0.00654
2	2.44	656	390	244.5	0.00511	475	5.33×10^5	0.01412
3	3.26	651	390	243.7	0.00649	604	5.31×10^5	0.0239
4	5.18	645	390	243.0	0.00964	897	5.29×10^5	0.0565
5	6.80	640	390	242.3	0.01220	1135	5.28×10^5	0.0941
6	8.45	635	390	241.5	0.01456	1353	5.26×10^5	0.1392
7	11.86	628	390	240.5	0.01869	1740	5.24×10^5	0.251
8	15.25	623	390	239.5	0.02262	2105	5.22×10^5	0.391
9	1.63	645	390	243.0	0.00342	318	5.29×10^5	0.00632
10	3.26	645	390	243.0	0.00669	542	5.29×10^5	0.0212

Auxiliary data:
Oscillator frequency—26.6 c.p.s.
Phase angle ϕ—90°
Specimen length—9¼ in.
Specimen diameter—0.622 in.

Applicable formulas:
$$* W=\frac{W_1\cdot W_2}{W_1+W_2} \quad ** E=\frac{L}{A}\frac{\omega^2}{g}W$$

acetate and methyl methacrylate and more nearly comparable to that of the phenolic laminates than to the other thermoplastics.

The damping capacity increases with stress in approximately the same manner for each of the materials of Table V. This is clearly shown by the comparable slopes ($n=2.3\pm$) of the data shown on the log-log plot of Fig. 10 for four phenolic laminates.

The experimental data thus seem to lead, both from the more extensive investigations on Lustrex samples and also from the separate series of tests on other high polymers, to the conclusion that the energy absorbed per cycle varies approximately as the 2.3 power of the maximum stress amplitude. This seems to differ with the conclusion of Robertson and Yorgiadis[8] that for all materials internal friction varies as the third power of the stress amplitude. However, only one of their test materials was similar to ours (Lucite) and for this material their reported data show considerable scatter, so much in fact that a 2.3-power law would appear to give just as good agreement with their data as a third-power law.

With the exception of methyl methacrylate, Table IV and Table V indicate that plastic materials of higher dynamic modulus exhibit, in general, lower energy absorption under dynamic loading. A similar trend has been previously reported by Robertson and Yorgiadis.[8]

CORRELATION OF CREEP AND DAMPING BEHAVIOR

Since both creep and damping are manifestations of anelasticity, it is appropriate to seek a correlation between measurements of the two quantities. In this investigation, both creep rate and damping capacity have been determined for polystyrene specimens subject to various values of stress amplitude. Both these quantities were found to vary as a power law of the stress amplitude, although the stress itself is constant in the creep tests and rapidly alternating from maximum tension to maximum compression in the damping tests. If, for a given stress amplitude, one plots the (1000-hour) creep rate as a function of damping capacity, one gets a straight line on a log-log plot (Fig. 11) having a slope of approximately 2. Thus, there appears to be a relation between creep rate and damping capacity of the form $C_r=K(\Delta W)^2$ where K is a constant.

This interrelationship of creep rate and damping capacity is significant from two points of view.

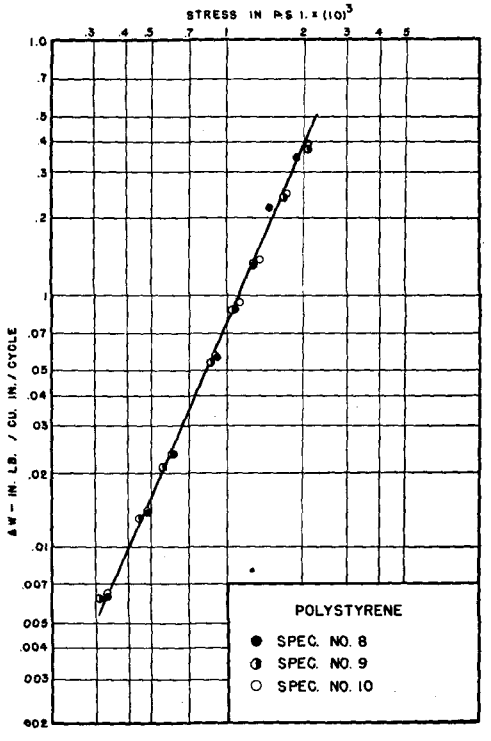


FIG. 8. Relation between damping capacity and stress amplitude.

First of all, if it is found that a similar relationship holds for other materials as well as for polystyrene, it should be possible to obtain knowledge of the deformation-time properties of any given substance by simply making damping capacity measurements at various stress amplitudes. Since damping capacity tests are relatively simple to run, and since measurements of damping capacity at various stress amplitudes can be obtained in a short period of time and from but a single specimen, this procedure would result in a considerable saving of time and effort.

Aside from this important practical consideration of the relationship between creep and damping capacity, the data would seem to imply that the same molecular mechanism must be responsible for both types of behavior. We shall first consider the bearing of the damping test data on molecular structure and then will consider the bearing of the creep data and of the "crazing" aspects of the creep measurements.

STRUCTURE OF HIGH POLYMERS AND DAMPING BEHAVIOR

The anelastic or viscoelastic properties of polystyrene and other high polymers have been considered from the point of view of molecular structure by a number of investigators.[4, 9–11] Linear

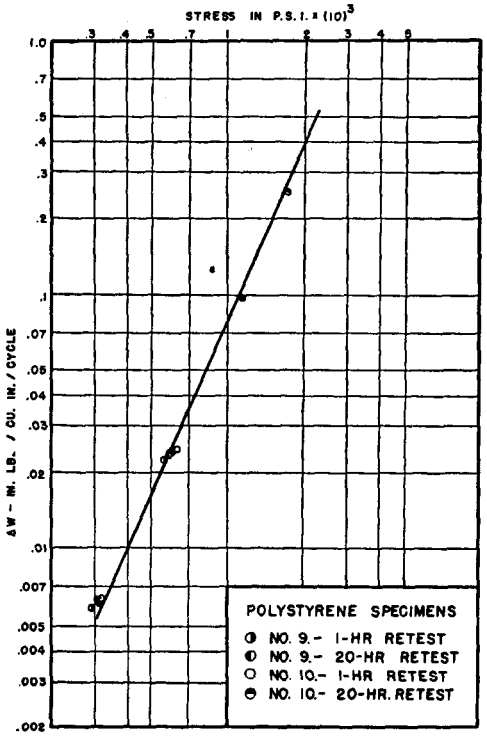


FIG. 9. Damping capacity data taken after one-hour and twenty-hour rest periods.

[9] H. Mark, Ind. Eng. Chem. 34, 449 (1942).
[10] A. Tobolsky and H. Eyring, J. Chem. Phys. 11, 125 (1943).
[11] T. Alfrey, Jr., J. Chem. Phys. 9, 374 (1944).

TABLE IV. Type of specimen and value of dynamic modulus for various high polymers.

Type of plastic	Cross-sectional dimensions (in in.)	Length of specimen L (in.)	Freq. of oscillation (c.p.s.)	Dynamic modulus E (10^5 p.s.i.)
Thermoplastic materials				
Cellulose acetate (FM6)	0.500 round	7.31	18.0	2.7
Methyl methacrylate (Plexiglas)	0.749 round	6.25	37.5	6.1
Polystyrene (Lustrex)	0.622 round	9.12	26.6	5.3
Thermosetting laminates				
Army duck base	0.513×0.500	9.00	37.5	13.3
Paper base (Grade XX)	0.500 round	8.00	37.5	14.3
Rayon base	0.508×0.615	7.50	60.0	17.2
Paper base (high strength)	0.502×0.508	8.94	60.0	33.1

Note: Dynamic modulus calculated on basis of length of specimen between grips (L).

polymers, of which natural rubber is an example, are generally considered to consist of long-chain molecules which, when unstressed, are in random curled positions because of the greater statistical probability of these configurations over extended ones. Under the action of stress, the entire system tends to straighten. This applies to local kinks, intermediate curls, and long range conformations. The rapidity with which each of these units can respond to stress is, however, quite different and depends on the nature of its environment. The local kinks will respond fastest to stress and the long range conformations slowest; there will thus be an elastic and a non-elastic response to applied stress.[4]

In the case of polystyrene, the non-elastic response is not due to any relaxation of primary bonds as, first of all, there are few, if any, primary bonds across chains and, secondly, the relaxation time of primary bonds would probably be quite high. Secondary bonds across chains are by comparison weaker, and slipping of chains or chain segments past one another is one possible mechanism contributing to creep, hysteresis, and internal friction. The mechanical properties are affected, however, not only by the intramolecular forces but also by geometric factors such as mechanical hindrances due to existence of bulky side groups or side chains. In polystyrene, the phenyl group prevents close fitting of chains and thus, the attractive power of the polymer per unit of chain length is reduced from that calculated by Mark[9] based on most efficient packing. Since, in general, internal friction is reported to be greater when the chains are well packed,[10] a reduction of attractive power (specific molar cohesion) should thereby decrease the damping capacity. This would appear to account for the comparatively low value of the damping capacity of polystyrene compared to that of cellulose acetate as shown by the data of Table V.

TABLE V. Comparative values of damping capacity of several thermoplastic materials and several thermosetting materials.

Type of plastic	Values of damping capacity (ΔW) (in. lb./cu. in./cycle) at $\sigma = 500$ p.s.i.	at $\sigma = 1000$ p.s.i.
Thermoplastic		
Cellulose acetate (FM6)	0.156	0.670
Methyl methacrylate (Plexiglas)	0.0882	0.430
Polystyrene (Lustrex)	0.0159	0.0782
Thermosetting phenolic laminates		
Army duck base	0.0129	0.0612
Paper base (Grade XX)	0.0108	0.0534
Rayon base	0.0085	0.0381
Paper base (high strength)	0.00324	0.0153

The still lower value for the thermosetting plastics is accounted for by the fact that they are three-dimensional polymers with primary cross linking and hence are more elastic and less inelastic in their response to load.

CRAZING EFFECTS IN POLYSTYRENE

One of the most striking manifestations of the anelastic behavior of polystyrene, observed particularly in the creep-time tests, was a tendency for the original transparent material to "craze." By crazing we simply imply a clouding or blushing of the originally transparent material which causes some of the light striking the material to be reflected instead of transmitted. Crazing occurs in methyl methacrylate as well as polystyrene and has been reported in the literature to be caused by solvent action as well as by applied stress. Crazing is frequently associated with mechanical cracks, and our tests show that even before fracture occurs crazing marks are sometimes evident at various points on the specimen where stress concentration occurs, such as at regions where the specimen changes its cross-sectional dimensions or at points of concentrated load application. Our observations of this phenomena may be summarized as follows:

(1) Crazing nearly always starts on the surface of the test specimen and works inward toward the center. Though more striking in long-time tests, some crazing seems even to occur in the short-time stress-strain tests. As noted previously, a small circular reflective area is sometimes visible on the otherwise amorphous fractured surfaces of the test pieces. This condition appears to generally occur when a noticeable defect or inhomogeneity is present.

(2) The amount of cross-sectional area of the specimen which crazes appears to be a function of both time of application of load and magnitude of applied tensile stress. For a given time, crazing increases with stress amplitude, and for a given stress, crazing increases with increase of time of load application. Maxwell and Rahm,[12] from measurements of reflected light intensity, report a similar behavior.

(3) Crazing seems to occur both on surfaces which have been machined and surfaces which have been cast without showing any preference for one over the other. In the tensile specimens, it seems also to occur uniformly along the longitudinal axis of the specimen.

(4) In some specimens in which the load remained on the specimen for a fairly long period of time (of the order of 1000 hours) the entire cross-sectional surface of the specimen crazed, but the specimen did not fracture.

(5) Fractured surfaces usually show definite evidences of cracks which appear to grow radially outward from the center of the disturbance, which itself may or may not be on the surface. The center of the cross section of many of the fractured specimens shows an amorphous region similar to that for the unstressed specimens.

(6) Crazing has been found to occur at low stresses and low strains (<0.5 percent elongation for 1000-hour tests) and also has been observed *not* to occur at high stresses and high strains (>1.3 percent) for rapid load application.

(7) Whenever cracks are noticeably present on the crazed surfaces, i.e., when the surface is the actual fracture surface and not a surface which has been cut from the stressed specimen, they occur on planes at right angles to the maximum principal stress direction.

(8) If sections of the specimen showing crazed regions along the edges are cut off and placed under high compressive loading, most of the crazing or cloudiness disappears.

Some of the manifestations mentioned above can be clearly seen in the photographs of Figs. 12 and 13, which depict specimens subject, respectively, to simple tensile creep and pure bending creep. These photographs reveal the highly reflective area which is usually found for a short distance all around the surface of the specimen and also the amorphous center area. They clearly show that the crazing cracks are at right angles to the direction of the maximum principal tensile stress.

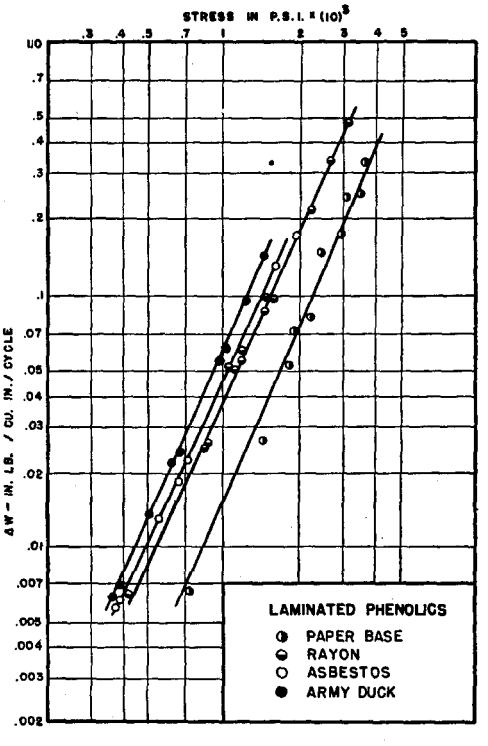


FIG. 10. Damping capacity *vs.* stress amplitude for four phenolic laminates.

[12] B. Maxwell and L. F. Rahm, Tech. Report 11B, Plastics Laboratory, Princeton University, Princeton, New Jersey (September, 1948).

In the case of the sample subject to bending, there is no evidence of crazing on the compression side of the specimen, while crazing is very apparent on the surface edges and for some distance inward on the tensile side of the specimen. Somewhat similar observations have been reported by Maxwell and Rahm,[12] Russell,[13] and others.

CURRENT THEORIES OF CRAZING

Several groups of investigators have studied the phenomena of crazing, have made measurements of crazing by recording the amount of reflected light, and have proposed certain theories to account for its occurrence. According to Maxwell and Rahm,[12] crazing is considered to be a system of very fine mechanical cracks which occur whenever the local deformation of the specimen exceeds a certain critical amount. This critical amount for clean, thermal stress-free samples of the polystyrene material which they tested was reported to be 0.75 percent. If their theory is correct, a clean stress-free specimen subject to tension should show no visible crazing until the local elongation exceeds their critical figure. It is difficult to see, however, why crazing should then occur only on the surface and not in the center, especially since the local elongation is approximately constant over the entire cross-sectional area. Also, in some of the short time stress-strain tests, the specimens were loaded until failure occurred at an elongation of about 1.4 percent and again no visible crazing was evident. It is, of course, quite conceivable that some crazing is present, but the amount is so small that it can be ascertained only by a sensitive light measuring method. Our tests also show that if the load is applied for a long period of time (several hundred hours or so), crazing will become evident at much lower strains than 0.75 percent. Maxwell and Rahm[12] believe this behavior to be due to contamination from the air. It is hoped that further tests under controlled atmospheres will clarify this point, but thus far our tests indicate that crazing is markedly dependent on the time of load application as well as on the stress or strain magnitude.

Some studies on the crazing of methyl methacrylate have been reported by Russell.[13] He noted that crazing cracks seem to be similar in nature whether caused by stress or by solvent action. He assumed that the crazing was produced by the same processes as are involved in normal tensile failure, and that the crazing condition occurs first on the surface because of the presence there of non-uniform randomly-directed residual stresses, which arise as a result of shrinkage due to non-uniform temperature conditions occurring in the casting

[13] E. W. Russell, Report No. Chem. 447, Part III, Royal Aircraft Establishment, Farnborough, England (August 1948).

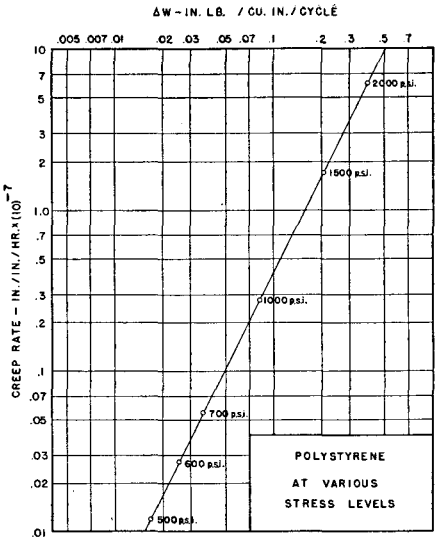


FIG. 11. Relation between creep rate and damping capacity for polystyrene.

process. This theory does not appear to be sufficiently adequate to explain our experimental results, *viz.*, that crazing can and does occur even when no appreciable residual stresses are present in the specimens. The presence or absence of residual stresses is determined by polariscope examination of all sheets from which the specimens are cut. Those showing any evidence of internal stresses are discarded. Furthermore, if any residual stress pattern should be present, it would be altered by the machining operation; yet, both the newly machined and the molded surfaces show identical crazing effects.

INTERPRETATION OF DATA IN TERMS OF MOLECULAR STRUCTURE

The results of the stress-strain studies, the creep studies, and the damping studies reported herein

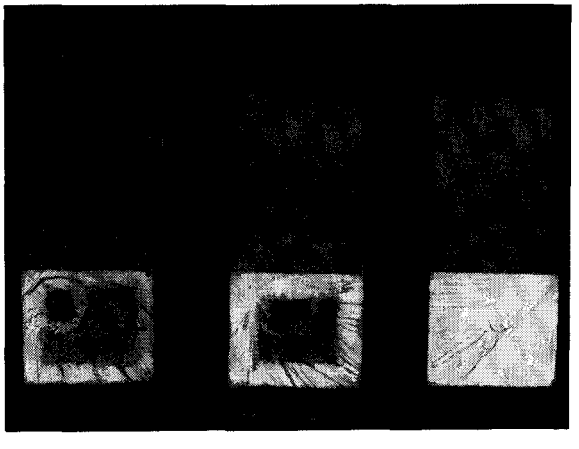


FIG. 12. Fractured surfaces of polystyrene tension creep specimens.

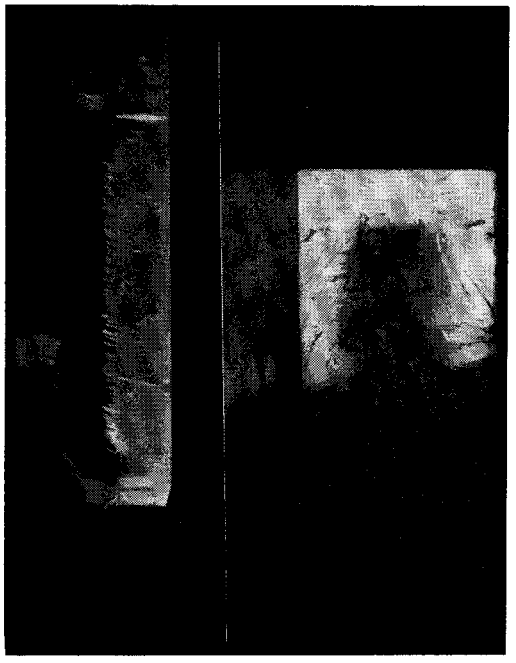


FIG. 13. Fractured surfaces of polystyrene bending creep specimens.

all seem to reveal that the molecular structure of polystyrene must, of necessity, be considerably different, at least at 20°C, from that of other linear super polymers such as synthetic or natural rubbers. First of all, the damping capacity data indicate that polystyrene, despite the absence of primary cross bonds, acts more in the fashion of the the three-dimensional cross-linked thermosetting materials than it does in the manner of the other thermoplastics. Secondly, the total elongation to failure under simple tensile loading is quite small—of the order of 1.4 percent at room temperatures as compared to about 50 percent for cellulose acetate. Thirdly, the material is found to creep under load at low stress values and to show crazing even at low elongations.

All this would seem to indicate that the structure of polystyrene below its second-order transition temperature does not consist of miscellaneous polymer chains that are predominately in the curled-up state. The data would appear rather to be more compatible with a polymer structure in which groups of polymer chains were in more or less ordered or partially extended positions, but the various groups or bundles themselves randomly orientated. In the usual Guth-James theory of rubber-like elasticity, the energy of all configurations is assumed to be alike, and hence, the curled-up state is considered the most likely one simply because of the greater number of ways in which this state can be statistically realized. There is no *a priori* reason why this condition should exist and is most unlikely in polystyrene, for example, in view of its observed mechanical behavior. The most probable state of the system as a whole may well be one in which various polymer chains are in ordered or partially extended positions if energy and stearic considerations as well as entropy ones are taken into account in the analysis.

The difference in behavior under tension and compression loading noted previously would appear to fit with the suggested picture of the polystyrene structure. Under fairly rapid tensile loading, very little additional elongation would be required before some of the already extended chains were stretched to their ultimate extensibility and the applied stress brought to bear on the primary bonds themselves. Under compressive loading, on the other hand, some secondary bonds might be broken and some chain slipping permitted, but no primary bonds would be separated, and hence, the deformation could become quite appreciable before any evidence of failure was observed.

In the tensile creep tests, as load is applied and maintained, some time dependent slipping will occur between chains and groups of chains, due to breakdown of secondary bonds. At the same time, there will be some general orientation of the polymer chains in the direction of the applied stress, although the tendency to orient will probably be restricted by the force field of the surrounding molecular chains and by mechanical hindrances. The longer the duration of load application, the greater will be the amount of orientation. It is

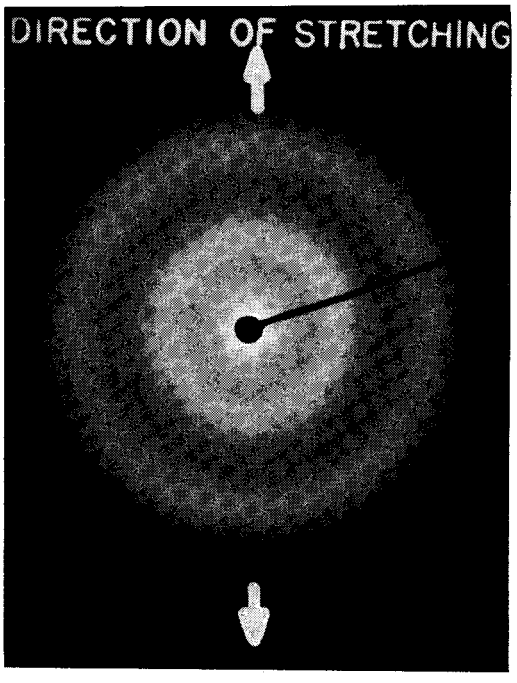


FIG. 14. X-ray diffraction pattern of polystyrene specimens.

possible that orientation will begin on the surface where the restrictive forces of the nieghboring polymer chains are perhaps somewhat less, because of the free air surface, than those acting on internal polymer molecules. Oxygen or moisture absorption may also play a part in reducing the value of these restraining molecular forces (and thereby permitting greater orientation), but sufficient experimental data has not yet been accumulated to decide this point.

If this view is correct, then crazing is a manifestation of orientation and the essential difference between the structure of noncrazed and crazed material is that in the first instance all the ordered regions or chain groups are randomly directed, while in the second instance the ordered regions show a preferred orientation in the direction of stretch. Additional evidence in support of this point of view arises from study of x-ray diffraction patterns taken on sections cut from the polystyrene creep specimens. Both the crazed and noncrazed regions of a specimen such as that shown in Fig. 12 were examined under Copper K radiation with the following results:

(1) The non-crazed regions showed a well defined uniform ring pattern. According to Fankuchen and Mark[14] this is indicative of random orientation of ordered regions or "crystallites" which are responsible for the scattering and in which the polymer chains show a high degree of local order.

(2) Transmission pictures taken on the crazed regions of the specimen with the x-ray beam perpendicular to the direction of stretching reveal a somewhat similar ring pattern with (to the eye) apparently comparable intensities. Figure 14 shows a typical x-ray pattern obtained under these conditions. Similar pictures have been obtained by Katz[15] who shows that the outside ring appears in x-ray pictures of the styrene monomer but the inside ring does not.

(3) However, photometer intensity curves of the crazed regions recorded by use of an x-ray spectrometer (Fig. 15) reveal that variations of diffracted ring intensity do occur (especially for the intense inner ring of Fig. 14) for different directions of the axis of rotation relative to the direction of stretching. This difference of intensity in the directions parallel and perpendicular to the applied stress is a definite indication of the existence of orientation. The photometer graphs also seem to show that the peak intensity of the inner ring shifts slightly inward toward the center as we pass from the parallel to the perpendicular direction. This would indicate an increase in some characteristic spacing caused probably by the same forces that produce the orientation tendency.

[14] I. Fankuchen and H. Mark, *Currents in Biochemical Research* (Interscience Publishers, Inc., New York, 1946), p. 439.

[15] J. R. Katz, Trans. Faraday Soc. **32**, 77 (1936).

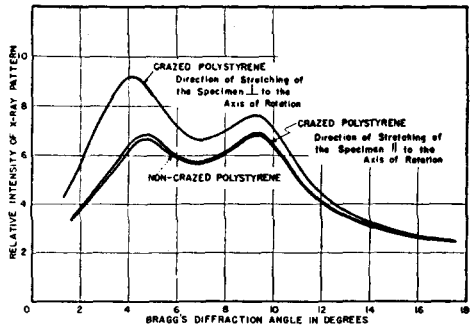


FIG. 15. X-ray spectrometer curves of crazed and non-crazed sections of polystyrene tension creep specimens.

The x-ray diffraction results thus appear to confirm the concept of the structure of polystyrene already discussed. The existence of the somewhat diffuse but nevertheless well defined rings in the immediate neighborhood of the incident beam indicates that geometrically ordered regions do exist in the otherwise amorphous structure and that within these regions there must be some periodic sequence of fairly well defined spacings. Furthermore, the results obtained on the crazed specimens by use of the x-ray spectrometer indicate the close tie-in between crazing and orientation and lend confirmation to the theory that crazing is essentially an orientation phenomena and not a mechanical crack phenomena, although it may be associated with cracks if the applied stresses are high enough to produce local or complete fracture.

It is hoped that more complete studies will permit the determination of the relative proportion of ordered or orientated regions to amorphous regions; will provide accurate quantitative values of the molecular or chain spacings; and will also shed more light on the effect of the surrounding atmosphere in the development of the crazing or orientated condition.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge our gratitude to the ONR and to the Mechanics and Materials Branch. Without their assistance and cooperation this project could not have been undertaken. We are indebted to Messrs. G. Cuff, D. Lemmon, W. Oliphant, and B. Black for assistance in obtaining the experimental data. Our thanks go also to Drs. E. Saibel and J. M. Robertson for advice and counsel, and to the Monsanto Chemical Company and Mr. H. Adams, in particular, for supplying us with the test material.