Investigation of Creep Phenomena in Polyethylene and Polypropylene

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Synopsis

Although creep in thermoplastics, especially for polyethylene, has been investigated thoroughly, not too much information exists to establish activation energies at different stress levels by the application of high stress-level, short-time creep tests.   Extrapolation of data to zero stress gives a true material activation energy which is a measure of internal resistance to deformation.   Descriptions of specific creep parameters and equipment with a relatively simple phototube recording device are offered along with a discussion of results and recommendations for future fields of investigation.

Introduction

Creep is generally defined as the time-dependent deformation of material under constant load or stress.   Although there has been much investigation of phenomenon of creep in metals, comparatively little information is available in the field of thermoplastics even though much theoretical work has been accomplished.

It is believed that creep is a result of a thermally activated process that is taking place in the material under consideration.   In metals, for example, three possible mechanisms combine during creep deformation to account for creep behavior.[1] These are: (1) true internal frictional forces, (2) thermally activated processes, and (3) quantum-mechanical "tunneling" effects.

True frictional forces give rise to a viscous or quasiviscous behavior such as a rigid body moving in a viscous fluid.

Thermally activated processes are due in part to insufficient forces to provide movement. Some internal obstacles can be overcome if local thermal fluctuations supply the necessary energy.   The rate that internal obstacles are overcome has been shown to depend on temperature in the form of $\exp\{-\Delta H/kT\}$, where ΔH is the activation energy of that specific process.

Quantum-mechanical tunneling effects are incorporated in the applied force or stress and are considered independent (or indirectly dependent) on temperature.

Since the creep process is thought to be temperature-dependent, the creep rate can generally be expressed as

$$\dot{\epsilon} = \sum f_i(\sigma, T, st)e^{-\Delta H(\sigma, T, st)/kT} \tag{1}$$

where $\dot{\epsilon}$ is the creep rate (sec^{-1}), f_i is a frequency factor or the flux of diffusing atoms or vacancies, ΔH is the activation energy which is dependent on stress (psi), temperature (°K), and a geometrical factor st of the material, and k is Boltzmann's constant (calories/mole-°K).

Time is not explicitly defined, although it is incorporated in the st term which takes into account the structural change during deformation.

Eyring[2] has developed a somewhat similar formula for rate diffusion ν, where a flow unit is considered to be a molecule:

$$\nu = (kT/h)e^{-\Delta f/kT} \tag{2}$$

where ν is the number of jumps per unit time, k is Boltzmann's constant (cal/mole-°K), h is Planck's constant (cal-sec), T is temperature (°K), and Δf is the free energy for activation (cal/mole).

Sherby[3] develops eq. (2) further by considering the work done by stress is equal to the force times the distance the flow unit has to move for activation and shows that:

$$\dot{\epsilon} = (2AkT/h)e^{-\Delta f/kT} \sinh(\tau A\lambda/2kT) \tag{3}$$

where A is the shear strain rate (sec^{-1}), τ is the shear stress (psi), and λ is the distance of separation of molecules (in metals this would refer to lattice dimensions).

The distance the flow unit would have to move, therefore would be $\lambda/2$.

Experimentation has shown the $2AkT/h$ term has very little influence on the creep rate in comparison to the temperature effect, and the hyperbolic sine term can be considered to be a constant to the first approximation.

Since $\Delta F = \Delta H' - T\Delta S = N\Delta f$ and $k = R/N$, the equation now becomes

$$\dot{\epsilon} = Ae^{-\Delta H'/RT}\sinh(\tau A\lambda/2kT) \tag{4}$$

where ΔF is the free energy (cal), $\Delta H'$ is the energy of activation (cal/mole), N is Avogadro's number, R is the gas constant, and τ is the shear stress (psi).

Letting a constant $B = A\lambda N/2$, τ = linear function of σ and approximating $\sinh B\sigma/RT$ by $e^{B\sigma/RT}/2$ leads to eq. (5):

$$\dot{\epsilon} = (A/2)e^{-\Delta H'/RT}e^{\sigma B/RT} \tag{5}$$

A more general equation can now be stated because of the two constant terms $A/2$ and $e^{\sigma B/RT}$.

$$\dot{\epsilon} = Ke^{-\Delta H'/RT} \tag{6}$$

Further study has shown that the constant K will depend on the parameters involved. Investigation of the effects of stress on the creep rate

at constant structure at intermediate or high stress levels have shown that K varies as follows:[4]

High stress: $K = Se^{\sigma B/RT}$

Intermediate stress: $K = S'\sigma^n$

where it has been found that the parameters B and n ($n \simeq 4$) are independent of temperature and S and S' are the stress levels involved.

Theoretical interpretation of the above equations, plus experimental observation show there is an idealized creep curve and that the material reacts ideally for strain versus time according to Figure 1. Creep study of nonmetallic material probably dates back to 1905 when Phillips published the results of his observations.[5] His work included creep observations of rubber and glass. In the late 1930's and early 1940's, much theoretical work was being carried out to establish mathematical models to describe creep experiments. Among the models proposed was the Voigt-Kelvin formulation which was based on a series of spring constants in parallel with dash pots. A similar model called the Maxwell-Wiechert Model consisted of parallel branches made up of one spring constant and a dash pot each.[6]
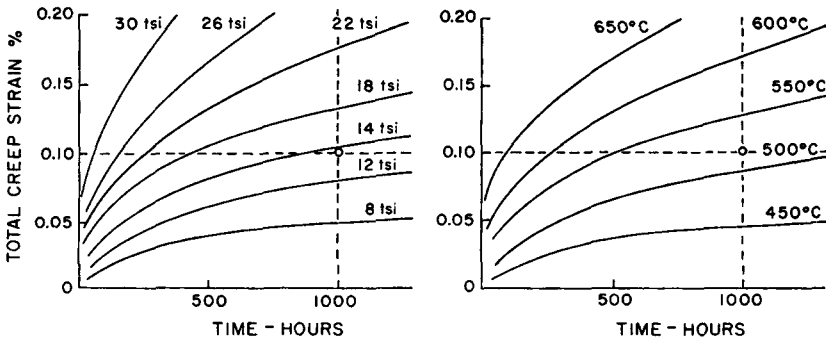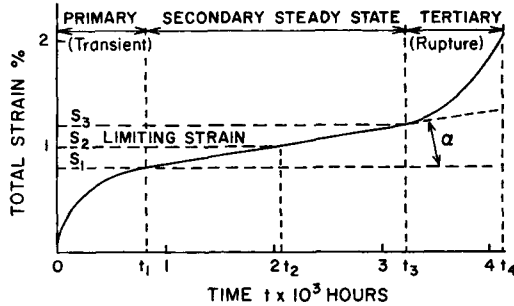

Fig. 1. Several idealized creep curves.

Reviewing concepts and definitions, Turner[7] lists as a basic total strain equation:

$$\epsilon_t = \epsilon_0 + \psi_{(t)} + \sigma t/n_0 \tag{7}$$

where ϵ_0 is instantaneous strain, $\psi_{(t)}$ is called the creep function, n_0 is the viscosity coefficient, t is time, and σ is stress.

The instantaneous strain component ϵ_0 is associated with bond angle distortion and bond stretching, $\psi_{(t)}$ is associated with the rotation of molecular segments or groups of segments, while the third term is associated with the large-scale relative movements of the whole molecule with respect to its neighbors.

All these terms appear to be associated with internal energies which to a great extent are temperature- and stress-dependent. In the examination of this equation one cannot help but to go back and compare term by term the basis of development of the rate equation for creep. Bond angle energy distortion can be compared to the Peierles force which holds a dislocation in its low energy position in a lattice. The creep function $\psi_{(t)}$ can be associated with dislocation tangles, and the large-scale relative movement of molecules can be associated with v (rate diffusion of a flow unit) which in turn can be associated with Fick's laws of diffusion, leading to a form of eq. (6) that was developed earlier.

Since the creep rate is a process of dislocation climbs in metals, it would not be surprising to find that, since polymers are long chain molecules, the movement of these chains past one another is also rate controlled. It is therefore, one of the goals of this paper to examine the activation energy $\Delta H'$ for the two polymers to find any correlation with stress or temperature.

Experimental Detail

Examination of creep data for metals shows that metals exhibit curves very similar to that of Figure 1. There is no real structure change, that is to say, crystal change, and resistance to deformation is caused by dislocations, tangles, inclusions, and vacancy diffusion if the temperature is low enough to discourage recrystallization.

The two plastics under investigation, however, do undergo a change from an amorphous or random material to that of a material showing orientation which can almost be called crystalline. Figure 2 shows a sample of polypropylene before and after deformation.

It may be that these two plastics might display not just the three creep stages as in the ideal curve but four states of creep, the second and third stages being those for the amorphous material and the oriented material, in that order. The creep studies for which this report is intended will be limited to the creep phenomena thought to be in the amorphous or random state material.

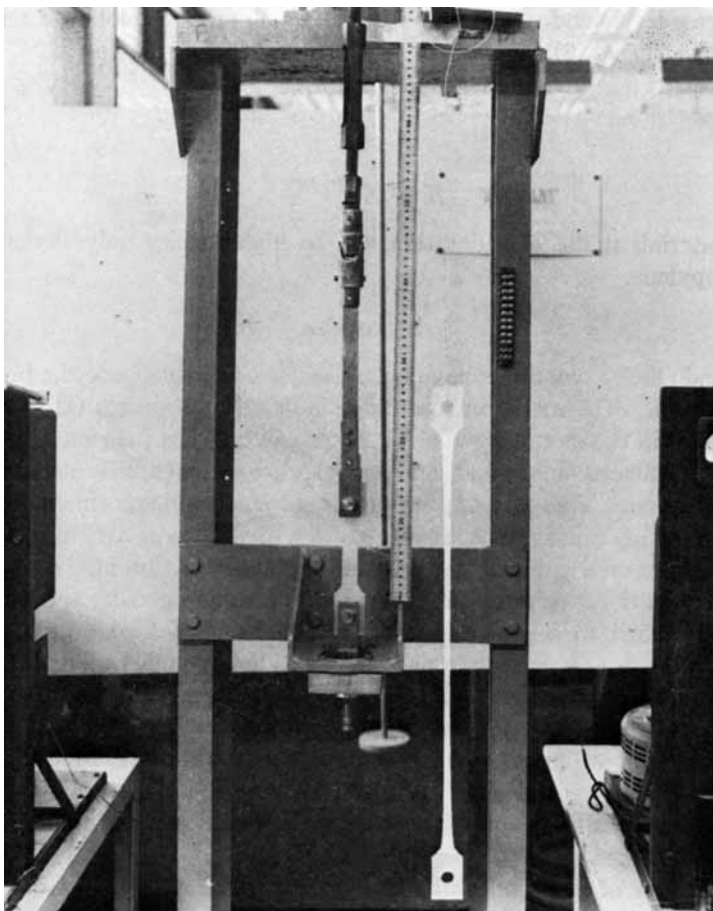There are many accepted methods for the determination of the activation

Fig. 2. Before and after picture of polypropylene.

energy ΔH. One method is the interrupted quench method where a material is subjected to a constant load at a constant temperature until a creep rate is established. Then it is immediately quenched to another temperature which is held constant. A second strain rate is established. With the help of eq. (6) the two different conditions are set up and equated to each other. Since it is assumed the process is only thermally activated, the constant K is the same for both conditions. ΔH is then computed.

A second method is that the tests are carried to failure which is called creep rupture. Here it is assumed that the constant K is a function of time. The two different conditions are then equated against each other, the only change is that K is replaced by the different rupture times. ΔH is then computed.

The intent of this study is to examine one of the proposed creep mechanisms which is not mentioned above. The object is to examine short-time

high-stress level conditions to see if the two polymers will follow a relationship such as in eq. (6):

$$\dot{\epsilon} = Ke^{-\Delta H'/RT}$$

where

$$K = Se^{\,B\sigma/RT}$$

The materials under consideration will be high-density polyethylene and polypropylene.

Apparatus

Several efficient methods have been designed to investigate the phenomena of creep. The method chosen here is based on a design that has long been in use in the metallurgy field. The basic unit is a fulcrum beam; the weights are placed on one end, and on the other end a cable is attached to a fixed specimen. This then applies a constant load to the specimen.

The weighing unit is basically a fulcrum with a ratio of 2.98 to 1 with the end cables set on a radius from the point of balance to eliminate a change in lever arm as the specimen is deformed. The cable opposite the weighted end is attached to a shutter that passes in front of a phototube. This shutter controls a beam of light passing from a light source to the phototube. The lower end of the shutter is connected to a bar which extends into the oil pot. At the end of this bar is the specimen which is fixed at the lower end. This phototube recorder is similar to that proposed by Scheer and Palmer.[10] The greatest asset this type of recording gear provides is that the instrument is fully automatic and produces a creep curve of specimen extension versus time.

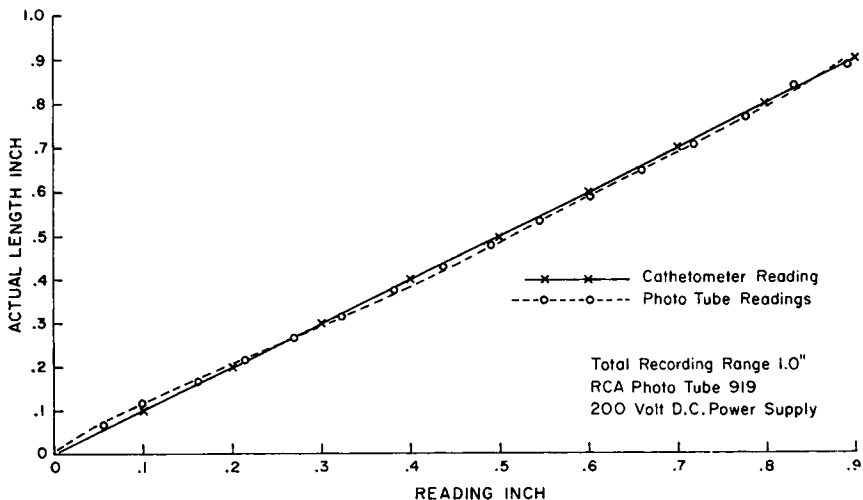Calibration of the phototube and readings taken by a cathetometer

Fig. 3. Calibration curve of cathetometer-phototube.

showed the phototube voltage output to be fairly linear (Fig. 3).   Figure
4 shows a schematic wiring diagram with the necessary power supplies re-
quired to activate this recorder.   The 250-V dc power supply is a Lambda
Regulated Power Supply Model 71.   The recorder is a standard 20 MV
range ̀Leeds and Northrup Speedomax Recorder, the light supply is a
collimated 6 V light bulb.   The phototube is an RCA 919 tube.

   Figure 5 shows a cutaway of the oil bath and the specimen mounting.
Although the two plastics in question are chemically inert to most solvents,
acids, and water, it was not known whether immersion in the silicone oil
bath would change the creep characteristics of the material.   In fact, much
work has been done in silicone oil baths.   In a review of brittle fracture of
glass by Phillips,[11] it has been shown that glass (and other materials)
materially increased in tensile strength properties on being tested when
completely immersed in water.   Since time would not allow testing both in
air and silicone oil to see if there was a material change in the properties,
it was elected to test the specimens in air by lowering the specimen down
inside a copper tube sealed at one end which is immersed in the oil bath.
A thermocouple attached to the specimen was used to check the tempera-
ture.   A Leeds and Northrup 110-V Controller was attached to the oil
bath for constant temperature control.

   The American Society for Testing and Materials has recommended
certain standards of procedure for long time creep tests of plastics under
compression or tension loads (ASTM designation D 674–56).   Even
though the ASTM recommends certain requirements and procedures to be
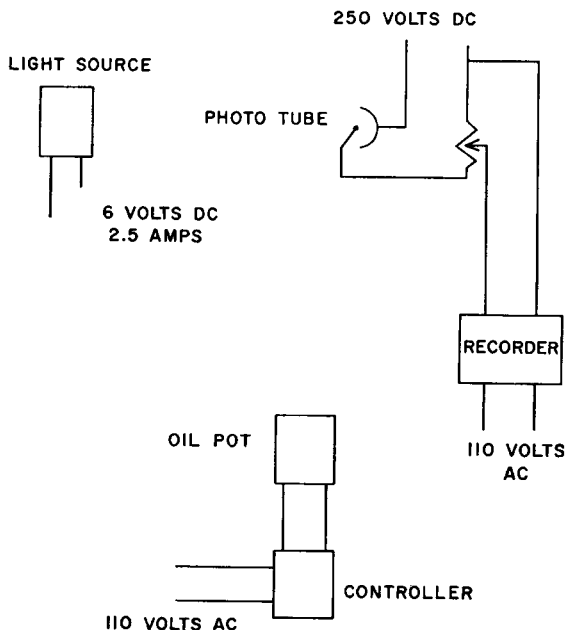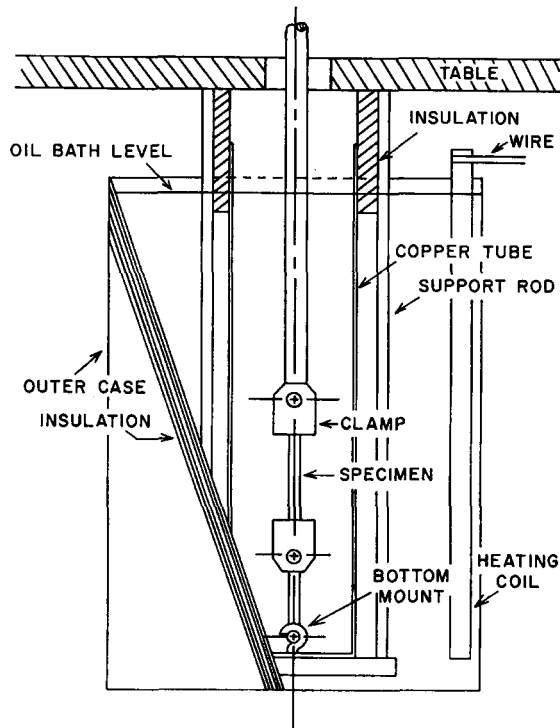

Fig. 4. Schematic wiring diagram.

Fig. 5. Mounted specimen and cutaway of oil bath.

followed, these are by no means standardized as concisely as the procedures used for metals. The ASTM standards were followed as far as temperature gradient of the specimen was concerned. For 36 hr the temperature gradient for a $2^{1}/_{2}$-in. length specimen was between 0.2 and 0.3°C. The specimen used for this study did not conform to the recommended ASTM standards. Since the phototube was limited to a 1-in. recording range and previous tests had shown that a constant strain rate was established in this range, the sample gage length was 1.625 in.

Results

When calculating an activation energy, it becomes necessary to define a few new terms. From an equation that was developed earlier,

$$\dot{\epsilon} = K e^{-\Delta H'/RT} \tag{10}$$

where

$$K = S e^{B\sigma/RT}$$

The terms, when rearranged, will yield eq. (11):

$$\dot{\epsilon} = S e^{-(-\Delta H' + B\sigma)/RT} \tag{11}$$

If one considers the term $(\Delta H' - B\sigma)$ to be a form of activation energy which is dependent on stress, then one can consider this to be a process activation energy ΔH, where

$$\Delta H = (\Delta H' - B\sigma) \tag{12}$$

Since the constant B is a material constant which is dependent only on the material, it can be seen that the process energy ΔH will equal the material energy $\Delta H'$, if the state of stress of the material is zero.

Another consideration is the structure factor S. It has been shown earlier that there is a structure change in both materials as deformation increases. This parameter can be eliminated by assuming that the structure change is proportional to the strain and suggests that for a given strain at constant stress the process activation energy could be calculated by setting up two contrasting temperature conditions for which the stress and strain are constant:

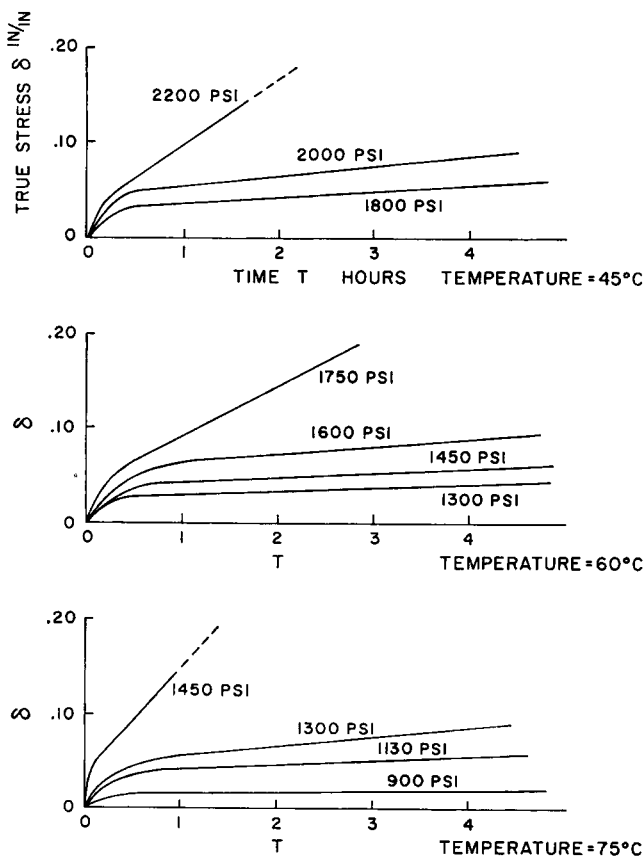$$\frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{Se^{-\Delta H'/RT_1}}{Se^{-\Delta H'/RT_2}} \tag{13}$$
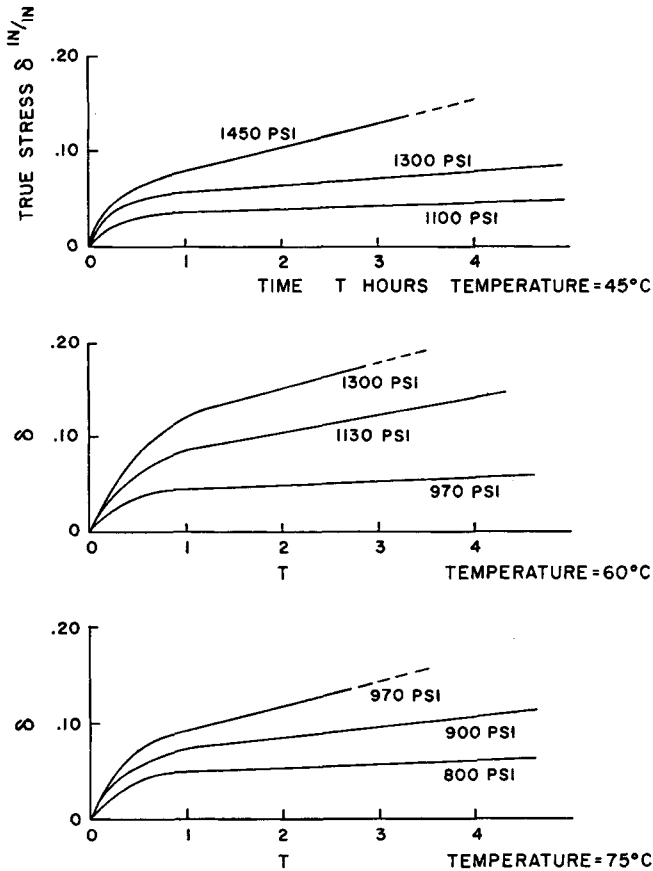

Fig. 6. True strain vs. time curve (polypropylene).

Fig. 7. True strain vs. time curve (polyethylene).

Rearranging yields

$$\ln\,(\dot\epsilon_1/\dot\epsilon_2)\ =\ -(\Delta H'/R)\,[(1/T_1)(1/T_2)]\tag{14}$$

and

$$\Delta H'\ =\ [T_2T_1/(T_2\ -\ T_1)]R\ln(\dot\epsilon_1/\dot\epsilon_2)\tag{15}$$

From the actual creep curves (Figs. 6 and 7), the instantaneous creep rates $\dot\epsilon$ and true strain δ were calculated at various points along each curve. The instantaneous creep rate and true strain were plotted as shown in Figures 8 and 9, from which were calculated the process energies $\Delta H'$. Considering a strain after the point at which the creep rates become constant will yield the energy $\Delta H'$ listed in Table I. The values from Table I for stress versus $\Delta H'$ are plotted in Figure 10. Extrapolating the data to zero stress will yield the activation energy which can be classified as a true activation energy of the material.
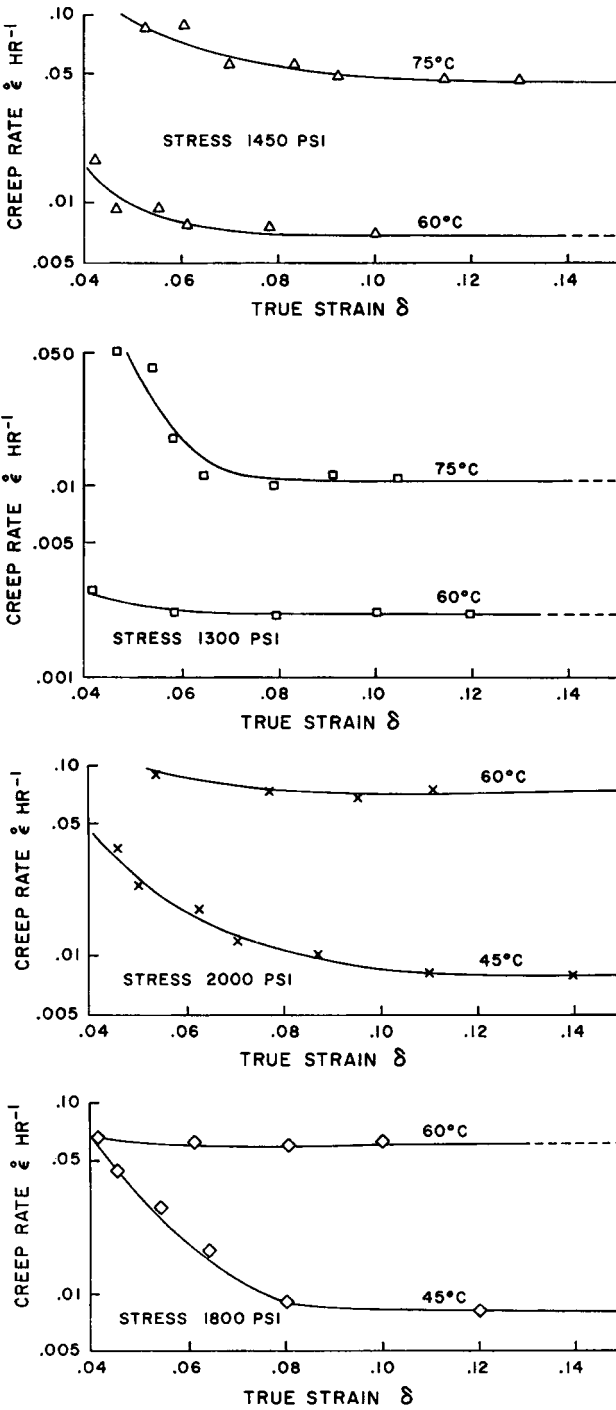
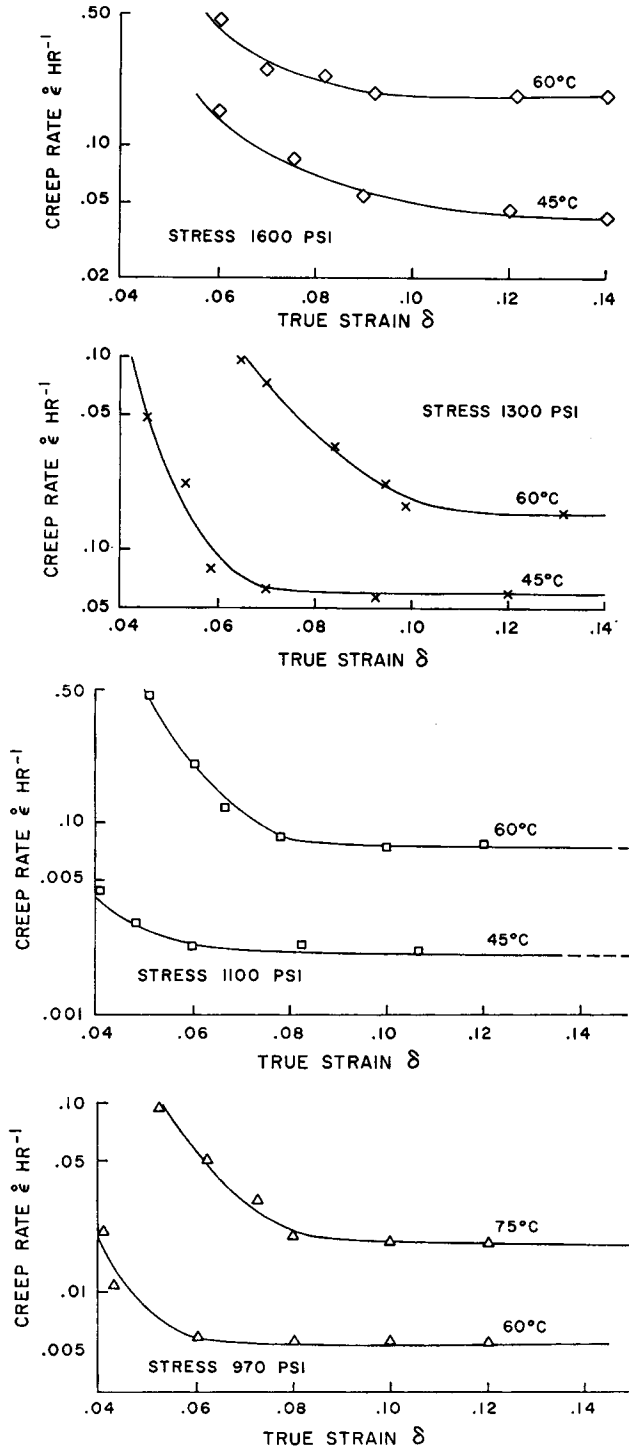Fig. 8. Creep rate vs. true strain curve (polypropylene).

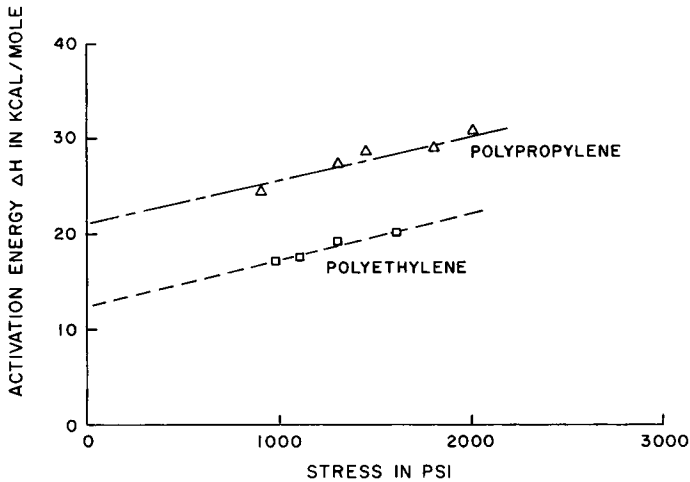Fig. 9. Creep rate vs. true strain curve (polyethylene).

Fig. 10. Process activation energy vs. applied stress curve.

TABLE I
Calculated Values for Activation Energies $\Delta H'$

Polymer	Stress, psi	$\Delta H'$, kcal/mole	True ΔH from Fig. 10, kcal/mole
Polypropylene	900	24.8	
	1300	27.1	21.5
	1450	28.6	
	1800	29.0	
	2000	30.8	
Polyethylene	970	17.0	
	1100	17.7	12.1
	1300	19.0	
	1600	20.1	

High-temperature viscosity measurements of high-density polyethylene have given activation energies of 12–14 kcal/mole at temperatures in excess of 400°K.[12–14] The extrapolated value of ΔH for polyethylene from Figure 10 agrees very favorably with accepted published values.

Conclusions and Recommendations

The main objective of this experiment was to calculate the activation energy of two different thermoplastic resins by use of a simply designed experimental set-up that would establish a constant creep rate for a high-stress, short-time creep test. This method gives a recorded trace of the whole history of a particular run, and is adequate for most of this work.

Although the apparatus gives satisfactory results for plastics, it is not suitable for work with metals or other material with a high modulus of elasticity. The recording ranges along with the light controlling source

will have to be modified to increase the ability to detect smaller changes in deformation.   Comparing the recorded creep traces at the same stress and temperature conditions showed very good agreement over 8-hr tests, indicating the data to be very reproducible.

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