Tensile Yield in Phenolphthalein Polyether Ketone

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SYNOPSIS

Uniaxial tension tests to the yield point were performed on phenolphthalein polyether ketone (PEK-C) from room temperature to near the glass transition temperature (T_g) at a constant rate of 0.02 min^{-1}. At room temperature, some measurements were also made at strain rates from 0.002 min^{-1} to 2 min^{-1}. Yield stress was a linear function of temperature and log strain rate. The temperature and the strain rate dependence of yield stress could be modeled using Eyring theory. Yield energy was found to be a linear function of temperature. Young's modulus, yield strain, elastic strain, and plastic strain all decreased with temperature. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Phenolphthalein polyether ketone (PEK-C) is an amorphous material
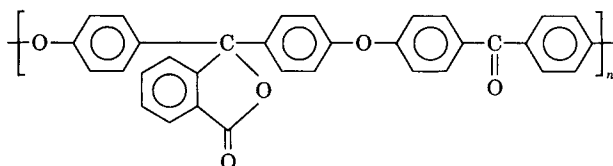
with a high T_g and can be used as an engineering thermoplastic and matrix of composites. As PEK-C is being increasingly used in engineering applications, there is also a need to understand temperature and strain rate effects on the yield properties of it. In this study, the tensile yield properties— yield stress, yield energy, yield strain, and Young's modulus—were determined as a function of temperature from room temperature to near the glass transition temperature. Some measurements were also made as a function of strain rate.

Many researchers[1-5] have chosen to consider yielding in polymers as a thermally activated process, following the formalism developed by Eyring and co-workers[6] for creep at constant applied stress.

On this dynamical view of the yield process, the yield stress denotes the point at which the internal viscosity falls to the value where the plastic strain rate equals the applied strain rate, $\dot{\epsilon}$. We can then write

$$\dot{\epsilon} = \dot{\epsilon}_o \exp\left(-\Delta H/kT\right) \sinh\left(\sigma_y v/kT\right) \quad (1)$$

where ΔH is the activation energy, which is a measure of the energy required by the segments of yield stress and thermal energy to jump from one equilibrium position to another, σ_y is the yield stress (usually tensile or compressive), v is the volume of a polymer segment involved in the yield process (activation volume), and $\dot{\epsilon}_o$ is a constant pre-exponential factor. This gives the yield stress as

$$\sigma_y = (kT/v) \sinh^{-1}\left[(\dot{\epsilon}/\dot{\epsilon}_o) \exp\left(\Delta H/kT\right)\right] \quad (2)$$

which for high values of stress reduces to

$$\sigma_y = \Delta H/v + (kT/v) \ln\left(2\dot{\epsilon}/\dot{\epsilon}_o\right) \quad (3)$$

Extensive studies by Roetling[3] and Bauwens-Crowet et al.[4] have shown that the yield stresses in general increase more rapidly at high strain rates and low temperatures than indicated by eq. (3). It has therefore been proposed that there is normally more than one activated rate process present with all species of flow units moving at the same rate, because the stresses are additive. Equations (2) and (3) can then be combined for two activated processes to give

$$\sigma_y = \Delta H_1 / v_1 + (kT/v_1) \ln (2 \, \dot{\epsilon}/\dot{\epsilon}_{o1})$$

$$+ kT/v_2 \sinh^{-1} [(\dot{\epsilon}/\dot{\epsilon}_{o2}) \exp (\Delta H_2/kT)] \quad (4)$$

where process 1 is considered to be in the high-stress condition so that the sinh term can be simplified to an exponential.

The success of this approach for many polymers has led us to analyse the yield behavior of amorphous PEK-C.

EXPERIMENTAL

Uniaxial tensile tests were made on phenolphthalein polyether ketone (PEK-C) performed in an Instron Universal Testing Machine model 1121 from room temperature to near the glass transition temperature. Some measurements were also made at the strain rates from 0.002 to 2 min^{-1}. The dumb-bell tensile specimens were used: thickness, 3.78 mm; width, 3.14 mm; gauge length, 25 mm. Five replicates were run at each temperature and strain rate, and all five specimens were put into the oven simultaneously.

Four parameters were determined for each stress–strain curve: yield stress, yield strain, Young's modulus, and yield energy. Yield stress and yield strain were determined by the inspection of the stress–strain plot. Young's modulus was calculated from the initial slope of the plot. Yield energy per unit volume of polymer was calculated from the area under the stress–strain curve from zero stress to the stress maximum.

RESULTS AND DISCUSSION

Yield Stress

In this study, the yield stress was calculated as the load at the first maximum on the load–extension curve, divided by the reduced cross-sectional area, calculated from the strain at this point, assuming deformation at constant volume. The significance of this definition of the yield point lines is the fact that when the load is stationary, the elastic strains in the material and in the tensile testing machine are constant. Thus, at the yield stress, the plastic strain rate produced in the sample by the stress is exactly equal to the imposed strain rate.

In general, the yield stress, σ_y, of a polymer is a function of both temperature and the entire strain history up to and including the yield point. Thus, a complete theory of the yield behavior would have to

embrace the nonlinear viscoelastic aspects and include the effects of interrupted loading programs, etc. We assumed that the yield stress as measured in these experiments is a function only of strain rate and temperature.

Figures 1 and 2 showed the yield stress as a function of temperature and strain rate, respectively. The yield stress decreased with increasing temperature and decreasing log strain rate. The temperature and the strain rate dependence of the yield behavior of polymers have been modeled using the Eyring theory of viscosity.[7-9] For high values of stress, it can be expressed by eq. (3). For a given material and for tests conducted at constant strain rate, the Eyring model predicts a linear relationship between yield stress and temperature. The results in Figure 1 confirmed the linear relationship for PEK-C of this study. Equation (3) indicates that the plot of σ_y/T versus ln $\dot{\epsilon}$ gives a linear relationship (Fig. 2). Values of ΔH and v can be obtained from the slope and the intercept of Figures 2 and 1; they are 60.9 kJ/mol and 0.9 nm^3, respectively. The value of ΔH for the activation energy is consistent with the α transition's.[10] This indicates that at high values of stresses, the yield process is governed by the α transition.

Young's Modulus

Young's modulus was calculated from the initial slope of the stress–strain plot. The Young's modulus for PEK-C as a function of temperature is shown in Figure 3. It decreases with increasing temperature.

Yield Energy

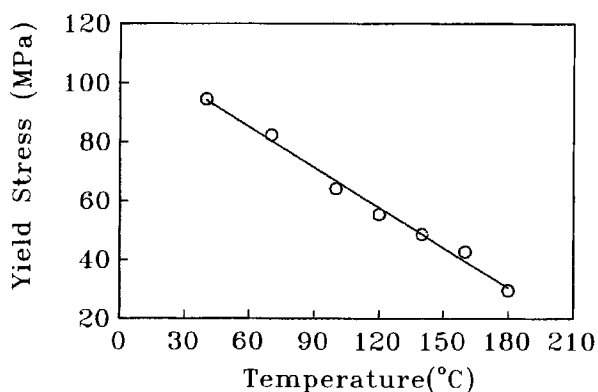Yield energy is calculated from the area under the stress–strain plot, and should therefore be related
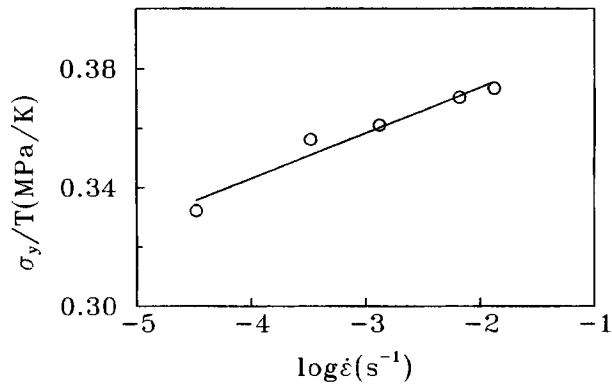

Figure 1   Yield stress vs. temperature.

Figure 2 Ratio of yield stress to temperature as a function of logarithm of strain rate for PEK-C.

Figure 4 Temperature-dependence of yield energy (E_y).

to the stress and strain. The temperature-dependence of the yield energy of PEK-C is shown in Figure 4. It was shown that the yield energy, E_y, was a linear function of absolute temperature, T.

Starita and Keaton[11] explained the relationship between the molar yield energy, E'_y, and deformation temperature using the following equation:

$$E'_y = b/b' \int_T^{T_g} \left(\frac{\partial U}{\partial T}\right)_p dT \qquad (5)$$

where b = fraction of thermal energy available to overcome activation energy barrier for flow; b' = fraction of mechanical energy available to overcome the same barrier; the sum of b and b' is equal to ΔH in the Eyring equations; and $\left(\dfrac{\partial U}{\partial T}\right)_p$ = the change in internal energy with temperature at constant pressure. Their reasoning is that the molar
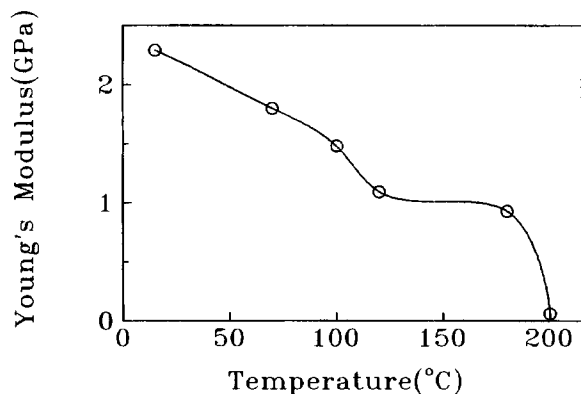

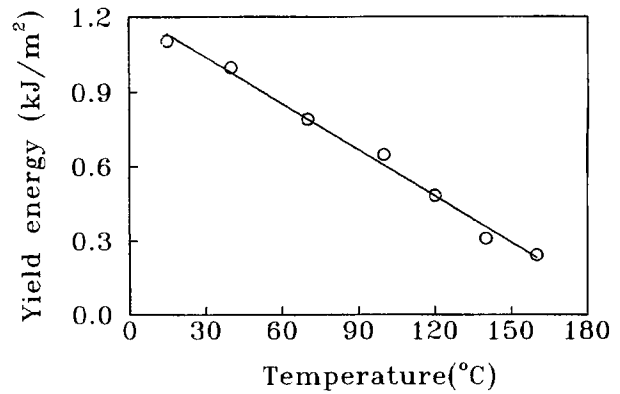**Figure 3** Young's modulus of PEK-C as a function of temperature.

energy causing a glassy polymer to flow or yield at a temperature below its glassy transition can be directly related to its internal energy. They further reduced the equation to measurable quantities through the use of thermodynamic identities given below:

$$E'_y = b/b' \int_T^{T_g} (C_p - \beta \rho v) \, dT \qquad (6)$$

where C_p = molar heat capacity at constant pressure, β = coefficient of volume expansion, and v = molar volume. More recently, Macosko and Brand[12] reduced eq. (6) to the following formula for amorphous polymers:

$$E'_y = b/b'(\bar{C}'_p - \bar{\beta}\rho\bar{v})(T_g - T) \qquad (7)$$

They further contended that at atmospheric pressures, the average molar heat capacity, $\bar{C}'_p$, was sufficiently greater than the quantity $\bar{\beta}\rho\bar{v}$ that eq. (7) could be further simplified:

$$E_y = (b/b')\bar{\rho}\bar{C}_p(T_g - T) \qquad (8)$$

where T_g is the glass transition temperature, $\bar{\rho}$ average density, $\bar{C}_p$ = average heat capacity per unit mass over the temperature range from T to T_g, and E_y = yield energy per unit volume. The temperature-dependence of the yield energy is:

$$- dE_y/dT = (b/b')\bar{\rho}\bar{C}_p \qquad (9)$$

If we know the slope of the yield energy versus temperature plot (dE_y/dT), the average heat capacity ($\bar{C}_p$), and the average density ($\bar{\rho}$), the value of $b/$

Table I Values of b/b' for Some Polymers

Polymers	b/b'
PCTFE	0.007
PVF$_2$	0.015
Polypropylene	0.012
Polypropylene	0.011
Poly(4-methyl pentene-1)	0.003
Nylon 6,6	0.007 (up to 160°C)
	0.055 (above 160°C)
PEK-C	0.02

b' can be obtained. A small value of b/b' implies that thermal energy is less effective compared with mechanical energy in producing yield than a large value of b/b' would imply. Values of b/b' of some polymers are shown in Table I. In glassy amorphous polymers, b/b' is larger than for semicrystalline polymers, and varies between 0.02 and 0.03.[13] Thus, mechanical energy is even less effective compared with thermal energy in semicrystalline polymers than in glassy amorphous polymers.

Yield Strain

Figure 5 shows the variation of yield strain as a function of temperature, but similar results would be obtained by changing the strain rate and maintaining a constant temperature. To examine this behavior more closely, it is of interest to look at the temperature-dependence of elastic and plastic components of the yield strain. Elastic strain can be determined from the dimensionless ratio of yield stress to initial Young's modulus, σ_y/Y. Plastic strain can be estimated by assuming the yield strain is the sum of an elastic component and a plastic component.
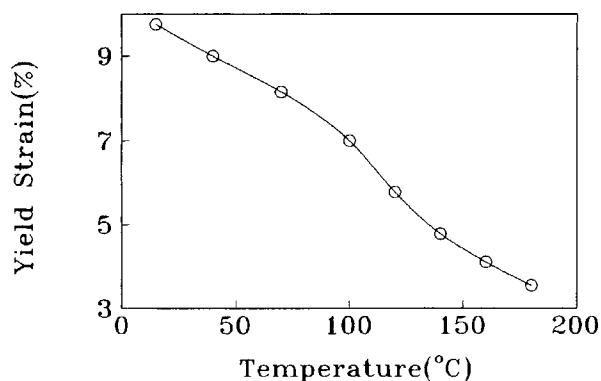
Figure 5 Temperature-dependence of yield strain.
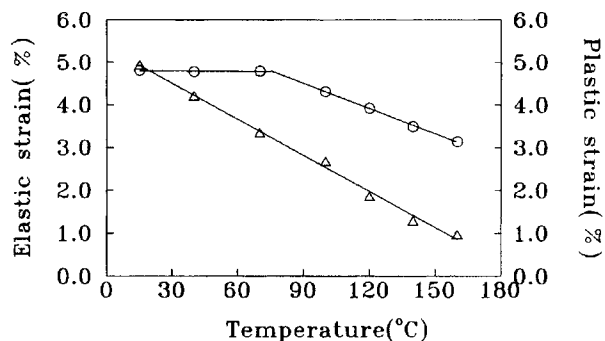
Figure 6 Elastic strain and plastic strain as a function of temperature.

$$\epsilon_y = \epsilon_{el} + \epsilon_{pl} \tag{10}$$

where the elastic strain is given by

$$\epsilon_{el} = \sigma_y/Y \tag{11}$$

Temperature-dependence of elastic strain and plastic strain are all shown in Figure 6. Both of them decrease with increasing temperature, but the temperature-dependence of elastic strain changes at about 70°C.

Yield strain is the only yield property that has a qualitatively different temperature-dependence in semicrystalline polymer than in glassy amorphous polymers. The yield strain in glassy polymers *decreases* with increasing temperature, while yield strain *increases* with increasing temperature for crystalline polymers.[13] In glassy amorphous polymers, the yield process, whatever it may be in detail, occurs at a given average intermolecular separation so that thermal expansion decreases the required mechanically induced strain. Thus, the yield strain decreases with increasing temperature in glassy amorphous polymers.

CONCLUSIONS

Tensile measurements were made on phenolphthalein polyether ketone (PEK-C) from room temperature to near the glass transition temperature. Some measurements were also made as a function of strain rate. Based on these measurements, the following conclusions were reached:

1. Yield stress is a linear function of temperature and log strain rate. The temperature and the strain rate dependence of the yield stress can be modeled by Eyring theory, and mean

time activation volume and activation energy can be obtained.

2. Yield energy is a linear function of temperature; from the slope, the ratio of thermal to mechanical energy required to produce yielding can be obtained.

3. Young's modulus, yield strain, elastic strain, and plastic strain all *decrease* with *increasing* temperature.

REFERENCES

1. Y. S. Lazurkin, *J. Polym. Sci.,* **30,** 595 (1958).
2. R. E. Robertson, *J. Appl. Polym. Sci.,* **7,** 443 (1963).
3. J. A. Roetling, *Polymer,* **6,** 311 (1965).
4. C. Bauwens-Crowet, J. A. Bauwens, and G. Homes, *J. Polym. Sci.,* **A27,** 735 (1963).
5. R. N. Haward and G. Thackray, *Proc. Roy. Sci.,* **A302,** 453 (1968).
6. G. Halsey, H. J. White, and H. Eyring, *Test Res. J.,* **15,** 295 (1945).
7. H. Eyring, *J. Chem. Phys.,* **4,** 283 (1936).
8. C. Bauwens-Crowet, J.-C. Bauwens, and J. G. Homes, *J. Mater. Sci.,* **7,** 176 (1972).
9. T. E. Brady and G. S. Y. Yeh, *J. Macromol. Sci. Phys.,* **B9,** 659 (1974).
10. Y. C. Han, Y. M. Yang, and B. Y. Li, *J. Appl. Polym. Sci.,* submitted for publication.
11. J. M. Starita and M. Keaton, *S. P. E. Tech. Papers,* **29,** 67 (1971).
12. C. W. Macosko and G. J. Brand, *Polym. Eng. Sci.,* **12,** 444 (1972).
13. S. Matsuoka, in *Failure of Plastics,* W. Brostow and R. D. Corneliussen, Eds., Macmillan, New York, 1986, pp. 24–59.