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INTRODUCTION

Polyethylene, which appears at first glance to be the simplest of polymers, displays properties which are surprisingly complex. One reason for this is the high degree of crystallinity in this "semicrystalline" polymer. This paper, which is a portion of a larger study (1), describes the compressive strain-rate/temperature behavior of highly linear, high density polyethylene and the success of an analysis of this behavior based upon techniques used successfully for other crystalline materials.

EXPERIMENTAL

Two highly linear, high density polyethylene resins were studied: Marlex 6009 (Phillips Petroleum Company, Bartlesville, OK), a high weight-average molecular weight (195,000), medium molecular-weight distribution (13.8) blow-molding resin, and Alathon 7050 (E. I. duPont de Nemours and Co., Inc., Wilmington, DE), a medium weight-average molecular weight (55,000), narrow molecular-weight distribution (3.1) injection-molding resin. To avoid anisotropy the polyethylenes were compression-molded into slabs which were annealed to relieve molding stresses, yielding materials which tested to be substantially isotropic. Cylinders having an aspect ratio (length/diameter) of 1.5 were machined from these slabs, with intermediate anneals used to maintain isotropy. Compression testing was done using a hydraulic servo-ram testing system. Temperatures from 23°C to 130°C were controlled by a resistance-heated, liquid-gas-cooled temperature chamber. In addition, the temperature gradient between the compression platens was controlled to less than 0.2°C. Barreling and other nonuniform deformation were successfully controlled by careful lubrication between specimen and platens. Strain rates ranged from 5×10^{-7} to 10^{-1} s^{-1}. The majority of the tests were performed at constant applied engineering strain rate. About 20% of the tests, however, were conducted at constant applied true strain rate, meaning that the compression rate was programmed to be continuously reduced as the overall specimen length was reduced.** In addition, some applied-true-stress (creep) testing was done.

RESULTS

A representative stress/strain curve is shown in Fig. 1. The curve is for Marlex 6009 tested in uniaxial compression, under applied true strain rate,

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**"Engineering" strain is the change in length divided by the initial length: $e = \Delta\ell_o/\ell_o$. "True" strain is the instantaneous change in length divided by the instantaneous length:
$\varepsilon = \Delta\ell/\ell = \int_{\ell_o}^{\ell} d\ell/\ell = \ln(\ell/\ell_o) = \ln(1 + e)$, where e is positive in tension and negative in compression. Similarly, "engineering" stress is the load divided by the initial area: $S = L/A_o$, while "true" stress is the load divided by the instantaneous area: $\sigma = L/A = S(1 + e)$.

at 88°C. The behavior for Alathon 7050 is similar, except that at this temperature the Alathon stress level is slightly higher. As can be seen from the figure, a constant stress is attained after an initial hardening period. At moderate temperatures and strain rates, where failure does not intervene (2) and in the absence of severe barreling, this stress remains constant to true strains as high as 200%. This behavior is analogous to that of most metals and other polycrystalline materials, and thus this stress will be referred to as the "steady state flow stress," with the symbol σ_{ss}.

The typical behavior obtained upon a change in true strain rate is also shown in Fig. 1. In the steady state flow region a change in strain rate first produces a short transient and then a new constant stress, which is in fact the steady state flow stress for the new strain rate. As demonstrated in Fig. 1, a large change in strain rate (a factor of 5) produces a small change in stress (a factor of 1.1). Because of this strain-rate insensitivity, the material is also very stress sensitive. Therefore, in applied stress testing (creep) a small deviation or change in stress produces a large change in strain rate. Because of this amplification of error in creep testing, applied-strain-rate testing was chosen as the primary mode of testing in this investigation. However, sufficient creep testing was done to confirm the relationship between applied-strain-rate and applied-stress testing. This was determined by tests where the steady state flow stress resulting from a given applied true strain rate was applied to another specimen in compressive creep. It was found that, as for other polycrystalline materials, within the uncertainties in the data the minimum or "steady state" creep strain rate attained in the creep test was the same as the applied true strain rate in the first test. Thus it was assumed that the "steady state" results of creep and applied-strain-rate tests are equivalent and reflect basic material behavior.

The relationship between applied stress and resulting creep strain rate as a function of temperature, or conversely the relationship between applied strain rate and resulting stress, are important to the understanding of the mechanical response of a material. A logarithmic plot of applied true strain rate versus steady state flow stress for Marlex 6009 at various temperatures is shown in Fig. 2. Statistical fitting indicates that in almost every case the data of Fig. 2 are well fit by a "broken" straight line changing from a slope of about 28 at low strain rates to a slope of about 10 at high strain rates.

Alathon 7050 exhibits similar behavior. At temperatures of 70°C and below the results for Alathon 7050 are statistically the same as those for Marlex 6009. At higher temperatures, however, the results for Alathon 7050 are shifted increasingly to higher stresses. Furthermore, when the logarithm of true strain rate is plotted versus the logarithm of stress at 5% or 10% true strain, the result is identical to Fig. 2, except that the stresses are shifted to lower levels. Thus, we assume that the behavior for Marlex 6009 in the steady state region is generally representative of the behavior of polyethylene both in the steady state region and at strains as low as 5%.

ANALYSIS AND DISCUSSION

The strain region of this study was far higher than the linearity limit for polyethylene, or for any other semicrystalline polymer (3,4). While a number of theories of nonlinear viscoelasticity have been developed, most of these have no physical significance (5) and would thus contribute little to our understanding of behavior. As an alternative, we will compare the behavior of polyethylene to the behavior of metals and other polycrystalline materials. Here creep has been demonstrated to be a thermally activated process which can be described by an Arrhenius relation of the form (6):

$$\dot{\varepsilon} = f(\sigma, z) \exp(-Q_{\dot{\varepsilon}}/RT) \qquad (1)$$

where $\dot{\epsilon}$ is the steady state creep rate; f is some function of applied stress, σ, and one or more unspecified variables, z; Q_f is the activation energy for flow; R is the universal gas constant; and T is the absolute temperature. Furthermore, for most polycrystalline metals and many alloys, at low to moderate stresses and at temperatures above half the absolute melting temperature, the stress dependence of the creep rate has been shown to obey a "power law" (6), namely:

$$\dot{\epsilon} \propto \sigma^n \qquad (2)$$

where n is the "stress exponent." Although the stress exponents observed for polyethylene are much higher than those of most homogeneous alloys (reflecting the unusually high stress sensitivity of this material), similar high exponents have been observed for metal-base particulate composites (6,7,8) and for dispersion-strengthened alloys (9).

Combining Eqs. (1) and (2) we get a strain-rate/stress/temperature relation of:

$$\dot{\epsilon} = K \sigma^n \exp(-Q_f/RT) \qquad (3)$$

where K is a constant and is not a function of stress. If K is also not a function of temperature, the activation energy for flow will be proportional to the slope of lines at constant stress on a plot of the logarithm of strain rate versus inverse temperature. Such a plot for Marlex 6009 is given in Fig. 3 for various values of stress. While theoretical bases for stress-dependent activation energies have been offered by other authors (10,11), the dependence seen here, where the activation energy increases as the stress decreases, is opposite to any theoretical expectation. Consequently we will explore other possible explanations for the behavior shown in Fig. 3.

Figure 3 indicates that the low stress data are associated with higher temperatures than are the high stress data, and further that some of the data show a tendency to upward curvature rather than constant slope behavior. This might indicate that the activation energy for flow is <u>temperature</u> rather than <u>stress</u> dependent. For linear polyethylene, a secondary transition region known as the α-transition, is encountered at about 75°C, with the exact temperature region depending on the specific polyethylene resin, its processing, and other such factors. It has long been recognized that as a transition region is approached, either from higher or lower temperatures, activation energies increase rapidly (12), and in fact the activation energy maximum is one definition of the "transition temperature." However, because even the lowest activation energies obtained for polyethylene in Fig. 3 are very high, this explanation seems unsatisfactory.

Another possible explanation for the observed behavior is that the "constant" K in Eq. (3) is temperature dependent. For many metals and alloys K has been observed to be somewhat influenced by temperature through its dependence on the microstructure of the material. Inclusion of the microstructure influence gives us a strain-rate equation of the form

$$\dot{\epsilon} = f(\sigma/\chi) \exp(-Q_f/RT) \qquad (4)$$

where χ is a term reflecting the temperature-dependent structure of the material. If the stress dependence is of the form of Eq. (2), we then have:

$$\dot{\epsilon} = k(\sigma/\chi)^n \exp(-Q_f/RT) \qquad (5)$$

where k is a constant. It has further been found that for pure polycrystalline metals the structure term χ is proportional to the elastic modulus of the metal (13).

The rationale behind a structure term is that temperature-dependent changes in internal material structure can influence the rate of the various mechanisms of deformation. In Fig. 2 we would presume that the two regions of differing stress exponents indicate that two different mechanisms for flow are rate controlling. Thus, if a structure term were used to remove the temperature dependence of the pre-exponential constant in Eq. (3), we might expect that at all temperatures the change from one mechanism to another would occur at the same value of "structure-compensated stress." Such behavior has in fact been observed with other materials (7,9,14). This would be the case if the structure term, $\chi(T)$, were proportional to the stress at which the change in slope occurs in the constant-temperature lines of Fig. 2. In Fig. 4 we show a logarithmic plot of true strain rate versus "structure-compensated stress" at various temperatures. Structure-compensated stress is taken as the steady state flow stress divided by the stress-at-change, σ_c, which is the stress at which the stress exponent changes from 28 to 10. Data at 23°C and 130°C were omitted since we could not determine an accurate σ_c for those temperatures. By definition all of the changes in slope now occur at a structure-compensated stress, σ_{ss}/σ_c, equal to one.

The activation energy for flow, taking into account this structure-compensation, can now be determined from Eq. (5) by plotting the logarithm of true strain rate versus inverse temperature at constant structure-compensated stress. Such a plot is shown in Fig. 5 for Marlex 6009. Remarkably, the slopes of the curves are all approximately the same, indicating a constant activation energy for flow over the full range of stress and temperature. In other words, Eq. (5) appears to be valid, with neither the activation energy for flow nor the constant k as a function of stress or temperature. The activation energy, which averages 64 kJ/mol (15.3 kcal/mol), is constant even in the region of the α secondary transition, and its value is low enough to be reasonable for a physical process in polyethylene.

Using the structure-compensated stress and the activation energy value of 64 kJ/mol we can now construct a "Master Curve" for deformation of polyethylene. Rearranging Eq. (4) we get:

$$\dot{\varepsilon}\ \exp(Q_f/RT) = f(\sigma/\chi) \tag{6}$$

If we substitute $c\sigma_c$, where c is a constant, for χ, and then assume that:

$$f(\sigma/c\sigma_c) = F(\sigma/\sigma_c)$$

we have:

$$\dot{\varepsilon}\ \exp(Q_f/RT) = F(\sigma/\sigma_c) \tag{7}$$

where $\dot{\varepsilon}\ \exp(Q_f/RT)$ is the "activation-energy-compensated strain rate," and σ/σ_c is the "structure-compensated stress." A logarithmic plot of activation-energy-compensated strain rate versus structure-compensated (steady state flow) stress for Marlex 6009 is given in Fig. 6. Results of similar form are obtained for Alathon 7050 and for stresses at strains of 5% and 10%. This "Master Curve" represents the deformation behavior over the strain-rate range from 5×10^{-6} to 10^{-1} s^{-1} and over the temperature range from 39°C to 126°C. The overall flow behavior can be represented by the relation:

$$\dot{\varepsilon}\ \exp(Q_f/RT) = k'(\sigma/\sigma_c)^n \tag{8}$$

where Q_f is 64 kJ/mol, k' is a constant, and n changes from 28 to 10 at an activation-energy-compensated strain rate of 10^6 s^{-1}.

While the above results are analogous to the findings for metals, the structure compensation effect is large for polyethylene and small for metals, while the activation energy compensation is small for polyethylene and large for metals. The implication is that temperature affects the internal structure and hence the rate of the deformation processes for polyethylene far more than it does the basic rate-controlling step(s) of the flow process. For metals the opposite is true. It is of further interest to note that the temperature dependence of the structure-compensation term, σ_c, is similar to that of the dynamic elastic modulus of polyethylene, indicating that as for metals the elastic modulus may reflect the internal structure of the material. (In fact, for creep of PMMA structure-compensation using the dynamic elastic modulus was found to yield a constant activation energy for flow and a master predictive relation (1).) For metals, the activation energy for flow obtained after structure compensation is found to be equivalent to that for self-diffusion. Similarly, the activation energy value for Marlex 6009 (and for Alathon 7050) of 64 kJ/mol is comparable to the values of 64 to 71 kJ/mol found for self-diffusion or diffusion of similar species in polyolefins (15,16). It would seem that the predictive relations derived for metals and other crystalline materials give significant insight into the deformation behavior of polyethylene as well.

CONCLUSIONS

We have successfully analyzed the compressive strain-rate/temperature behavior of high density polyethylene in terms of the predictive relations developed for other crystalline materials. The resulting activation energy for flow was found to be constant over the temperature range from 39°C to 126°C, even though a secondary transition of polyethylene occurs at about 75°C. The success of this approach is significant in that it implies a greater similarity than has been generally recognized between the deformation behavior of polyethylene and that of other crystalline materials.

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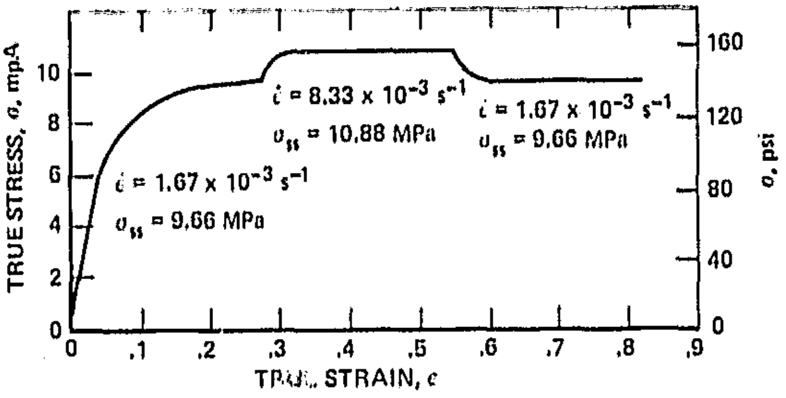


Fig. 1 Representative stress/strain curve for true-strain-rate-change testing of high density polyethylene in uniaxial compression. The curve is for Marlex 6009 tested at 88°C.

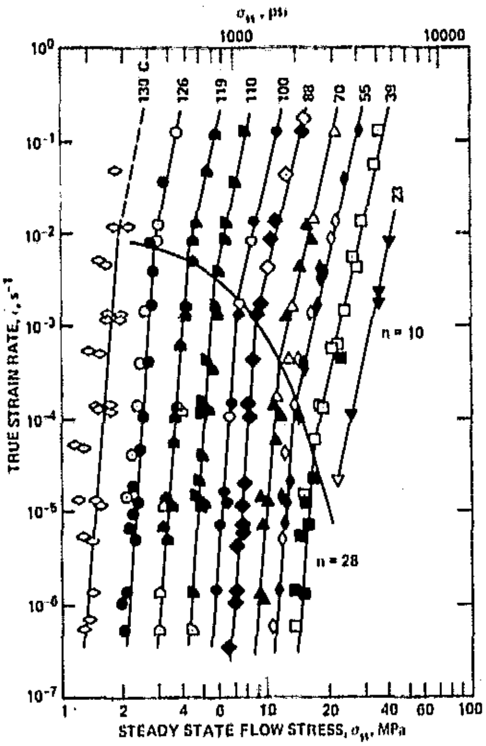


Fig. 2 Logarithmic plot of true strain rate versus compressive steady state flow stress for Marlex 6009 at various temperatures. Stresses represented by closed symbols are valid to ±5% or better; stresses represented by open symbols are valid to about ±10%.

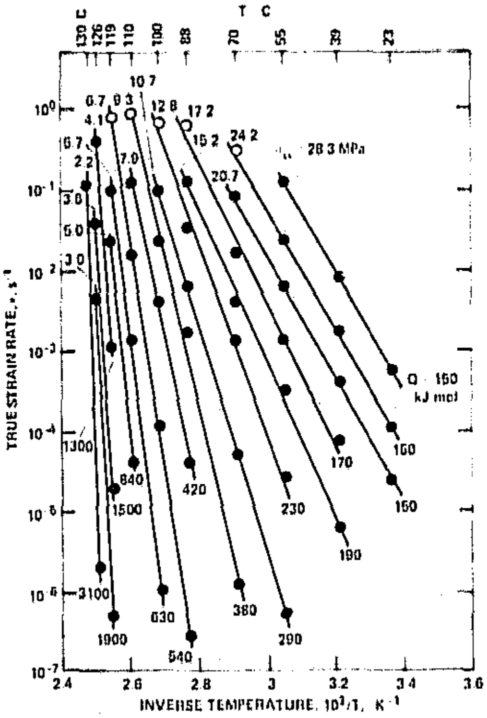
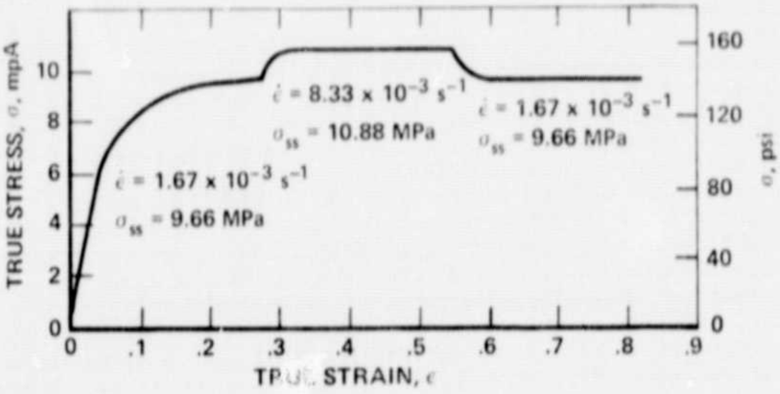


Fig. 3 Activation energy plot: semi-logarithmic plot of true strain rate versus inverse temperature for Marlex 6009 at various stresses. Open symbols indicate extrapolated data.



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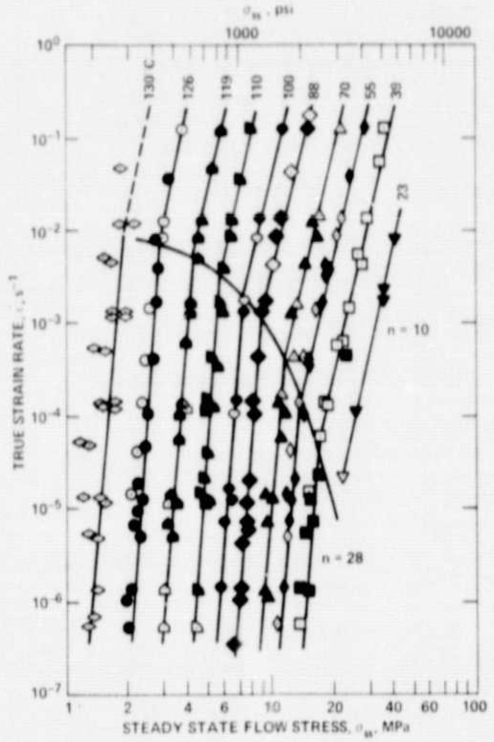

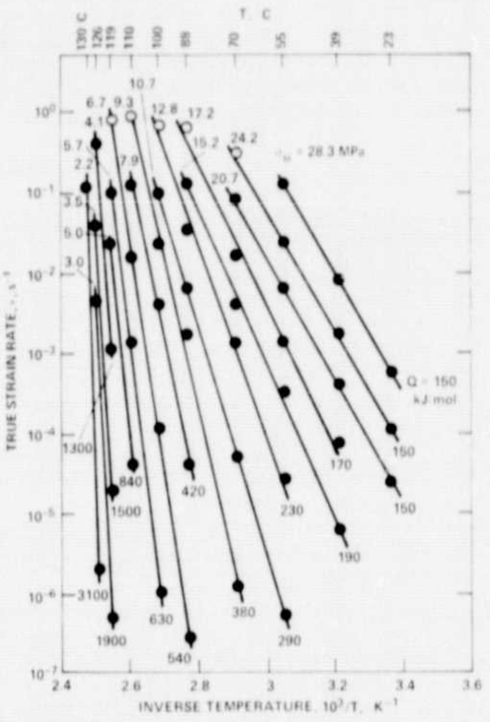

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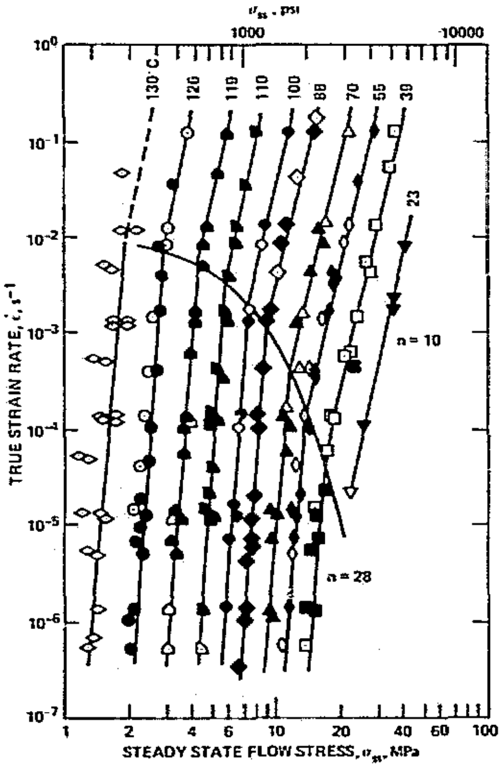


Fig. 4 Logarithmic plot of true strain rate versus "structure-compensated stress" for Marlex 6009. Stresses represented by closed symbols are valid to ±5% or better; stresses represented by open symbols are valid to about ±10%.

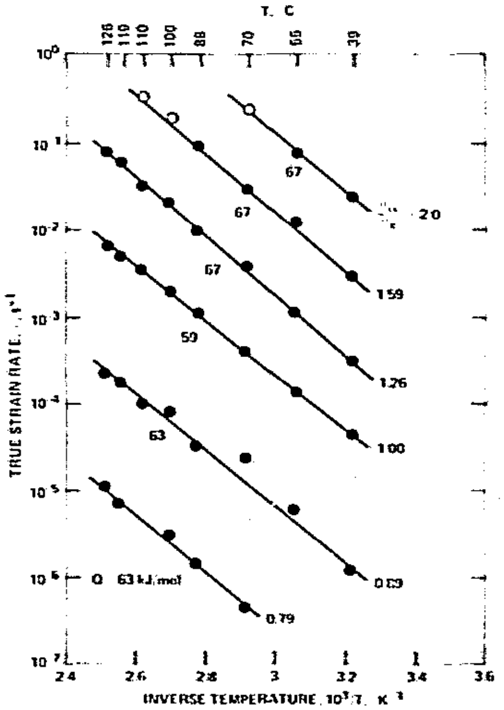


Fig. 5 Activation energy plot: semi-logarithmic plot of true strain rate versus inverse temperature for Marlex 6009 at various structure-compensated stresses. Open symbols indicate extrapolated data.

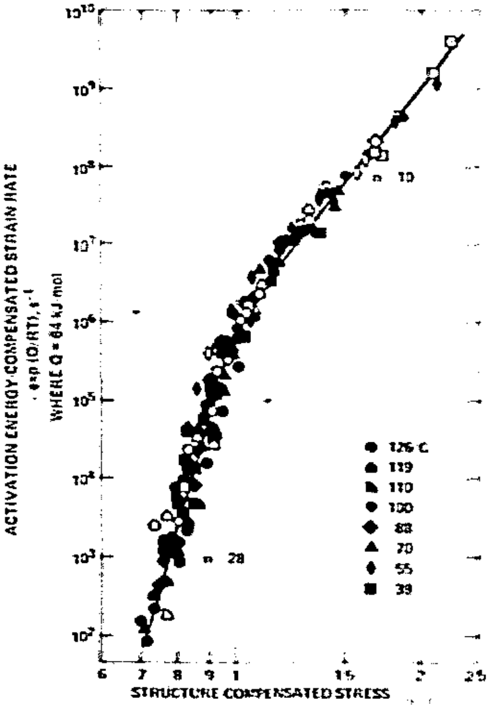
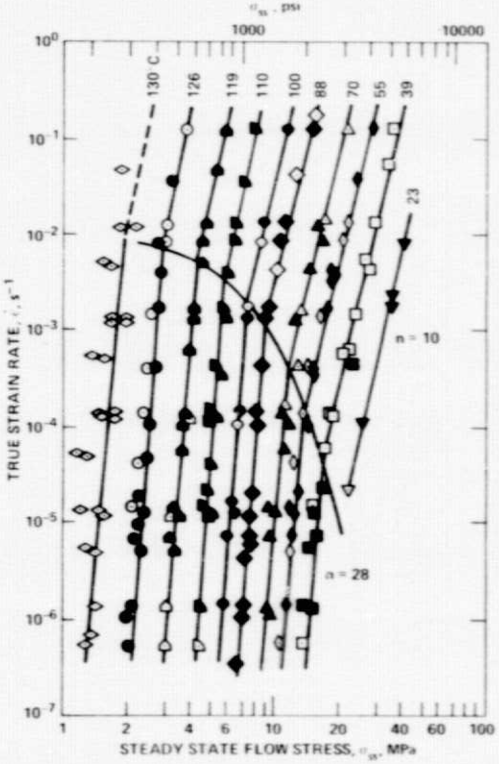


Fig. 6 "Master Curve": logarithmic plot of activation-energy-compensated strain rate versus structure-compensated stress for Marlex 6009. Stresses represented by closed symbols are valid to ±5% or better; stresses represented by open symbols are valid to about ±10%.



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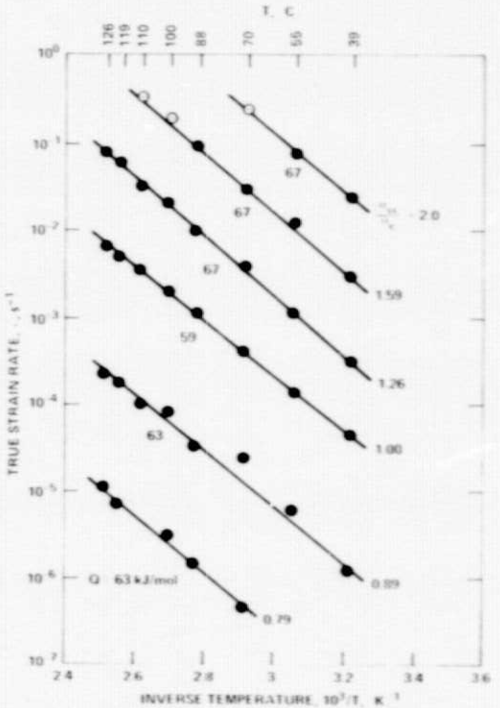
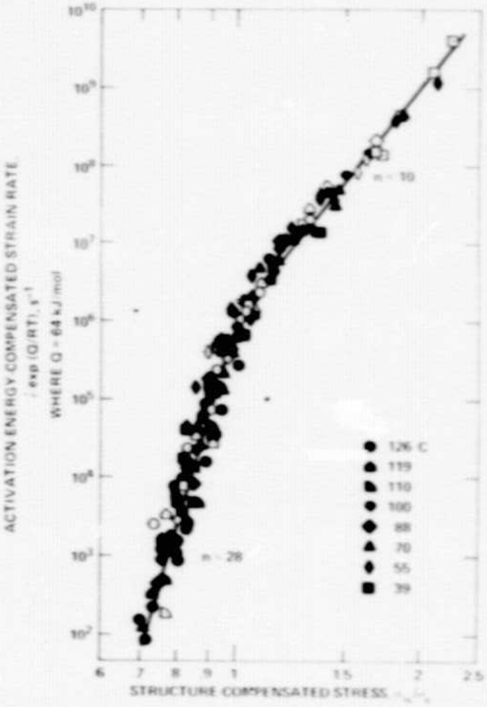


Fig. 5 Activation energy plot: semi-logarithmic plot of true strain rate versus inverse temperature for Marlex 6009 at various structure-compensated stresses. Open symbols indicate extrapolated data.



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