

## Delayed Yielding of Epoxy Resin. II. Behavior Under Constant Stress

ORI ISHAI,\* *Department of Mechanics, Technion, Israel Institute of  
Technology, Haifa, Israel*

### Synopsis

Creep tests were carried out on epoxy resin specimens at room temperature and at different high stress levels under tension, compression, and flexure. Compared with the behavior at constant strain rate (CSR) reported in Part I of this work, creep strain-time curves revealed a distinct delayed yielding region of constant minimum rate (secondary creep) followed by a post-yielding region of increasing slope (tertiary creep). In all cases, results indicate linearity between creep stress and log secondary creep rate, which is almost coincident with the corresponding relationship between yield stress and strain rate obtained in subsequent CSR loading cycles with the same specimens. The similarity in behavior under both the creep and CSR modes conforms to Eyring's theory of non-Newtonian viscous flow at high stress levels and low temperature. Theoretical analysis yields reasonable values of the activation volume, which is unaffected by the loading and test modes or by loading history, and could thus be regarded as an intrinsic parameter of the microstructure, inherently related to the viscoplastic process involved. The above considerations indicate a deviatoric stress-biased diffusional mechanism as the predominant factor in the yielding of an amorphous glassy epoxy system.

### INTRODUCTION

Part I of the present work<sup>1</sup> dealt with the yielding characteristics of ductile epoxy specimens loaded at constant strain rate (CSR), from which a clear relationship between yield stress and strain rate, in agreement with Eyring's theory of non-Newtonian viscous flow, was established. It is assumed that the same fundamental laws are valid for other test modes, by which the same material parameters could be derived.

Creep of glassy polymers at low stress levels was widely investigated and reviewed.<sup>2-4</sup> Their behavior was found, in most cases, to be governed by linear viscoelastic laws. Creep tests of glassy polystyrene<sup>5,6</sup> reveal predominantly anelastic characteristics. The nonlinear time-behavior of glassy polymers at high stress levels was reviewed and discussed by Ferry,<sup>7</sup> Bueche,<sup>8</sup> Rosen,<sup>8a</sup> Ward,<sup>9</sup> and Vincent,<sup>10</sup> mainly based on creep and CSR data for PMMA and polystyrene given by Sauer,<sup>5</sup> Findley,<sup>11,12</sup> and others. Analogy between macrocreep behavior of glassy polymers under high stresses and that of metals at high temperature was recognized by Sully,<sup>13</sup>

\* Present address: Material Research Laboratory, Washington University, St. Louis, Missouri.

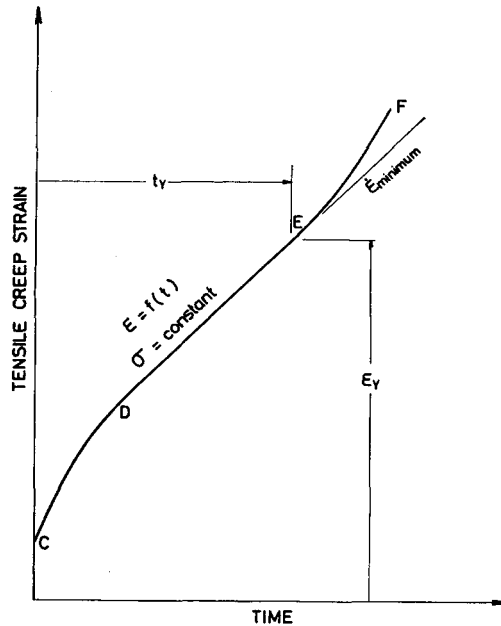


Fig. 1. Typical creep curve at high stress level.

based on Chasman's experimental work<sup>14</sup> on methyl methacrylate and cellulose acetate specimens loaded for more than 1000 hr. at room temperature. Additional data and discussion by Bueche,<sup>3b</sup> Landel,<sup>15</sup> and Rosen<sup>8b</sup> deal with creep-fracture phenomena, and are mainly concerned with the delayed-failure mechanism and the respective ultimate stress-time relationship which is of primarily engineering importance.

Much less attention has been paid to the creep behavior of ductile glassy polymers under high stresses. Study of the cold-drawing mechanism of polystyrene<sup>16</sup> and nylon 66<sup>17,18</sup> under dead load revealed a distinct "delayed yielding" region analogous to that usually observed at constant strain rate.

Three main regions are usually distinguished in such creep curves (Fig. 1): (1) primary creep (C-D), decreasing slope with predominantly anelastic characteristics; (2) secondary creep (D-E), minimum constant slope with predominantly viscous characteristics; (3) tertiary creep (E-F), increasing slope, terminating in fracture in the case of brittle-ductile characteristics, but tending to stabilization and showing a decrease in strain rate with time in the case of cold-drawing characteristics.<sup>16,17</sup>

The analogy between creep and CSR behavior in the case of ductile polymers can be demonstrated by comparing the two following functions:\*  $\sigma = f(\epsilon)$  for CSR and  $\dot{\epsilon} = f(\epsilon)$  for creep.

These relationships are given for the same material, the first representing

\* A similar analogy may be found between  $\sigma = f(t)$  for CSR and  $\dot{\epsilon} = f(t)$  for creep.

TABLE I

Region	CSR loading [ $\sigma = f(\epsilon); \dot{\epsilon} = \text{const.}$ ]	Creep [ $\dot{\epsilon} = f(\sigma); \sigma = \text{const.}$ ]
C-D C'-D'	Pre-yielding $\partial\sigma/\partial\epsilon > 0$	Primary creep $\partial\dot{\epsilon}/\partial\sigma < 0$
D-E D'-E'	Yield plateau $d\sigma = 0$ $\sigma = \sigma_{\text{max}}$	Secondary creep $d\dot{\epsilon} = 0$ $\dot{\epsilon} = \dot{\epsilon}_{\text{min}}$
E-F E'-F'	Post-yielding $\partial\sigma/\partial\epsilon < 0$	Tertiary creep $\partial\dot{\epsilon}/\partial\sigma > 0$

its stress-strain curve and the second obtained from its creep curve at a constant stress level, i.e., that of the yield stress of the first curve. The constant strain rate of the first curve thus equals the minimum rate of the creep curve.

The three regions, defined above for the creep and CSR test modes in Part I,<sup>1</sup> can now be compared from the viewpoint of this analogy as follows shown in Table I.

If the analogy described in Table I actually exists, the  $\sigma$ - $\dot{\epsilon}$  relationship at the yield level must be identical for both the creep and CSR modes, and secondary creep must be merely another manifestation of the yield plateau.

Hence, yield time and yield strain have, in the case of creep, the same physical significance according to their definition in Part I,<sup>1</sup> namely, they represent the values of time and strain at the onset of instability, at which the creep strain rate increases (Fig. 2).

Creep tests were carried out in Part II of this work, mainly with a view to examining the validity of the above analogy and to applying its physical significance for further development of the viscoplastic hypothesis postulated in Part I.<sup>1</sup>

## EXPERIMENTAL

### Preparation of Specimens

A cold-setting mix (1:1) of Versamide 140 and Epicote 815 was used as in Part I. The same curing conditions were applied, and the same types of specimens prepared according to the three modes of loading, namely: 7/12/120 mm. bars for tension, 18/36 mm. cylinders for compression, and 20/16/130 (80 mm. span) and 20/16/400 (320 mm. span) beams for flexure.

### Test Procedure

Tests were again conducted at an almost constant temperature level of  $26 \pm 1^\circ\text{C}$ . To minimize scatter, all specimens of each group were first

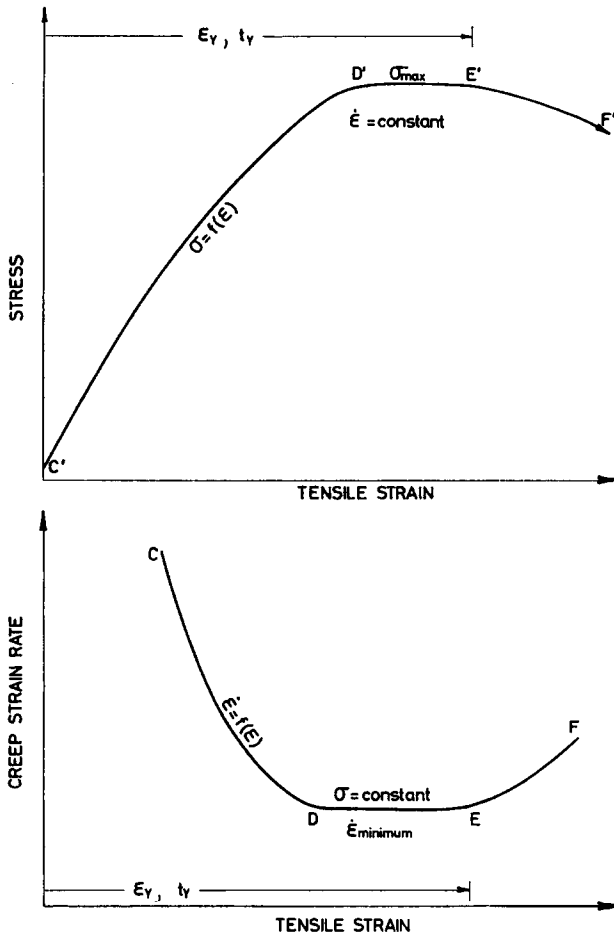


Fig. 2. Comparison of the typical modes of behavior at constant strain rate  $\sigma = f(\epsilon)$  and constant stress level  $\dot{\epsilon} = f(\sigma)$ .

subjected to a CSR loading cycle at the same rate up to yield, thereby permitting exclusion of specimens showing high deviation from the average yield value. In the second CSR cycle, the strain rate was varied, and yield values were determined for each rate. The third cycle was the creep test. Specimens were loaded up to a chosen level (maintained throughout the test), and deformations recorded with time. Eight different load levels were chosen for each mode of loading, in the range of high yield stresses obtained in the previous CSR cycle. The creep test terminated where a marked increase in slope was detected in the tertiary region. In the fourth cycle, the same specimens were subjected to an additional CSR run up to yield.

The effect of stress relief was examined on tensile specimens by application of heat treatment (80°C., 2 hr.), following the CSR cycle and prior to the creep test. The findings of Part I<sup>1</sup> have shown that each loading cycle

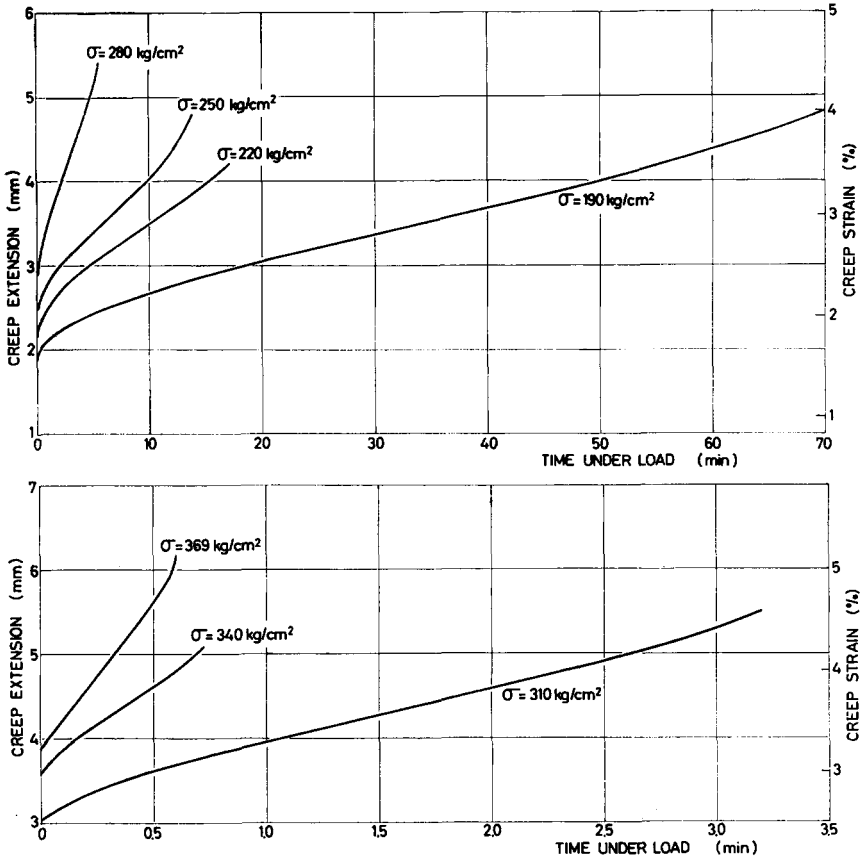


Fig. 3. Tensile creep curves at different high stress levels.

resulted in a lower yield level in the subsequent one. It was concluded, however, that the constant slope of the yield stress versus log strain rate relationship (the major characteristic parameter involved) is unaffected by loading history. Use of the same specimens in both the CSR and creep test modes has an important advantage and is justified when the main object is a characteristic of the material common to all modes.

An additional creep test was run on the longer (320 mm.) beams by loading in flexure at four different dead-load levels at midpoint for 1 hr., followed by unloading. Midpoint deflections were measured by means of mechanical dial gages (reading up to  $10^{-4}$  in.) during creep and creep recovery. The main object of this series was investigation of the creep behavior at low stress levels within the linear viscoelastic range.

### TEST RESULTS AND DISCUSSION

Creep curves reveal the common trends described in Figure 1 under the three modes of loading (Figs. 3-5), namely, a short region of decreasing

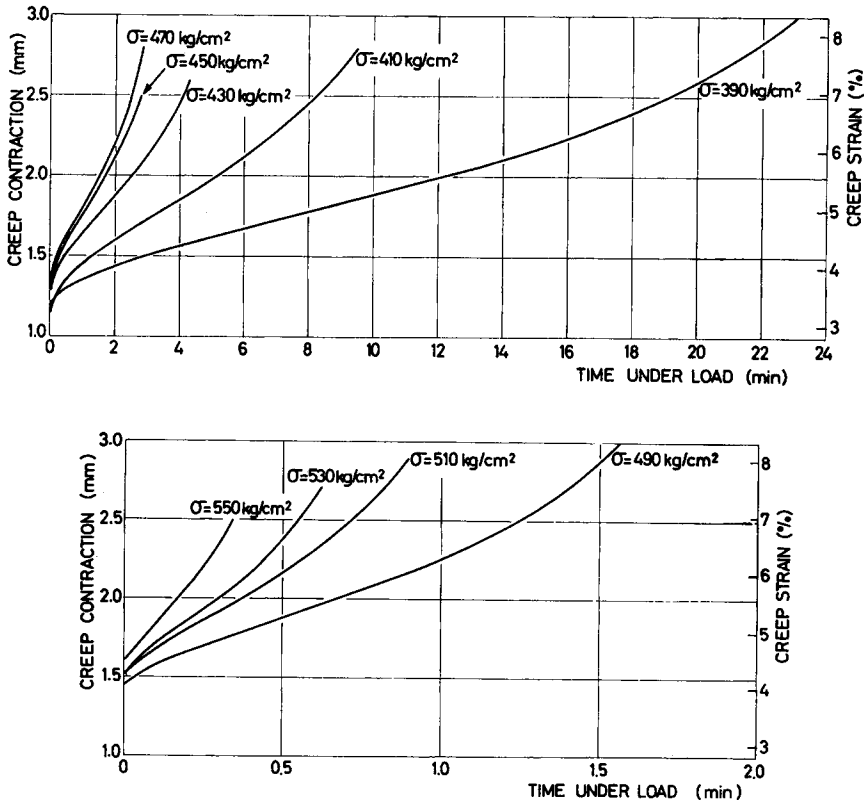


Fig. 4. Compressive creep curves at different high stress levels.

strain rate and a longer region of constant minimum rate, followed by one of increasing slope. In most cases unloading took place when tertiary creep set in. Where the creep test had been continued, necking was detected in the post-yielding stage, and in extreme cases tensile specimens underwent brittle-ductile fracture shortly afterwards.

The minimum strain rate was derived from the slope of the linear region (secondary creep), whose terminal point represents the yield time and yield creep strain for the different constant stress levels. Stress versus log minimum strain rate in creep was obtained as a straight line, with the slope almost the same as obtained for yield stress versus log strain rate in the CSR tests. This common trend was obtained for the three modes of loading (Figs. 6-9). Creep stress versus log strain-rate points in the tension and compression tests (Figs. 6 and 8) lie between the first and second CSR curves. This is clearly attributable to the loading-history effect, the difference between creep and CSR levels being almost identical with that between the second and third CSR cycles (Fig. 6). In the case of heat-treated tensile specimens, in which the load-history effect was probably

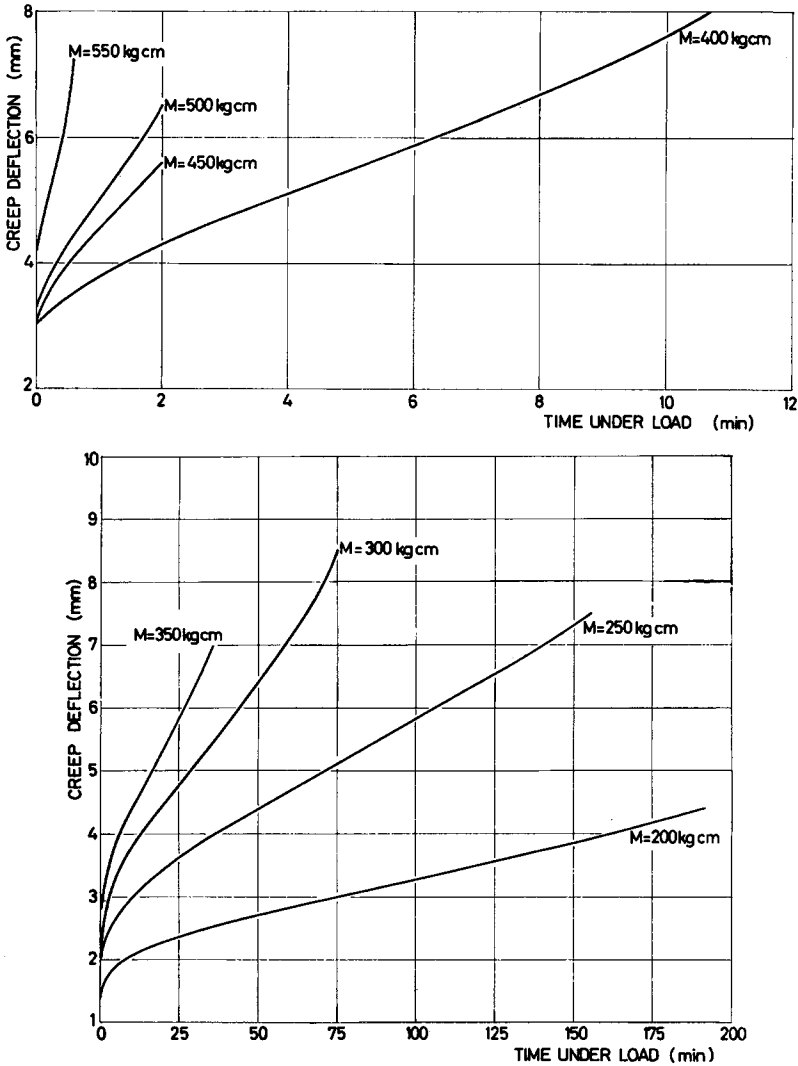


Fig. 5. Flexural creep curves at different high bending-moment levels.

neutralized by stress relief, creep and CSR points are almost colinear on the same straight stress versus log strain-rate line (Fig. 7).

In the flexure tests, where creep preceded CSR loading, the same trend is evident, namely, the stress versus creep-rate line lies above the yield stress versus strain-rate line, and both have nearly the same slope (Fig. 9). The tensile creep yield strain versus log creep-rate curves show higher values compared with the same relationship in the CSR cycles (Fig. 10). Tensile and compressive stress versus log yield time in creep were obtained as a straight line with high scatter—almost the same trend as in the CSR tests, but at a lower level (Figs. 11 and 12).

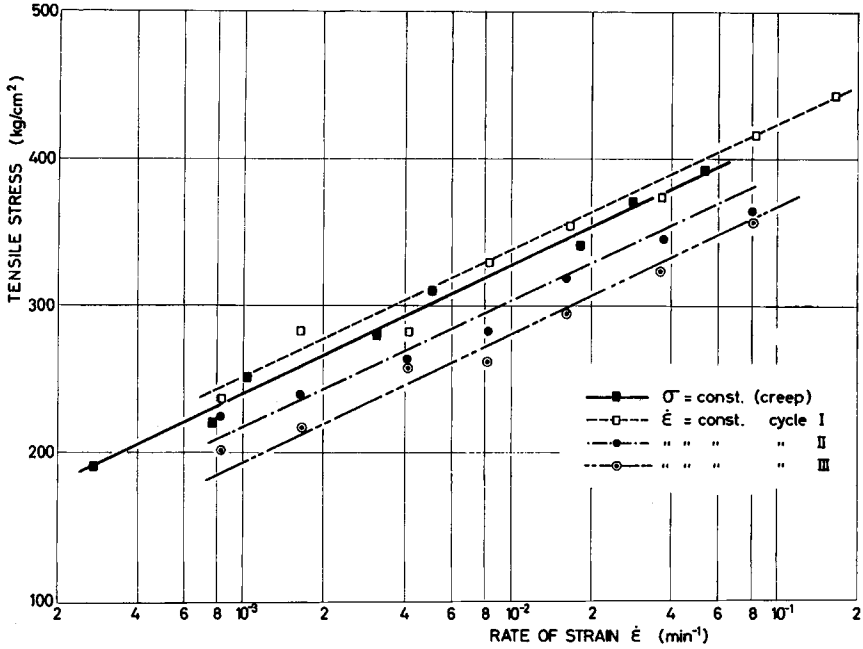


Fig. 6. Tensile stress vs. log strain rate at subsequent creep and CSR loading cycles.

Creep and creep-recovery curves at low stresses (Fig. 13) show almost full recovery 3–4 days after unloading, an indication of the anelastic creep behavior at this region.

The linearity of creep rate versus maximum bending stress in the same time interval is evidence of the predominance of linear viscoelasticity at the low stress levels in question.

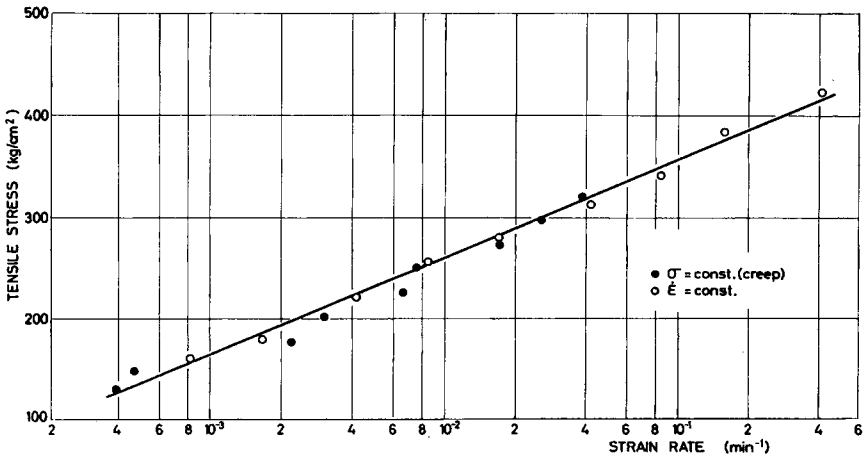


Fig. 7. Tensile stress vs. log strain rate at subsequent creep and CSR cycles for heat-treated specimens.



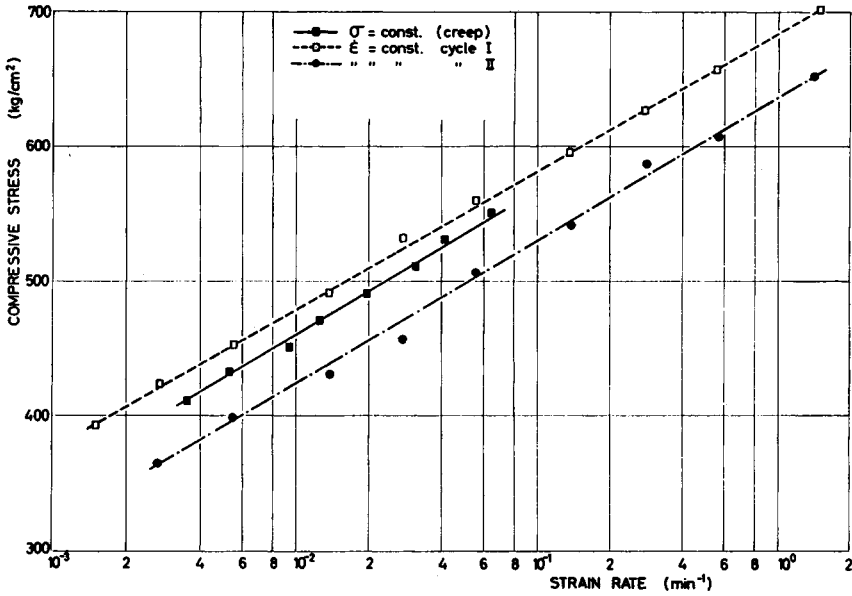


Fig. 8. Compressive stress vs. log strain rate at subsequent creep and CSR loading cycles.

**Theoretical Analysis**

The main significance of the experimental results lies in the almost identical  $\sigma$  versus  $\log \dot{\epsilon}$  relationship established for the respective delayed-yield regions in both the creep and CSR test modes. Another important conclusion is the interchangeability of the minimum creep rate and maximum yield stress plateau in the CSR mode.

It could thus be concluded that the laws governing the delayed-yield stage are in principle the same for both modes and probably for other ones as well, and that the  $\sigma$  versus  $\log \dot{\epsilon}$  relationship is an inherent law character-

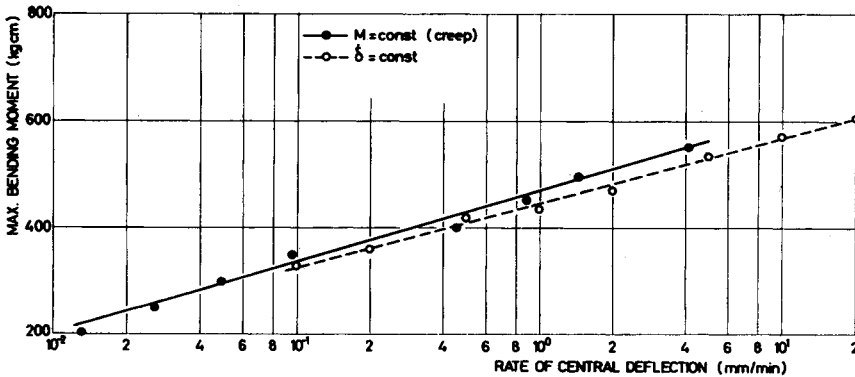


Fig. 9. Maximum bending moment vs. log deflection rate at subsequent creep and CSR loading cycles.

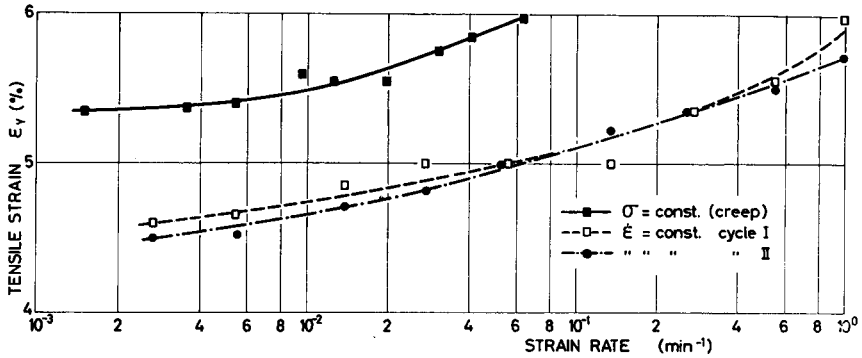


Fig. 10. Tensile yield strain vs. log strain rate at subsequent creep and CRS cycles.

izing the material during the viscoplastic process involved. As the slope of this relationship is almost unaffected by the loading and test mode or by loading history, it is apparently related to a parameter of the material. The above arguments, supported by evidence of the residual shear pattern prior to and during yielding, point to a predominantly viscoplastic mechanism governed by the principal shear stresses.

The apparent yield plateau in the CSR mode and the delayed-yield region of secondary creep justify the assumption that such a mechanism only be-

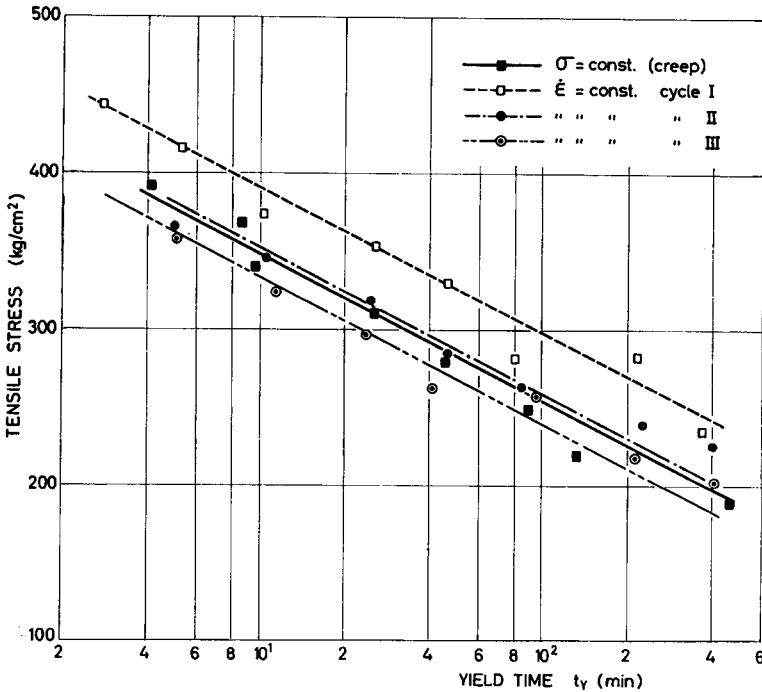


Fig. 11. Tensile stress vs. log yield time at subsequent creep and CRS cycles.

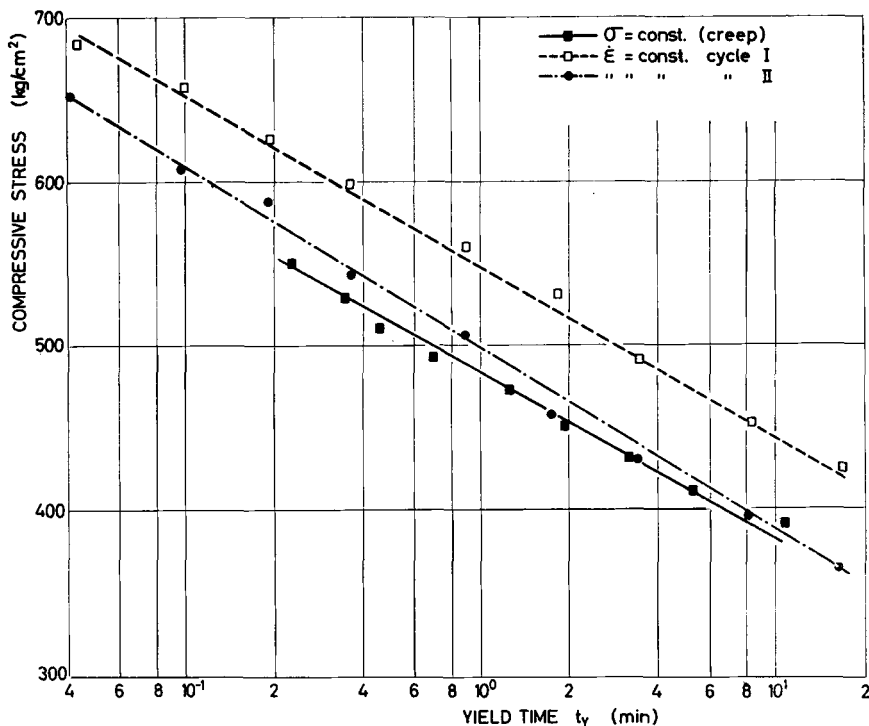


Fig. 12. Compressive stress vs. log yield time at subsequent creep and CSR cycles.

comes fully activated above a certain stress, strain, or (in general) energy level, which is in turn inherently related to the corresponding strain rate. This mechanism could thus be regarded as a time-dependent biased segmental-motion process which is, at a high stress level, mainly governed by external deviatoric energy activation.

The theory of such a mechanism at low temperature and high stress levels, in which the external mechanical energy outweighs thermal effects, has been widely studied by many authors. A general evaluation of this mechanism as a rate process was given by Eyring;<sup>19,20</sup> it was also discussed by Freudenthal<sup>21</sup> as "athermal inelasticity" with reference to plasticity of crystalline materials. Bueche<sup>3b,22</sup> developed a delayed-rupture theory for glassy polymers based on Eyring's hypothesis, which was supported by experimental data.

Lazurkin<sup>23</sup> and more recently, Robertson,<sup>24</sup> Arends,<sup>25</sup> and Ward and Pinnock<sup>9</sup> found this non-Newtonian viscous theory most applicable to formulation of delayed-yielding behavior of ductile glassy polymers.

At first approximation, the activation energy may be considered independent of stress and temperature. In that case the basic relationship would be formulated as shown in eq. (1)

$$\dot{\gamma} = \text{const.} (kT/h) \exp \left\{ -Q/kT \right\} \sinh [s\lambda_1\lambda_2\lambda_0/2kT] \quad (1)$$

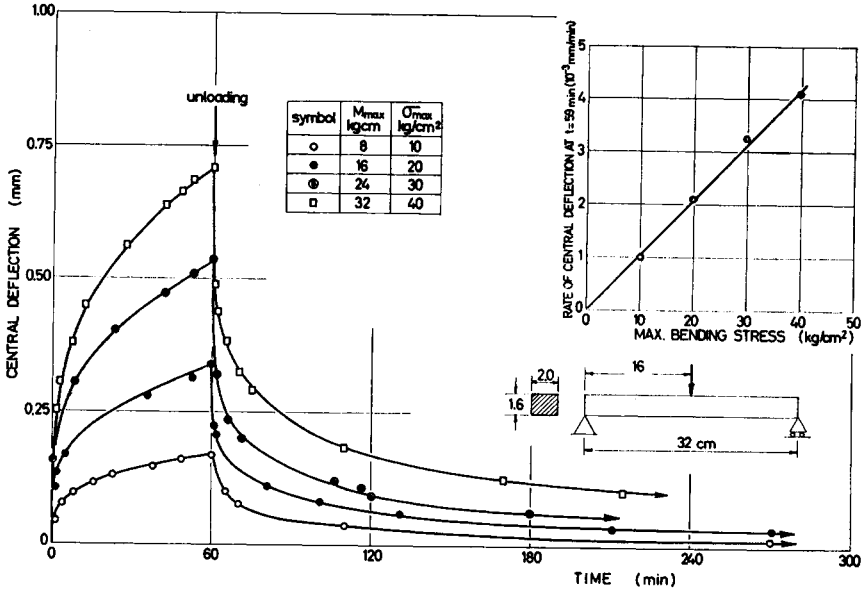


Fig. 13. Creep and creep recovery in flexure at different low stress levels.

where  $\dot{\gamma}$  is the rate of shear flow,  $k$  is Boltzmann's constant,  $T$  is temperature (Kelvin),  $h$  is Planck's constant,  $Q$  is activation energy,  $s$  is the mean shear stress, and  $\lambda_1, \lambda_2,$  and  $\lambda_0$  are, respectively, the interatomic (within the molecule), intermolecular, and jump distances.

At low temperature and high stress level with  $s\lambda_1\lambda_2\lambda_0 \gg 2kT$ , eq. (1) reduces for isothermal conditions to

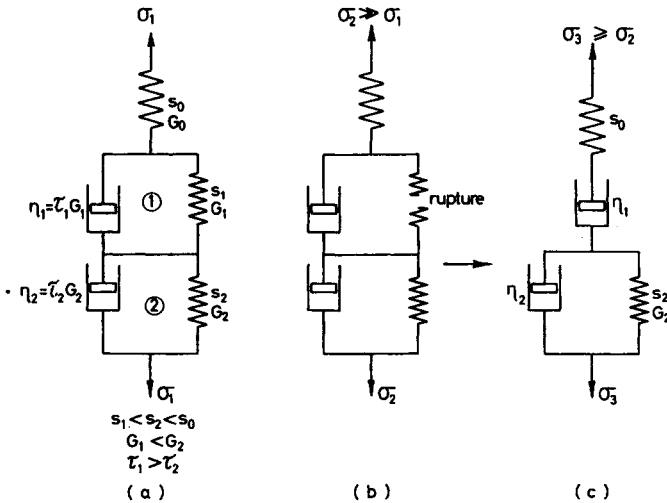


Fig. 14. Rheological models representing the delayed yielding mechanism.

$$\dot{\gamma} = B \exp \{bs\} \quad (2)$$

where

$$B = \text{const. } (kT/h) \exp \{-Q/kT\}$$

and  $b = V_0/2kT$  are temperature-dependent parameters, where  $V_0 = \lambda_1\lambda_2\lambda_0$  is the activation volume.\*

The longitudinal strain rate  $\dot{\epsilon}$  may be considered as proportional to the rate of shear flow; hence eq. (2) can be modified accordingly:

$$\dot{\epsilon} = B_1 \exp \{b\sigma/2\} \quad (3)$$

where  $\sigma = 2s$  — mean normal flow stress and  $B_1 \propto B$ .

Finally eq. (3) can be rewritten in its familiar logarithmic form:

$$\sigma = c_1 + c_2 \log \dot{\epsilon} \quad (4)$$

where  $c_1$  and  $c_2$  are stress-independent parameters.

Equation (4) describes a linear relationship between log strain rate (in tension or in compression) and the corresponding flow stress. Such a relationship, established in the present work in all cases for epoxy resin, was also found predominant in other experimental works. It refers to yielding, at constant strain rate, of several polymers in the glassy state, namely: polystyrene in compression,<sup>26</sup> plasticized PVC and PEMA, crystalline silicone rubber, polyethylene,<sup>23</sup> and Lexan polycarbonate<sup>24</sup> in tension.

A similar relationship in agreement with Eyring's theory was established between creep stress and log creep strain rate, or log yield time, in several works<sup>3a, 5, 8b, 12, 16</sup> as well as in relaxation tests.<sup>24</sup>

Using eqs. (3) and (4), the activation volume  $V_0$  is obtainable from the average slope of the  $\sigma$  versus  $\log \dot{\epsilon}$  lines as follows:  $V_0 = 4200 \text{ \AA.}^3$  in tension; and  $V_0 = 3800 \text{ \AA.}^3$  in compression.

It is noteworthy that the slopes and derived  $V_0$  values are almost unaffected by the test mode and by the loading and curing history, and the discrepancy between compressive and tensile values may be considered as insignificant.  $V_0$  may thus be regarded as an intrinsic value related to the molecular microstructure of the epoxy resin.

A value of  $V^0 = 4400 \text{ \AA.}^3$ , was also obtained by Bueche<sup>3b</sup> on the basis of entirely different data of tensile strength of polystyrene near its glass temperature, PEMA,<sup>22</sup> and SBR.<sup>27</sup>† Different values of  $V_0$ , but still of the same order of magnitude, were obtained for Lexan film by Robertson<sup>24</sup> and for "rubber-modified" polystyrene by Arends.<sup>25</sup>

By providing data about the microstructural dimensions  $\lambda_1$  and  $\lambda_2$  of the tested epoxy system, the jump distance  $\lambda_0$  could be evaluated. It would be

\* The structural parameter  $V_0$  may be regarded as a measure of the volume of the activated segmental unit involved in the diffusional process.

† The value of  $V$  used by Bueche and others is associated with  $\delta = \lambda_0/2$  (half the jump distance), and thus  $V = V_0/2$ .

most interesting to compare this value with the flow segmental unit of about 32 carbon atoms obtained by Kauzmann and Eyring<sup>28</sup> for polyester molecules.

For the mechanical yielding energy level, a value of  $V_{0s}/2kT > 10$  is obtained, which justifies the approximated form of eq. (2). While the constant  $b$  in eq. (3) is almost invariant, the constant  $B_1$ , although almost unaffected by the test mode, is closely dependent on the loading mode, loading history, and other variables. Although the activation energy (the main factor affecting  $B_1$ ) could not be obtained from existing data for a single temperature level, it can be assumed that this parameter, which represents the intermolecular energy barrier to diffusional movement, would be higher for compressive loading, where internal friction would be augmented by the applied isotropic pressure component. Similarly, after the material has undergone a preliminary yield process, a lower resistance reflected in lower activation levels can reasonably be expected on subsequent loading.

### Rheological Interpretation

The microstructural characteristics of a crosslinked polymer can be represented by an infinite spectrum of Kelvin models, with viscous elements coupled by springs. At low stress levels such a model behaves anelastically and is characterized by delayed (but fully recoverable) viscoelastic deformation. This characteristic, demonstrated in Figure 13, was manifested in creep and relaxation tests on epoxy resins up to a creep strain of 3%.<sup>29</sup> Beyond a certain stress or energy level, progressive scission of weak secondary bonds is likely to set in, leading to dissipation of deviatoric energy. Rheologically, this could be described as progressive failure of weak elastic bonds (represented by the springs) in the three-dimensional network, with gradual increase of the contribution of released viscous elements to the overall deformational behavior. As long as continuity of the network is maintained, most of the external energy input is stored in the elastic system. At a certain point, when the rate of input is outweighed by that of scissional dissipation, the structure loses its capacity for absorbing additional energy, and a short-term equilibrium prevails. This stage, termed here "yielded plateau" or secondary creep, could be defined as non-Newtonian viscous flow, being characterized by full deviatoric energy dissipation. It differs, however, from Newtonian flow in that it only becomes activated when enough mechanical energy has been generated to surmount the structural potential-energy barrier, and in its nonlinear characteristics. As for the delayed-yield stage, it is characterized by temporary predominance of viscous Maxwell elements, free to operate owing to failure of the coupling springs. The anelastic behavior of the network of primary and secondary bonds may thus be regarded as temporarily out of action on yielding. This hypothesis is partly confirmed by the tensile behavior under successive repeated loadings, shown in Figure 12 of Part I.<sup>1</sup> The decrease of the apparently linear region from cycle to cycle,

and the increase of the subsequent yield plateau, are evidence of the reduced contribution, due to the yielding effect, of the anelastic (Kelvin) elements to the overall mechanical behavior.

The above arguments could be illustrated as follows.

Figure 14a describes a unit rheological model consisting of Kelvin elements. This model could represent the anelastic behavior of the virgin polymeric system under low stresses. Above a certain stress level, the lower strength of spring  $S_1$  is exceeded (Fig. 14b), and the model is converted into one consisting of a free Maxwellian element (Fig. 14c).\*

Above these levels the model would reveal a certain degree of free viscous behavior, which at the high mechanical energy involved will follow the exponential relationship between stress and strain rate.

A more realistic representation of the microbehavior would consist of an indefinite number of Kelvin models characterized by a spectrum of varying spring strengths and the corresponding retardation times.

This would represent the distribution of primary and secondary binding energies of the microstructure. At a certain stress level, depending on rate or time, a certain strength is exceeded and the corresponding viscous element would be released and contribute to the progressive viscoplastic deformational component of the whole mechanism.

It is thus expected that the stress strain or energy at which deviation from linear viscoelastic behavior sets in would be time-dependent. The deviation-stress versus time relationship could probably be associated with the binding-energy distribution and the corresponding retardation-time spectrum.

Repeated loading and relaxation tests indicate that the sliding process during yielding involves probably only temporary disruption of secondary intermolecular bonds. At this stage there is only a remote possibility of scission of primary crosslinks. Such scission would only prevail in the post-yield region and terminate with failure of the whole system.

Full dimensional thermorecovery of the slightly yielded specimens is evidence that, in spite of the viscoplastic process, the external system of the crosslinked polymer is still intact and its predominantly anelastic behavior recoverable.

## CONCLUSIONS

A ductile epoxy resin in a glassy state reveals, on loading at a constant strain rate and constant stress level, respectively, a distinct delayed-yield region, followed by a stress decrease in the first mode and an increased rate in the second.

Linearity between stress and log strain rate (or log yield time) on yielding

\* The retardation time  $\tau_1$  of element (1) is much longer compared with that of element (2). Hence  $s_1$  would be exceeded first only at a slow strain rate. If the test duration is much shorter, element (2), with the shorter retardation time  $\tau_2$ , would operate more rapidly at a high strain rate and  $s_2$  would be exceeded first under a higher applied stress.

was established for tensile, compressive, and flexural loading with a common characteristic for the CSR and creep test modes.

The relationship was formulated, for the isothermal glassy state, in accordance with Eyring's theory of non-Newtonian viscous flow as follows:

$$\dot{\gamma} = B \exp \{bs\}$$

The constant  $b$  derived from experimental data yields reasonable values related to the activation volume of the molecular segment involved in the process and is almost unaffected by the loading and test modes, by the loading history, and by heat treatment, so that it can be considered as an intrinsic microstructural parameter. The above evidence is also in agreement with observations of the residual shear pattern, as well as with the thermorecoverability of dimensional changes, and thus indicates that the prevalent mechanism is a (non-Newtonian) viscous one.

Yielding of the epoxy system in question and of similar amorphous linear or crosslinked materials is a form of viscous flow, fully activated only beyond a certain level which mainly depends on the rate of input of external mechanical energy.

Such a process is governed by deviatoric energy and oriented by the principal shear stresses. Four regions are distinguishable, especially for the creep and CSR modes: (a) pre-yielding, with linear viscoelasticity prevalent; (b) transitional, where nonlinear viscous behavior probably sets in; (c) delayed yield, with a unique relationship between stress and strain rate in accordance with the non-Newtonian viscous theory; (d) post-yielding, where instability due to interstructural changes sets in, terminating with complete disintegration of the three-dimensional system.

A comprehensive theory on the mechanical behavior of glassy polymers at high stress levels calls for further extensive experimental work. To determine the activation energies involved, a study of the influence of temperature on yielding characteristics would be required. It appears that relaxation or constant stress-rate tests would reveal the same general trend as found for the creep and CSR modes.

A study of the interrelationship of crosslink density and yielding can be expected to shed more light on the contribution of the microstructure to the dynamic and permanent changes involved, and quantitative photoelastic or other auxiliary techniques would probably provide more direct physically significant evidence for the proposed mechanism.

The author wishes to express his gratitude to Ing. E. Goldberg for editorial assistance and advice. He would also like to thank P. Shechter of the Department of Mechanics for assistance in conducting the tests and for preparing the drawings.

### References

1. O. Ishai, *J. Appl. Polymer Sci.*, **11**, 963 (1967).
2. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 47-71.



3. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962, (a) pp. 248-256; (b) pp. 262-268.
4. P. D. Ritchie, *Physics of Plastics*, Plastics Institute, Iliffe, London, 1965, pp. 43-49.
5. J. A. Sauer and J. Marin, *J. Appl. Phys.*, **20**, 507 (1949).
6. J. Marin and G. E. Cuff, *Proc. ASTM*, **49**, 1158 (1949).
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, pp. 317-318.
8. B. Rosen, in *Fracture Processes in Polymeric Solids*, B. Rosen, Ed., Interscience, New York, 1964, (a) pp. 96-98; (b) pp. 302-317.
9. I. M. Ward and P. R. Pinnock, *Brit. J. Appl. Phys.*, **17**(1966).
10. D. I. Vincent, in *Physics of Plastics*, P. D. Ritchie, Ed., Iliffe, London, 1965, pp. 75-84.
11. W. N. Findley and G. Khosla, *J. Appl. Phys.*, **26**, 821 (1955).
12. W. N. Findley, *J. Appl. Phys.*, **21**, 258 (1950).
13. A. H. Sully, *Progr. Metal Phys.*, **6**, 135 (1956).
14. B. Chasman, *Mod. Plastics*, **21**, 145 (1944).
15. R. F. Landel and R. F. Fedors, in *Fracture Processes in Polymeric Solids*, B. Rosen, Ed., Interscience, New York, 1964, pp. 408-423.
16. D. H. Ender and R. D. Andrews, *J. Appl. Phys.*, **36**, 3057 (1965).
17. M. L. Williams and M. F. Bender, *Textile Res. J.*, **33**, 1023 (1963).
18. M. L. Williams and M. F. Bender, *J. Appl. Phys.*, **36**, 3044 (1965).
19. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
20. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941, pp. 477-551.
21. A. M. Freudenthal, *The Inelastic Behavior of Engineering Materials and Structures*, Wiley, New York, 1950, p. 137.
22. F. Bueche, *J. Appl. Phys.*, **28**, 784 (1957).
23. J. S. Lazurkin, *J. Polymer Sci.*, **30**, 595 (1958).
24. R. E. Robertson, *J. Appl. Polymer Sci.*, **7**, 443 (1963).
25. C. B. Arends, *J. Appl. Polymer Sci.*, **10**, 1099 (1966).
26. C. C. Hsiao and J. A. Sauer, *ASTM Bull.*, No. **172**, 29 (1951).
27. T. L. Smith, *J. Polymer Sci.*, **32**, 99 (1958).
28. W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.*, **62**, 3113 (1940).
29. P. S. Theocaris and C. HadjiJoseph, paper presented at 4th International Congress of Rheology, Brown Univ., August 1963; *Proceedings of the Fourth International Congress on Rheology*, E. H. Lee and A. L. Copley, Eds., Interscience, New York, 1965.

### Résumé

Des tests de rétrécissement ont été effectués sur des échantillons de résine époxy à température ordinaire et à différents niveaux d'étirement élevés sous tension, compression et flexion. Comparées au comportement à vitesse de tension constante, (C.S.R.) rapporté dans la Partie I de ce travail, les courbes de tension-rétrécissement, en fonction du temps révèlent une région de rendement retardé de vitesse minimum constante (rétrécissement secondaire) suivie d'une région ultérieure à tangente croissante (rétrécissement tertiaire). Dans tous les cas, les résultats indiquent une linéarité entre la tension de rétrécissement et le logarithme de la vitesse de rétrécissement secondaire qui est pratiquement en coincidence avec la relation correspondante entre le point de rendement et la vitesse de tension obtenue dans les cycles de charge subséquents C.S.R. avec les mêmes échantillons. La similitude de comportement entre à la fois le rétrécissement et les modes C.S.R. est conforme à la théorie de Eyring de l'écoulement visqueux non-Newtonien à des niveaux d'étirements élevés et basse température. L'analyse théorique fournit des valeurs raisonnables du volume d'activation qui est non-affecté par la charge et par le mode d'essai ou par l'historique de la charge, et peut donc être regardée comme un para-

mètre intrinsèque de la microstructure inhérent au processus viscoplastique considéré. Les considérations ci-dessus indiquent un mécanisme de diffusion étirement-biaxial comme facteur prédominant dans la formation d'un système époxy vitreux amorphe.

### Zusammenfassung

Kriechtests wurden an Epoxyharzproben bei Raumtemperatur bei verschieden hoher Spannung unter Zug-, Druck- und Biegebeanspruchung durchgeführt. Im Vergleich zu dem in Teil I beschriebenen Verhalten bei konstanter Verformungsgeschwindigkeit (C.S.R.) wiesen die Kurven für Kriechverformung gegen die Zeit einen deutlichen Bereich verzögerten Fließens bei konstanter Minimalgeschwindigkeit (sekundäres Kriechen) auf, auf welchen ein Nach-Fließbereich mit zunehmender Neigung (tertiäres Kriechen) folgte. In allen Fällen zeigen die Ergebnisse eine lineare Beziehung zwischen Kriechspannung und  $\log$  sekundäre Kriechgeschwindigkeit, was fast mit der entsprechenden Beziehung zwischen Fließgrenze und Verformungsgeschwindigkeit bei späteren C.S.R.-Belastungszyklen an den gleichen Proben zusammenfällt. Die Ähnlichkeit im Verhalten beim Kriechen und beim C.S.R. entspricht der Eyring'schen Theorie des nicht-Newton'schen viskosen Fließens bei hoher Spannung und niedriger Temperatur. Die theoretische Analyse liefert plausible Werte für das Aktivierungsvolumen, welches durch die Belastung die Testmethode und die Belastungsvorgeschichte nicht beeinflusst wird und daher als spezifischer, für den auftretenden viskoelastischen Prozess charakteristischer Parameter der Mikrostruktur betrachtet werden kann. Die obigen Betrachtungen lassen einen spannungs-gelenkten Deviations-Diffusionsmechanismus als dominierenden Faktor beim Fließen eines amorphen glasigen Epoxysystems erkennen.

Received February 1, 1967  
Prod. No. 1578