

The Modulus and Yield Stress of Glassy Poly(methyl Methacrylate) at Strain Rates up to 10^3 Inch/Inch/Second

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Synopsis

Specimens of poly(methyl methacrylate) (PMMA) were compressed at nominally constant strain rates ranging from 10^{-5} to 10^3 in./in./sec. at 0, 22, 50, and 115°C. A plot of stress at a small fixed strain (2%) and constant temperature versus logarithm of strain rate is sigmoidal in shape and, furthermore, time-temperature superposition could be used to construct a master curve of stress versus temperature-compensated strain rate. It is suggested that the sigmoidal curve is a manifestation of the β transition in PMMA, and this is supported by the measured value of activation energy and the strain rate value at the point of inflection on the curve. By contrast, yield stress varies linearly with $\log \dot{\epsilon}$. Time-temperature superposition could not be applied. Rationalizing on the basis of the high stress form of the Eyring equation, yielding is by a yet unspecified molecular mechanism in which activation volume has the order of magnitude of a monomer unit but increases with increasing temperature.

INTRODUCTION

The intent of the present work was to study both the small strain (modulus) and the large strain (yield) behavior of glassy poly(methyl methacrylate) (PMMA) compressed at large, constant strain rates (up to 10^3 in./in./sec.) and to correlate the results with those reported in the large body of literature on dynamic (oscillatory) measurements and stress relaxation.¹⁻⁷

Smith has pointed out that in linear viscoelastic theory the tangent modulus in a constant strain-rate deformation is equal to the relaxation modulus $G(t)$ at a corresponding time.⁸ Measurements of relaxation modulus cannot be made at times shorter than the load-up time, so that, unless low-temperature data are available and resort is made to time-temperature superposition, this correlation cannot be used directly to obtain high strain-rate moduli. However, $G(t)$ is approximately $G'(w)$, where $w = 1/t$, the storage modulus,⁹ so that constant strain-rate moduli at high strain rates can be compared with the results of dynamic (oscillatory) modulus measurements. Of particular interest is that dynamic

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measurements on PMMA have clearly established a secondary (β) transition (attributed to movement of the ester side groups). This should be reflected in a plot of modulus, or stress at a fixed strain, in a constant strain-rate test, versus strain rate as a sigmoidal curve. Furthermore, the inflection point on the curve should shift along the strain-rate scale with temperature, just as does the inflection point in the plot of $G'(w)$ versus frequency, or the peak in the loss tangent for the β transition.¹

It seems intuitively obvious that side-group movement will not make a major contribution to strain at yield. Gross movement of molecular chains is required, which requires a different treatment.¹⁰ Yielding at constant strain rates has been studied by a number of workers.^{6,11-13} Lohr⁶ applied time-temperature superposition to plots of yield stress (σ_y) versus strain rate ($\dot{\epsilon}$) at different temperatures and approximated the master curve by $\sigma_y = A + B \log \dot{\epsilon}$, a relation similar in form to the high stress form of the Eyring equation and one that is followed very often by metals.¹⁴⁻¹⁶ There are discrepancies, however; for the high stress form of the Eyring equation does not predict time-temperature superposition. In the present paper the dependence of yield-stress on strain rate and temperature is analyzed on the basis of the Eyring equation, and the variation with temperature of activation volume is calculated.

EXPERIMENTAL

Material

Commercial Plexiglass II, supplied by Cadillac Plastic and Chemical Company as 0.5 in. diam. rod, was machined to compression specimens 0.375 in. diam. and 0.50 in. long. After machining, the specimens were stored in a desiccator for at least 500 hr., to give a uniform, low moisture content, which was not measured. The molecular weights were measured as, number-average, 7.2×10^5 and, weight-average, 4.4×10^6 .

Procedure

Three testing machines were used to cover the total strain-rate range (10^{-5} to 10^3 in./in./sec.): between 10^{-5} and 10^{-2} in./in./sec. an Instron Machine; at approximately 10 in./in./sec., a medium-rate machine, which is a gas-operated device similar in principle to machines used by Clark and Wood¹⁷ and Campbell and Marsh,¹⁸ in which the specimen is compressed by a piston traveling at a controlled velocity;¹⁹ and between 10^2 and 10^3 in./in./sec., a Split Hopkinson Bar. In the latter technique, stress-strain curves are derived by considering the transmission of a stress wave through the specimen, which is sandwiched between two elastic bars.¹⁹ The method of data-reduction for this machine and the medium-rate machine can be found in Maiden and Green.²⁰

In all cases correction was made for machine stretch. Repeatability fell within 3% for the Instron and medium-rate machine and within 10%

for the Split Hopkinson Bar. Temperatures of 50, 82, and 115°C. were maintained by a furnace surrounding the specimen. No provision was made for controlling the humidity or, therefore, the moisture content during testing, except that the specimens were not removed from the desiccator until the beginning of the test. A few additional stress-strain curves were obtained at 0°C. in a bath of water and ice.

RESULTS AND DISCUSSION

The plot of stress σ at 2% strain versus the logarithm of strain-rate ($\log \dot{\epsilon}$) is sigmoidal in shape (Fig. 1). At a larger strain, say 4%, the S shape is less pronounced and finally the plot of yield stress σ_y versus $\log \dot{\epsilon}$ is approximately linear (yield stress was defined as the stress at the maximum on the stress-strain curve, which is at approximately 8-10% strain). The same trend was found previously in a different batch of plexiglass.²⁰ In that work an Instron Machine was not used; tests at low rates were made on the medium-rate machine. Therefore, the sigmoidal curves cannot be attributed to the use of different machines over the different ranges of strain-rate.

Specimens deformed in the Split Hopkinson Bar do not reach a uniform stress until after a number of wave reflections, so that stress at 2% strain calculated by the usual analysis²⁰ is in some doubt. For this reason a few specimens were tested in which stress was measured by a quartz crystal located between specimen and anvil bar and strain was measured by a strain gage attached to the specimen as close as possible to the quartz crystal. A strain of 2% was reached before the first wave reflection, and stress at this strain was 22 ksi. The strain rate was approximately 2×10^3 in./in./sec., so that measurements by this technique were only 10% higher than by the usual method (Fig. 1). The result that the plot of σ

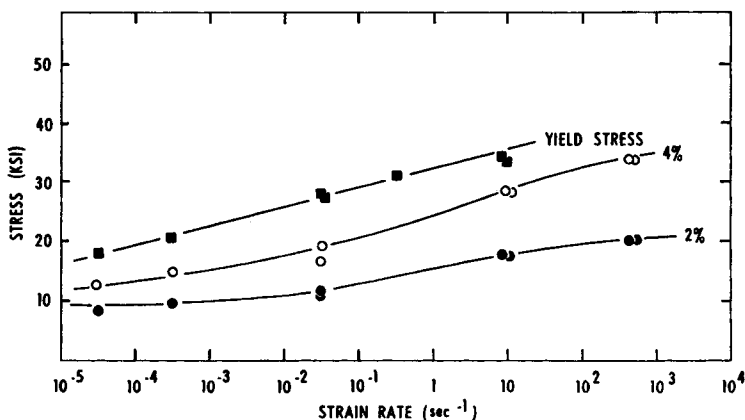


Fig. 1. Stress versus strain rate for poly(methyl methacrylate) at 2% strain, 4% strain and yield.

at 2% strains versus logarithm of strain rate is sigmoidal in shape does not change.

As mentioned previously, such S-shaped curves of σ at constant strain (or modulus) versus $\log \dot{\epsilon}$ can be rationalized by considering the operation of a specific (secondary) relaxation mechanism, perhaps in PMMA, the movement of ester side groups.¹ At low strain rates the ester groups have time to readjust and relax the stress; at higher rates they are "frozen," and stress is higher for the same strain. If this suggestion is to be supported, then, first, the strain rate at the point of inflection on the curve of σ versus $\log \dot{\epsilon}$ should relate to the frequency at the secondary transition observed in plots of storage modulus versus frequency² and, second, the inflection strain rate should shift with temperature, just as does the dynamically observed transition.¹ From Figure 1 the inflection strain rate is approximately 0.3 in./in./sec. With $\epsilon = 2\%$ the equivalent

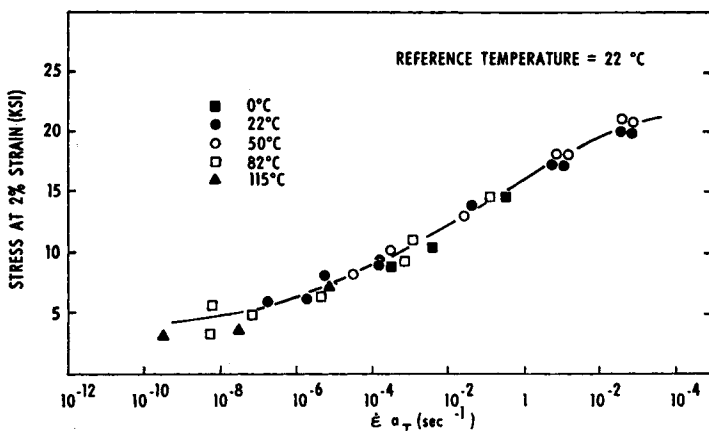


Fig. 2. Stress at 2% strain versus temperature-compensated strain rate $\dot{\epsilon} a_T$ for poly(methyl methacrylate) in compression.

time is 0.06 sec., and the equivalent frequency is $1/2\pi \cdot 0.06 \approx 2.6$ cps, which can be compared with the value of approximately 20 cps found by Koppelman for the frequency of the inflection point in the storage modulus $G'(w)$ at the β transition.² It is suggested that at least part of the reason for the discrepancy might be found in the presence of second components in the PMMA, such as impurities and moisture. For a verification of the temperature dependence of the inflection strain rate, curves of σ (at 2% strain) versus $\log \dot{\epsilon}$ at 0, 22, 50, 80, and 115°C. were shifted along the $\log \dot{\epsilon}$ axis to give a master curve (Fig. 2). The activation energy calculated from the plot of shift factor ($\log a_T$) versus reciprocal temperature (Fig. 3) is 18 kcal./mole. This agrees quite well with the value of 20 quoted by Deutsch et al. on the basis of dynamic measurements.¹ It is concluded that the sigmoidal curve of σ versus $\log \dot{\epsilon}$ observed at small strains is another manifestation of the β transition that has been observed in dynamic

oscillatory studies and has been attributed to movement of ester side groups.

As yielding sets in, side-group motion is no longer the predominant molecular movement, and the S shape is smoothed out. Yielding must involve the straightening and movement of molecular chains.¹⁰ At all

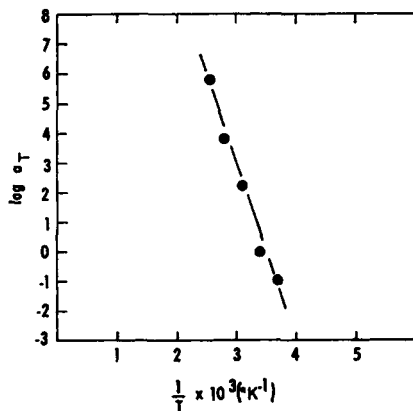


Fig. 3. Logarithm of shift factor $\log a_T$ versus reciprocal temperature. Shift factors were calculated during construction of Figure 2.

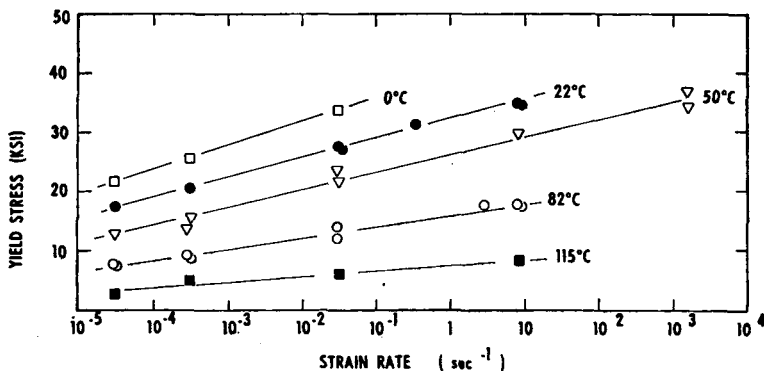


Fig. 4. Yield stress versus strain rate for poly(methyl methacrylate) in compression at 0, 22, 50, 82, and 115°C.

temperatures and over the strain-rate range where it was experimentally possible to measure yield stress, σ_y varies approximately linearly with $\log \dot{\epsilon}$. However, the slope varies with temperature, so time-temperature superposition is not possible (Fig. 4). From reaction-rate theory

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp \left\{ -\frac{(U_0 - \sigma_y v)}{kT} \right\} \tag{1}$$

where U_0 is an activation energy for yielding in the absence of stress; v is an activation volume, k is Boltzmann's constant, T is the absolute temper-

ature, and $\dot{\epsilon}_0$ is a function of the size and number of sites at which molecular movement occurs. Rearranging gives

$$\sigma_y = U_0/v + (kT/v) \ln \dot{\epsilon}/\dot{\epsilon}_0 \quad (2)$$

which has the form experimentally observed and is incidentally observed often in metals.¹⁴⁻¹⁶ Not as in metals, however, $[\partial\sigma/(\partial \ln \dot{\epsilon})]_T$ decreases with increasing temperature, which requires that activation volume should increase. An average value of v is 3×10^{-22} cm.³, which is of the order of magnitude of one monomer unit.¹⁰ The conclusion is that yielding is by a still unspecified mechanism, for which activation volume increases with temperature.

SUMMARY

At small strains the curve of stress versus the logarithm of strain rate is sigmoidal in shape, and this is suggested to be a result of the β transition in PMMA. At larger strains the effect of the β transition is masked, as movement of molecular chains becomes more predominant. Yield stress varies linearly with logarithm of strain rate, but activation volume, though of the order of the monomer size, increases with increasing temperature.

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