Discussion

O. D. Sherby.[5] The authors are to be congratulated in attempting to tackle the difficult problem of predicting creep and tensile data from stress-relaxation experiments.

It is interesting to note that the stress-strain curves for the plastics studied by the authors at room temperature and above appear similar to the curves typical of metals that strain-harden. Obviously, considerable plastic deformation is taking place in these plastics under action of stress. The creep curves, shown in Figs. 10 to 12 of the paper, also resemble those for metals, revealing in all cases pronounced transient stages of creep. It is unfortunate that the authors discontinued their tests after such short intervals of testing; it is thought that with extended deformation a steady-state creep rate eventually would have been achieved.

If plastics deform under stress in a way similar to metals then some of the laws which are obeyed by metals also might be obeyed by plastics. In recent investigations[6,7] on the deformation of pure metals and simple alloys at elevated temperatures it was shown that tensile data at various temperatures and strain rates could be correlated by means of the equation

$$\sigma = f(\dot{\epsilon}e^{\Delta H/RT}) \quad \ldots\ldots\ldots\ldots\ldots\ldots [12]$$

where σ = ultimate tensile strength, $\dot{\epsilon}$ = rate of tensile straining, R = gas constant, T = absolute temperature, and ΔH is the activation energy of the deformation process. It was further shown[7] that the activation energy of the deformation process for a given metal was equal to the activation energy for self-diffusion. Thus it might be interesting to see if the data reported in Table 1 of the paper can be analyzed by means of the foregoing equation (assuming that the maximum stress recorded in Table 1 is about equal to the ultimate tensile strength).

Fig. 17 of this discussion shows such a correlation attempt for 0, 10, 20, and 30 per cent plasticized methacrylate. The following remarks are pertinent to the resulting correlation: (*a*) Equation [12] of this discussion appears valid for correlating tensile data on plastics. The 5 per cent plasticized methacrylate also correlated well by means of Equation [12] but was not included in the graph in order to avoid unnecessary confusion owing to the additional datum points. (*b*) The data below room temperature cannot be used in this correlation attempt. This is in the range where the stress-strain curves exhibit negligible plastic flow (Figs. 1 and 4 of the paper). Also, the 122 F (323 K) temperature tensile data for 20 per cent plasticized methacrylate did not correlate well with the other two temperature data and consequently were not plotted in Fig. 17, herewith. It was noted that the maximum stresses achieved at 122 F were considerably less than the stresses which would have been anticipated from extrapolation of the curve in Fig. 17, suggesting that perhaps some auxiliary weakening effects were present at 122 F to cause this anomaly. (*c*) The activation energy obtained for the various polymethyl methacrylates is about equal to 38,000 cal per mole, independent of the plasticizer content. The exact significance of the 38,000 cal per mole is not clear to the writer. Furthermore, it is surprising that the activation energy remains constant. It might be added that metals behave similarly in that dilute solid-solution alloying does not change the activation energy for plastic flow.[6]

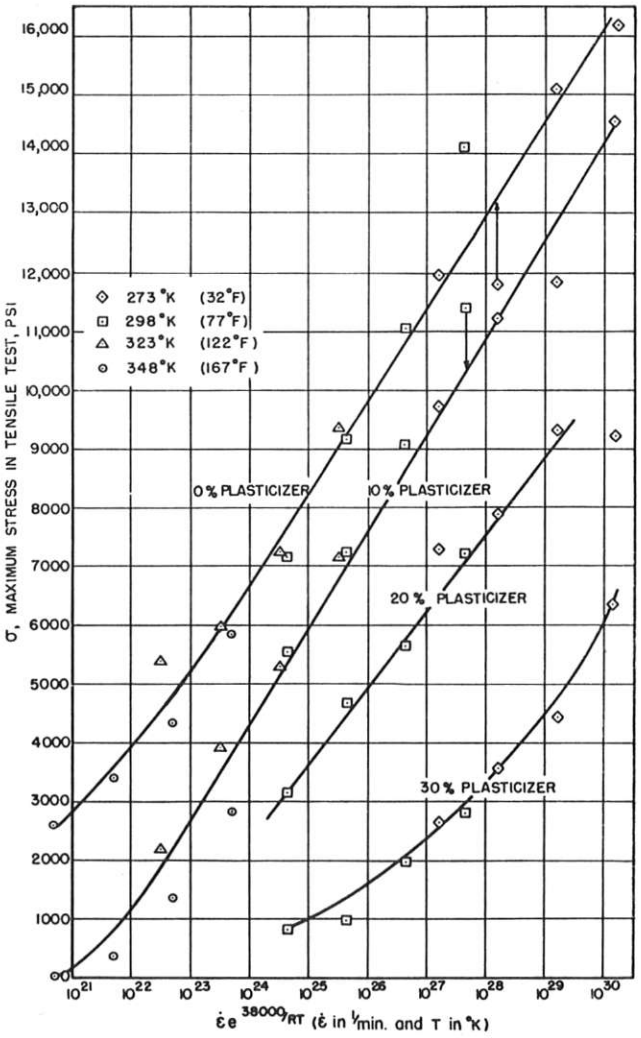

Fig. 17 Correlation of Tensile Data of Polymethyl Methacrylate at Various Strain Rates by Relation $\sigma = f(\dot{\epsilon}e^{\Delta H/RT})$

If Equation [12] were valid for any given strain condition, that is, $\sigma_\epsilon = F(\dot{\epsilon}e^{\Delta H/RT})$ where the function F depends on the strain under consideration, then it might be suggested that the authors' Equation [9] can be generalized for the solution of the stress at a given strain at any temperature where ρ now equals

$$\frac{\dot{\epsilon}e^{\Delta H/RT}}{e^{38,000/2\times 298}}$$

here then $\dot{\epsilon}$ = constant strain rate of tensile test at temperature T and T = absolute temperature of test. However, a more careful examination of Equation [9] indicates that the curve deduced from this equation does not follow the form of the curves in the writer's Fig. 17 and, therefore, the two equations cannot be combined.

In Fig 18, herewith, it is attempted to plot the curve for σ at a strain of 0.04 as a function of strain rate as deduced from the authors' Equation [9] for the 10 per cent plasticized methacrylate. It will be observed that there is no strain-rate effect below a strain rate of about 10^{-3} per min and above about 10 per min. Only between 10^{-3} per min and 10 per min is there a normal strain-rate effect. The writer is not sure that many (or any) materials follow this trend. On the other hand, the tensile stress for 10 per cent plasticized methacrylate can be predicted approximately for 0.04

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[6] "Creep Correlations in Alpha Solid Solutions of Aluminum," by O. D. Sherby and J. E. Dorn, *Journal of Metals*, AIME, vol. 4, 1952, pp. 959–964.

[7] "Creep Correlations of Metals at Elevated Temperatures," by O. D. Sherby, R. L. Orr, and J. E. Dorn, *Journal of Metals*, AIME, vol. 6, 1954, pp. 71–80.

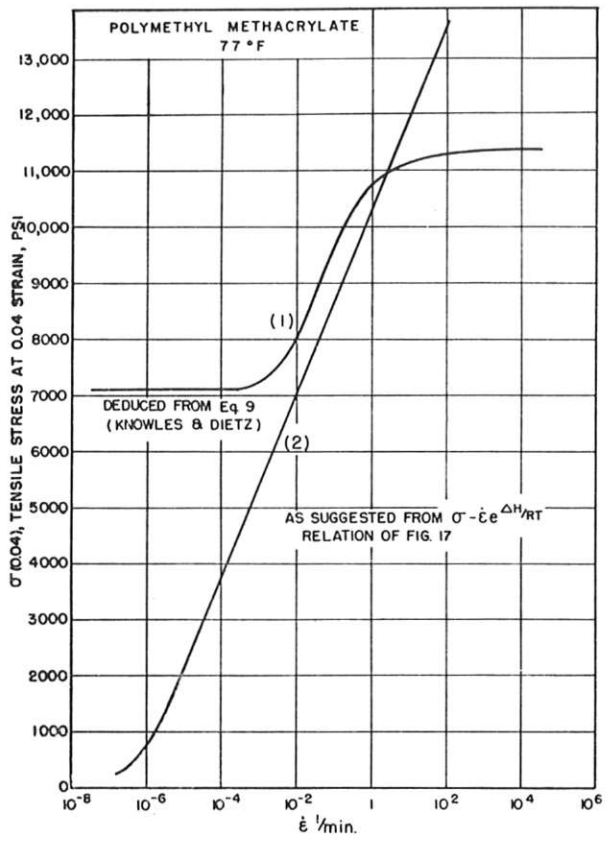

FIG. 18 CORRELATION BETWEEN TENSILE STRESS AT GIVEN STRAIN AND STRAIN RATE FOR 10 PER CENT PLASTICIZER

(Curve 1 is deduced from authors' Equation [9] and curve 2 is suggested from the $\sigma - \dot{\epsilon} e^{\Delta H/RT}$ curve of Fig. 17.)

strain at 77 F from Fig. 17 of this discussion, if 0.04 strain is assumed to be the point of maximum stress (as suggested by the data in Figs. 2, 3, 5, and 7 of the paper). Such a curve is plotted in Fig. 18. Most materials behave more like curve (2) than curve (1).[7] It is believed also that curve (2) approximately represents the creep stress-steady state creep-rate relation[6,7] for 10 per cent plasticized methacrylate.

Have the authors performed any creep tests at various temperatures? It would be interesting to know if the temperature laws[6,7,8] for elevated-temperature creep of metals also apply to plastics as the writer is now convinced they should. Thus it has been shown[6,7,8] that $\epsilon = f(\theta, \sigma)$ where ϵ = creep strain, $\theta = te^{-\Delta H/RT}$, t = time under stress σ, and ΔH = activation energy for creep. For a given creep stress σ, various temperature tests should correlate on a single curve when ϵ is plotted again θ and ΔH should again be equal to about 38,000 cal per mole. If such correlations are valid for plastics, the number of tests can be reduced materially to characterize the material for wide ranges of stress and temperature.

C. R. STOCK.[9] Most knowledge of industrial products or services can be expected to progress through three stages, starting as an art, developing via the empirical correlation of cause and effect, and finally achieving a logical foundation on verified theoretical principles. Electronics represents the one extreme of rapid advance to the third stage, while some long-established industries are hardly past being an art. It probably would be agreed by most that that part of the technology of plastics having to do with mechanical application and design is not far beyond the middle ground of empiricism.

Efforts to provide for the thermoplastics the ultimate goal of a sound descriptive theory of mechanical behavior based on internal structure doubtless will continue to be retarded by the extreme complexity of the problem; the outcome of experiment can so far be predicted only approximately at best. Until this goal is eventually realized, advances must continue to be made at the empirical level, to provide more satisfactory criteria for design than either cut-and-try methods or classical elastic theory can supply.

The present paper describes an approach based on cause and effect, that has a good chance of providing a satisfactory means of predicting the exterior mechanical behavior of methacrylate and hence possibly of other thermoplastics. The analytical power of the modified Boltzmann equation gives promise of this because it eschews elegance of form in favor of realistic recognition of the nonlinear response observed experimentally, providing means for taking this more complex reaction to stress into account. Obviously, the work reported here for one plastic constitutes only an encouraging indication when viewed against the broader field of linear high polymers in general; it cannot even be said to have defined the mechanical behavior of methacrylates unequivocally. But over the range of variables covered, correlation between prediction and experiment has been closer than in any earlier attempt. If further work is equally encouraging, there may be a possibility of characterizing at least some plastics by parameters that will permit of intelligent engineering design.

AUTHORS' CLOSURE

The authors wish to thank Dr. Sherby and Dr. Stock for their interesting comments.

The first discusser's correlation of the tensile data presented in Table 1 is indeed interesting. Calculations based on the nonlinear Eyring three-element mechanical model were carried out some time ago on a series of methacrylates of varying molecular weights using data obtained by creep and relaxation testing.[10] Despite some scatter the activation energies thus calculated (between 25 and 40 kilo calories/mole, in most cases) appeared to be independent of molecular weight over the range considered.

The authors have not studied the creep behavior of the plasticized-methacrylate series at various temperatures. Data on the varying molecular-weight series, however, are available.[10] The suggestion, made by the first discusser, that various temperature creep tests should correlate on a single curve was apparently verified in Yurenka's work.

A remark relevant to Dr. Sherby's Fig. 18: It should be pointed out that plotting the authors' Equation [9], using the constants [10], in the form of stress versus strain rate at a fixed strain $\bar{\epsilon}$ is significant only when $p \geq \bar{\epsilon}/100$; i.e., $p \geq 4 \times 10^{-4}$ per sec, or $p > 2 \times 10^{-2}$ per minute, since the constants [10] were obtained from relaxation tests of one-hundred seconds' duration and, as pointed out previously, the resulting equations describe adequately only those experiments whose durations are roughly the same as that of the relaxation tests from which the values [10] were obtained.

[8] "Some Observations on Correlations Between the Creep Behavior and the Resulting Structure in Alpha Solid Solutions," *Journal of Metals*, AIME, vol. 5, 1953, pp. 324–330.

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[10] "Creep and Relaxation Properties of Polymethyl Methacrylate," by S. Yurenka, ScD. thesis, M.I.T., Department of Mechanical Engineering, 1950.