

The Brittle Fracture of Amorphous Thermoplastic Polymers

A. T. DiBENEDETTO and K. L. TRACHTE,* *Materials Research Laboratory, Washington University, St. Louis, Missouri*

Synopsis

The brittle fracture properties of polyphenylene oxide, polysulfone, polycarbonate, and poly(methyl methacrylate) thermoplastic polymers were investigated over a wide range of temperatures. Fracture energy measurements were made using double edge-notched tensile samples. Tensile strength, tensile strain, and initial elastic modulus were measured for calculation of the fracture energy and further analysis of the polymer behavior. It was found that mechanical transitions in the tensile properties corresponded reasonably well with transitions in the fracture energy in the temperature range investigated. Fracture surface photographs permitted visual analysis of the fracture process. It was found that the roughest fracture surface corresponded to the maximum in the fracture energy for a given polymer. A theory for prediction of polymer tensile yield strain is presented, based on the volume dilation concept. The implications of this theory are discussed in terms of the crack tip flow process leading to brittle fracture.

INTRODUCTION

There is substantial evidence in the literature that viscous flow or plastic deformation occurs near the tip of an advancing crack in glassy amorphous polymers. The measured fracture energy for glassy polymers is approximately 1000 times greater than the theoretical surface energy of the solid. This increase has been attributed to the energy requirements for viscous flow and polymer crazing at the crack tip.

It is reasonable to expect that, as plastic deformation becomes more inhibited by successive hindrance of the side group and main chain motions of the polymer molecule, the fracture energy should decrease toward the theoretical surface energy, which involves only breaking of atomic bonds.

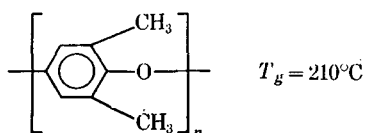
Unexpectedly, it has been found that for poly(methyl methacrylate) (Plexiglas II UVA), the fracture energy continues to increase with decreasing temperature, at least to -50°C . A threefold increase in fracture energy was found as the test temperature was reduced from the main glass temperature, T_g , at 105°C to -50°C . These data are in agreement with previous work^{1,2} on the same grade polymer. This is surprising in that one would expect plastic deformation to be already considerably reduced at this

* Present address: Esso Research Corporation, Baytown, Texas.

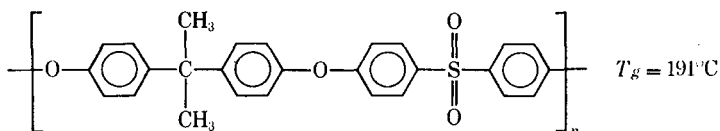
lower temperature, which is about 145°C below the main glass temperature.

Since it was presumed that a maximum in the fracture energy must occur somewhere between the main glass temperature and absolute zero temperature, three amorphous polymers with high main glass temperatures were investigated, allowing a wide temperature range for testing. The four polymers investigated were:

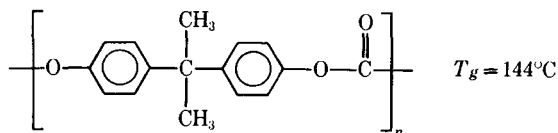
1. Polyphenylene oxide (General Electric Grade 631-111):



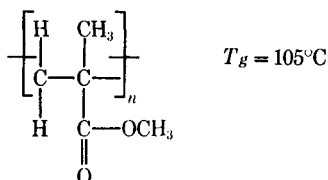
2. Polysulfone (Union Carbide Grade 1700):



3. Polycarbonate (General Electric "Lexan")



4. Poly(methyl methacrylate) (Rohm and Haas Plexiglass II UVA):



THEORY

The fracture mechanics of Irwin³ were used to calculate the plane strain fracture energy γ required for catastrophic failure of the polymers. The sample geometry used is shown in Figure 1. An iterative technique utilizing a computer was used to solve Irwin's approximation for the chosen geometry:

$$K_{Ic} \simeq \sigma_n \left\{ W \left[\tan \frac{\pi [a + (K_{Ic}^2 / 2\pi \sigma_y^2)]}{W} + 0.1 \sin \frac{2\pi [a + (K_{Ic}^2 / 2\pi \sigma_y^2)]}{W} \right] \right\}^{1/2} \quad (1)$$

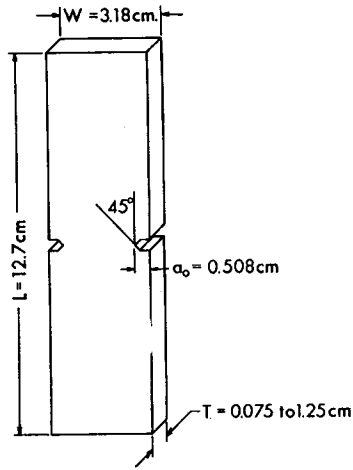


Fig. 1. Sample geometry for fracture energy test.

where K_{Ic} = critical stress intensity parameter at the crack tip; σ_n = brittle tensile strength of a notched sample, based on the gross cross-sectional area; W = sample width; a = half-crack length at fracture; and σ_y = tensile yield strength at the notch tip. The plane strain fracture energy γ was calculated from

$$\gamma = K_{Ic}^2(1 - \nu^2)/2E \quad (2)$$

where ν = Poisson's ratio of the polymer (taken as 0.35 for the four polymers); and E = initial elastic modulus of the polymer.

From the notched sample, the experimental values of W , σ_n , and a were obtained. The brittle tensile strength, σ_n , was calculated directly from the load-deformation curve for the sample. The value of a , which includes the initial machined notch length and the slow crack growth prior to failure, was measured from the fractured sample surface to the nearest ± 0.003 cm under a microscope.

The values of σ_y used in the calculation of γ were obtained from a standard ASTM tensile test, D1708.⁴ A 3-in. gauge length was used with all other dimensions as specified by ASTM. The strain rates used in our testing program were 0.013/min for the tensile tests and 0.25/min for the notched sample tests. The strain rate at the crack tip, however, is likely to be much higher than that of the applied strain rate.⁵ Since polymer properties are strain-rate sensitive, the value of σ_y obtained from the tensile test is expected to be lower than the actual yield strength at the crack tip. However, an error analysis based on eq. (1) indicates that this uncertainty in σ_y does not significantly affect the calculated fracture energy within a three-decade range of strain rates.⁶

The values of initial elastic modulus E used in the calculations were those obtained from the unnotched tensile tests.

The test temperature was varied from -50°C to the main glass transition temperature of the polymer. The sample preparation and testing procedures have been discussed in more detail elsewhere.^{6,7}

EXPERIMENTAL RESULTS

The effect of temperature on the energy required for polymer brittle fracture is shown in Figure 2. A maximum in γ was observed for poly(phenylene oxide) and polysulfone about 85°C below the main glass transition temperature. Our testing procedure did not allow for thick enough samples of polycarbonate to be tested to keep the fracture in a plane strain mode; consequently, some macroscopic yielding was observed around the fracture plane above 27°C . This is shown in Figure 3. Gross yielding at the notched section resulted in high values of γ , which are not reported with the plane strain data. The plane strain fracture data obtained for polycarbonate are similar to those of poly(phenylene oxide) and polysulfone.

The degree of roughness of the fracture surface is a qualitative measure of the fracture energy. For instance, the maxima in fracture energy for poly(phenylene oxide) and polysulfone occur at 121°C and 105°C , respectively. This is also the temperature region of maximum roughness, as seen from Figures 4 and 5. Polymethylmethacrylate exhibits a continuing increase in γ with decreasing temperature, with a corresponding increase in surface roughness, as can be seen in Figure 6. As the test temperature approached the main glass temperature (105°C) for this polymer, a near-perfect cleavage surface was formed (104°C). A temperature increase of

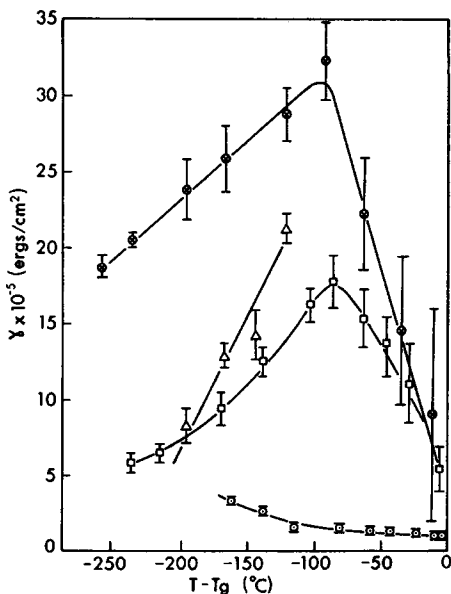


Fig. 2. Polymer fracture energy as a function of temperature.

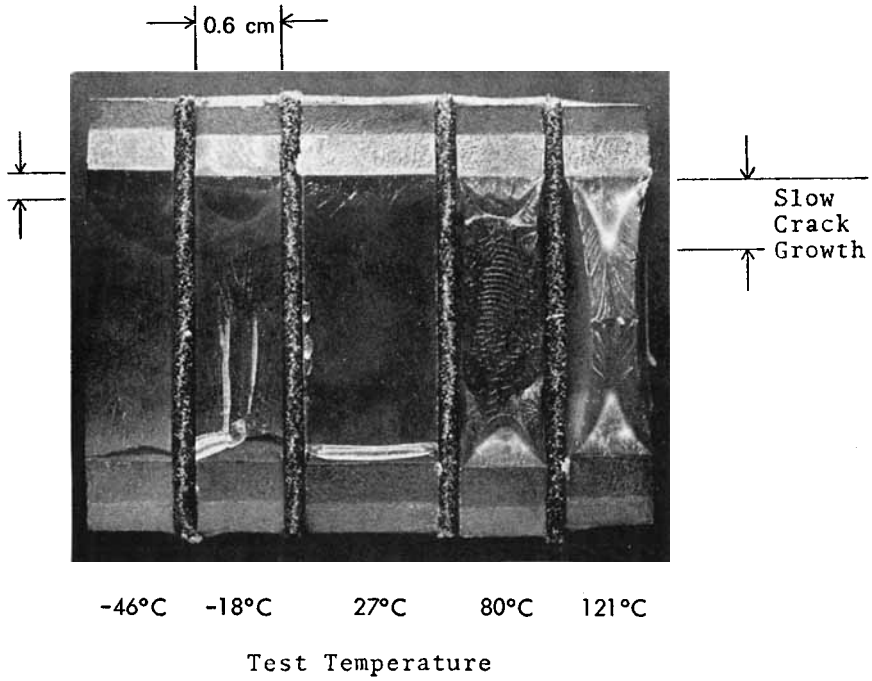


Fig. 3. Polycarbonate fracture surfaces.

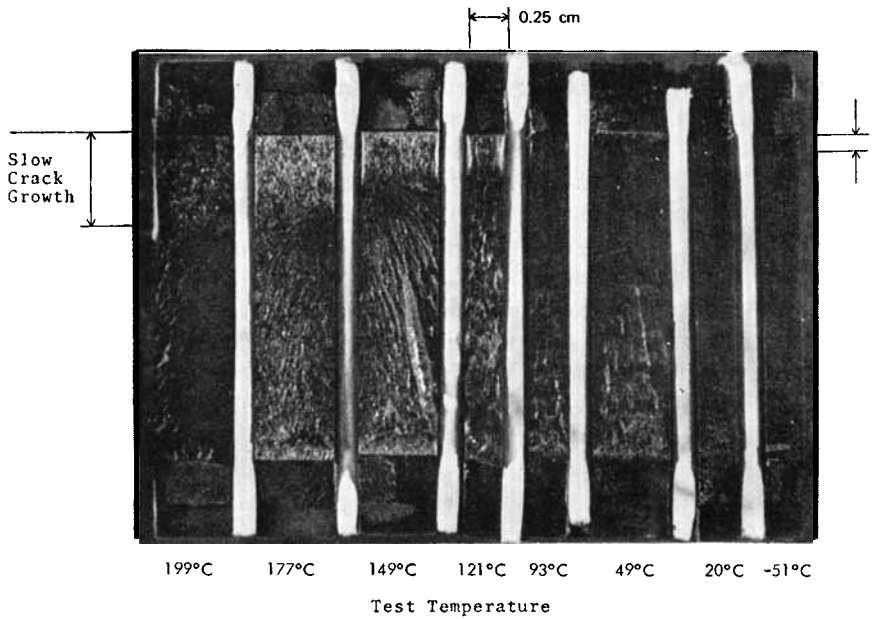


Fig. 4. Polyphenylene oxide fracture surfaces.

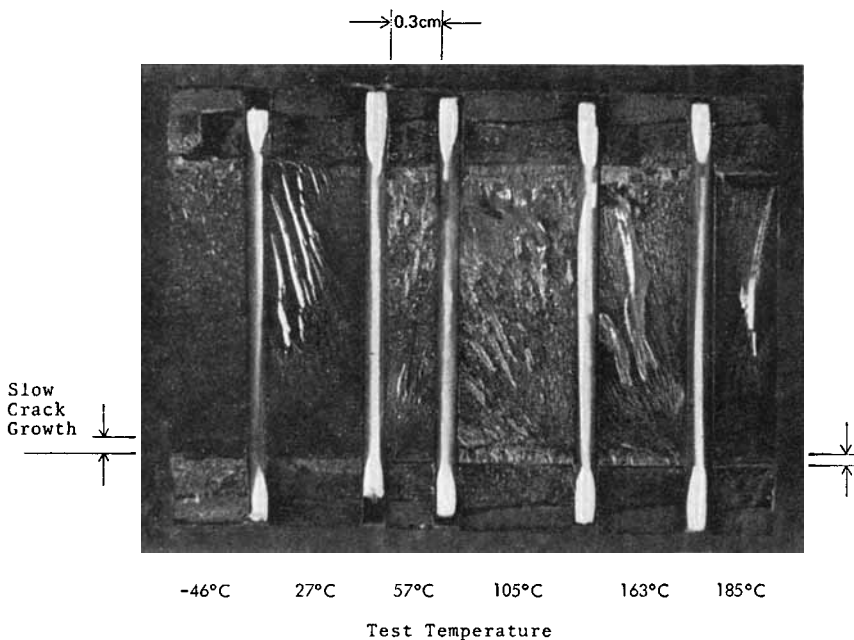


Fig. 5. Polysulfone fracture surfaces.

only a few degrees completely changed the fracture mode. At 106°C, gross yielding occurred, resulting in shear failure at the notched section. This same phenomenon was observed with polysulfone and poly(phenylene oxide) just above T_g .

Over the past few years there have been numerous attempts to relate impact strength to secondary glass transitions. Perhaps the best survey to date is that of Boyer.⁸ A comparison of the observed temperature response of γ with known secondary transitions for the four polymers⁹⁻¹³ showed no apparent correlation between fracture energy and secondary transitions. In fact, the data did not reflect any change in γ at any of the secondary glass transitions.

For this reason, we concluded that the maximum in the plane strain fracture energy for polysulfone, poly(phenylene oxide), and presumably polycarbonate is a manifestation of the approaching main glass temperature. This is supported by the tensile yield strength, yield strain, and initial elastic modulus data for the four polymers, as shown in Figures 7, 8, and 9. As the test temperature is lowered from the main glass transition, the fracture energy increases for all four polymers. The tensile yield strength, yield strain, and initial elastic modulus also increase, at the same rate for all four polymers. Between $T_g - 30^\circ\text{C}$ and $T_g - 60^\circ\text{C}$ the rate of increase in the tensile properties decreases abruptly for poly(phenylene oxide), polysulfone, and polycarbonate. Considering the difference in strain rates between the tensile and notched tests, this mechanical transi-

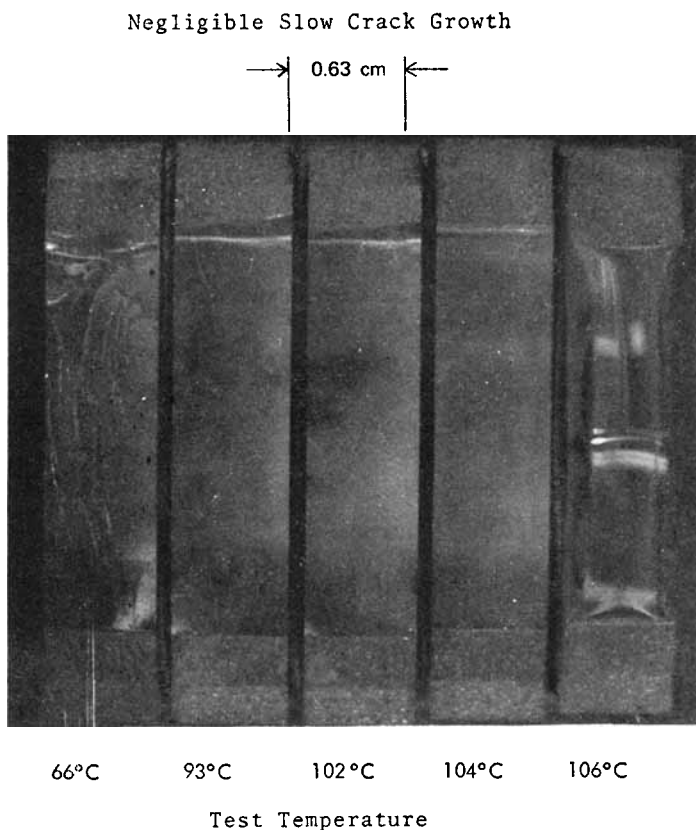


Fig. 6. Polymethylmethacrylate fracture surfaces.

tion compares reasonably well with $T_g - 85^\circ\text{C}$, at which temperature the maximum in γ is observed for poly(phenylene oxide) and polysulfone (and presumably polycarbonate in plane strain fracture mode). The tensile properties of Plexiglass II UVA increase linearly throughout the temperature region investigated, with no change in slope with temperature. Similarly, γ for Plexiglas II UVA continues to increase as the test temperature is reduced.

According to the above interpretation, the maximum and consequent decreases in γ as T_g is approached is the result of increased polymer softening, as indicated by the tensile data.

ANALYSIS OF DATA

The mechanism causing the onset of polymer flow has been a subject for speculation for considerable time. There is reason to believe that temperature rise, volume dilation, and a number of molecular factors such as chain entanglement, backbone flexibility, side group size, etc., are involved in the plastic deformation process. There has been considerable support in the

literature for the concept of volume dilation as at least a partial cause of yielding in polymers.¹⁴⁻²¹ Our tensile yield data appear to further support this concept. The volume dilation theory suggests that as a uniaxial stress is applied to the polymer, the volume increases according to the following relation:

$$\Delta v = (1 - 2\nu)v\epsilon \quad (3)$$

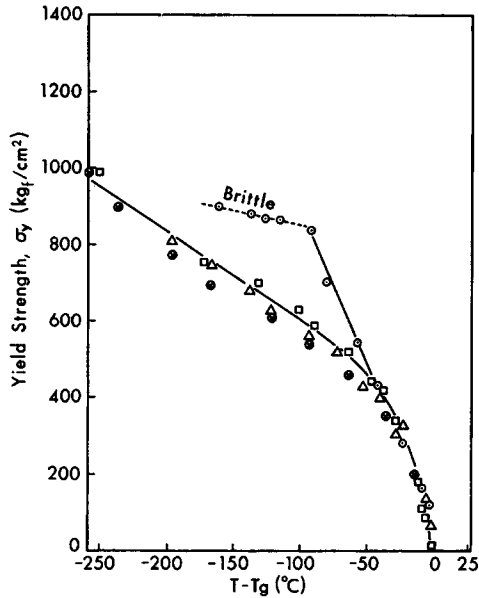


Fig. 7. Effect of temperature on polymer yield strength.

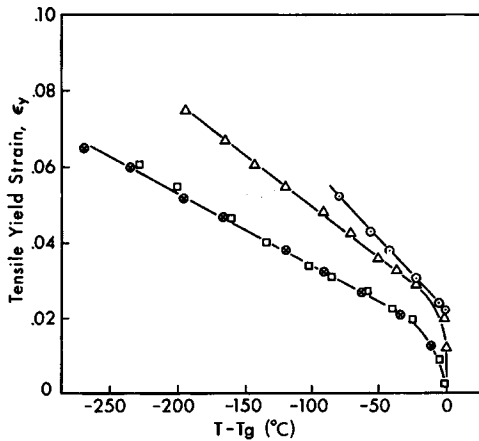


Fig. 8. Effect of temperature on polymer yield strain.

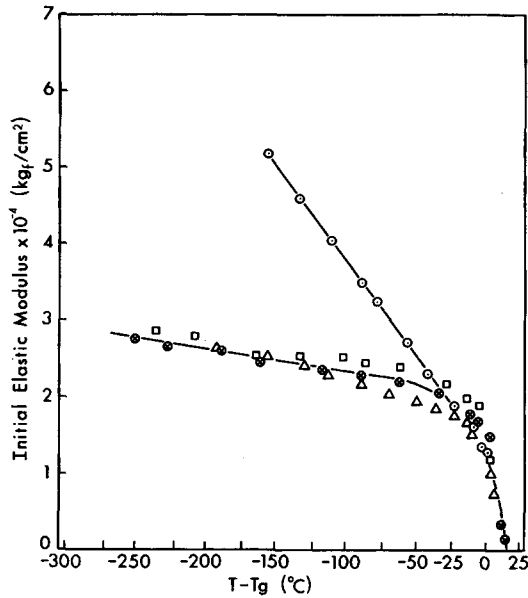


Fig. 9. Effect of temperature on polymer initial modulus.

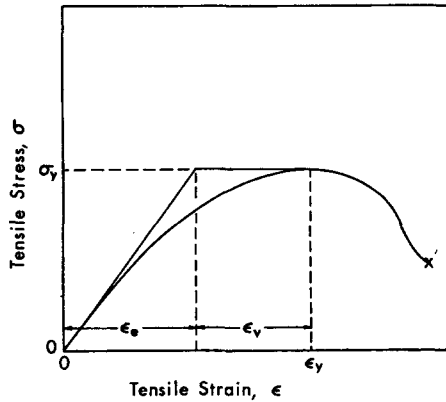


Fig. 10. Schematic diagram of the proposed elastic and viscous strains.

where Δv = increase in polymer volume; v = volume of the polymer in the unstressed state; ν = Poisson's ratio; and ϵ = uniaxial tensile strain.

If part or all of this volume increase corresponds to polymer free volume generation, then yielding will occur when the free volume generated at the test temperature equals that needed for the polymer molecules to "feel" as though they are at the main glass temperature. This yield process is then dependent on what is referred to as a "pseudo" reduction of the main glass temperature, i.e., $\Delta T_g = T_g - T_{\text{test}}$.

There have been at least two theories developed which propose that all of the volume increase from an applied load becomes free volume.^{16,18}

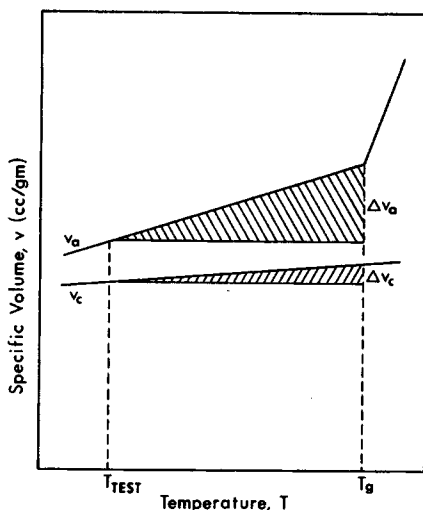


Fig. 11. Polymer free volume defined to include changes in amorphous and close-packed volume.

Although our yield strain data can be fitted to portions of each of the proposed theories, neither theory successfully predicts the yield strain over the entire temperature range tested.

We propose that not all of the increase in volume during loading becomes free volume, but rather that the dilatation associated with the initial linear elastic response of the polymer does not result in free volume. The total strain to yield is expressed as the sum of two terms, a linear elastic strain, ϵ_e , and a nonlinear strain, ϵ_v , which for lack of a better name will be called a viscous strain. This is shown schematically in Figure 10.

The elastic component is given by σ_y/E , where E is the initial elastic modulus. This is the strain which would be present in the polymer at the yield stress level if no nonlinear deformation occurred. One might visualize this to be the strain in the material if there were no change in the conformation or orientation of the molecules in the glassy state. Rather, the dilation occurs, as it does in simple crystals, with essentially no change in molecular conformation other than an increase in the average spacing between molecules. It is assumed that this elastic deformation does not generate additional free volume.

All of the free volume needed to cause gross yielding is assumed to come from the nonlinear increment ϵ_v to the total strain. It is emphasized that this viscous flow model represents plastic deformation on a microlevel, perhaps the same as in craze formation. It should not be confused with the postyield homogeneous plastic flow that occurs during cold drawing of a polymer. Thus, the nonlinear incremental strain results in a molecular rearrangement that causes an increase in the free volume of the polymer. This latter effect may or may not be accompanied by an additional macroscopic volume change. The relationship between ϵ_e and the free volume

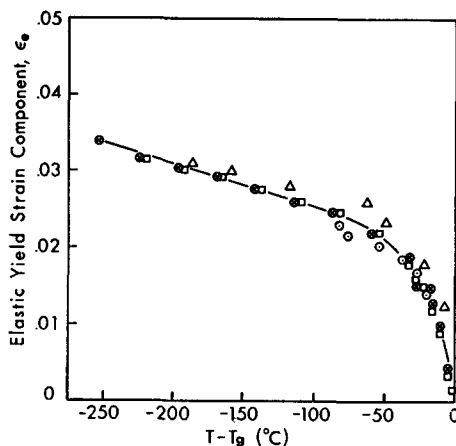


Fig. 12. Variation in the elastic strain with temperature.

is shown with the aid of Figure 11. Our definition of free volume is identical to that used by Litt and Tobolsky¹⁶:

$$\Delta v_{\text{free}} = \Delta v_a - \Delta v_c = \alpha_{ga} \Delta T_g v_a - \alpha_{gc} \Delta T_g v_c \quad (4)$$

where Δv_{free} = change in specific free volume (cc/g); Δv_a = change in amorphous specific volume (cc/g); Δv_c = change in close-packed specific volume (cc/g); α_{ga} = volumetric coefficient of thermal expansion in the amorphous glassy state (1/°C); α_{gc} = volumetric coefficient of thermal expansion in the close-packed glassy state (1/°C); v_a = amorphous specific volume (cc/g); v_c = close-packed specific volume (cc/g); and $\Delta T_g = T_g - T_{\text{test}}$ (°C).

It should be emphasized that although the polymers investigated are highly amorphous, under certain conditions a close-packed or crystalline-like structure can be induced. For instance, the close-packed specific volume of polycarbonate¹⁷ was taken as that value of specific volume obtained from x-ray scattering data on well-annealed polymer samples.

Incorporation of eq. (4) into eq. (3) results in the following expression:

$$\epsilon_y = \frac{\Delta v_{\text{free}}}{v_a(1 - 2\nu)} = \left(\alpha_{ga} - \alpha_{gc} \left(\frac{v_c}{v_a} \right) \right) \Delta T_g / (1 - 2\nu). \quad (5)$$

Thus, the yield strain for the polymer is given by

$$\epsilon_y = \sigma_y / E + \left[\left(\alpha_{ga} - \alpha_{gc} \left(\frac{v_c}{v_a} \right) \right) \Delta T_g / (1 - 2\nu) \right]. \quad (6)$$

The elastic component of the yield strain appears to be the same for all four polymers, as shown in Figure 12. Whether this is true for all amorphous polymers is not known, but it is not too likely. Subtraction of the experimental elastic strain in Figure 12 from the experimental yield strain in Figure 8 results in the viscous strain ϵ_v for the four polymers. As shown

TABLE I
Comparison of the Predicted and Measured Values of
($\alpha_{ga} - \alpha_{gc}(v_c/v_a)$)

Polymer	($\alpha_{ga} - \alpha_{gc}(v_c/v_a)$), (1/°C)	
	From Figure 13	Measured value
PPO	3.6×10^{-5}	—
PS	3.6×10^{-5}	—
PC	6.1×10^{-5}	6.5×10^{-5} ¹⁶
PMMA	12.6×10^{-5}	

n Figure 13, except for the initial 30°C below T_g , the data appear to be linear with ΔT_g . Since at T_g no viscous strain is needed to cause yielding, the data lines were drawn through zero at T_g . In accordance with eq. (5), the slope of the line is equal to $(\alpha_{ga} - \alpha_{gc}(v_c/v_a))/(1 - 2\nu)$. Table I shows the values of $(\alpha_{ga} - \alpha_{gc}(v_c/v_a))$ for the four polymers as determined from Figure 13. The range of values between 3.6 to 12.6×10^{-5} (1/°C)

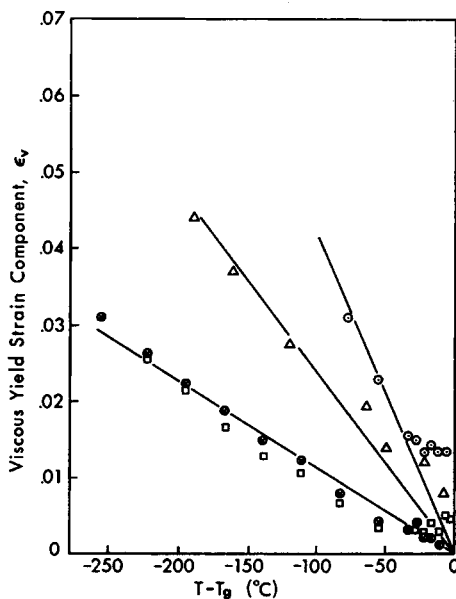


Fig. 13. Variation in the viscous strain with temperature.

appears to be reasonable. The only data available to check the theoretical slope were for polycarbonate,¹⁷ and, as seen, the agreement is excellent. Specific volume measurements on the close-packed state were found at room temperature for poly(phenylene oxide) and poly(methyl methacrylate),¹⁶ but a value of α_{gc} could not be found or reasonably calculated to check the theory for either polymer.

Within 30°C of the main glass transition temperature, there appears to be a small deviation in the linearity between ϵ_s and temperature, with the experimentally determined values being slightly higher than the linearly extrapolated values. If one includes a temperature dependence in ν , α_{ga} , and α_{gc} , the value of viscous strain would be increased in the region near T_g , further improving the fit. In particular, α_{ga} for poly(methyl methacrylate) has been shown to increase rapidly above 95°C.²² Poisson's ratio would also be expected to be increasing toward a value of 0.5 in this temperature region. A more correct form for viscous strain is then

$$\epsilon_s = \left[\alpha_{ga}(T) - \alpha_{gc}(T) \left(\frac{v_c(T)}{v_a(T)} \right) \right] \Delta T_g / [1 - \nu(T)]. \quad (7)$$

Although the yield strain data at these temperatures are not sufficiently accurate to merit calculations of this type, eq. (7) will undoubtedly give a better fit of the experimental data.

CONCLUSIONS

The fracture energy of poly(phenylene oxide), polysulfone, and polycarbonate increases with decreasing temperature to a maximum at roughly 85°C below the main glass transition temperature of the polymers. The maximum appears to be associated with the general changes in viscoelastic properties accompanying the main glass transition temperature and can be correlated with changes in strength and modulus in this temperature region. A similar maximum in γ with corresponding changes in strength and modulus was not observed for poly(methyl methacrylate) at as low a temperature as we could study. Presumably poly(methyl methacrylate) must also show the same type of behavior, but at a much lower temperature than the other three polymers. Below this maximum, the fracture energy decreases almost linearly with decreasing temperature. If one extrapolates the data for three of the polymers to the temperature region of absolute zero, the fracture energy appears to have decreased to the order of the theoretical surface energy.

In addition, the volume dilation theory has been further supported by our polymer yield strain data. Although no definite mathematical analysis involving strain at the crack tip has been developed as yet, in light of the correlation of the transitions in the fracture energy with the tensile data, the same equations which describe the onset of yielding in a tensile sample may also be applicable to the crack tip yielding process. If this is true, further work of this nature should provide a method for predicting the fracture energy from tensile stress-strain properties.

This work was sponsored by the Advanced Research Projects Agency, Department of Defense, and Office of Naval Research, under Contract No. N00014-67-C-0218 (formerly N00014-66-C-0045).

References

1. J. P. Berry, *J. Polym. Sci. A*, **1**, 993 (1963).
2. L. J. Broutman and F. J. McGarry, *J. Appl. Polym. Sci.*, **9**, 589 (1965).
3. G. R. Irwin, *Fracture of Hi-Strength Sheet Materials Under Conditions Appropriate for Stress Analysis*, U. S. Naval Laboratory, Washington, D. C., NLR Report 5486, 1960.
4. American Society for Testing and Materials Standards, *Plastics—General Methods of Testing-Nomenclature*, Part 27, 1966, p. 568.
5. G. R. Irwin, *Trans. ASTM*, **86A**, 444 (1964).
6. K. L. Trachte, *The Brittle Fracture of Thermoplastic Polymers and Composites*, D. Sc. Thesis, Materials Research Laboratory, Washington University, St. Louis, Missouri, 1970.
7. A. Wambach, K. Trachte, and A. DiBenedetto, *J. Composite Materials*, **2:3**, 266 (1968).
8. R. F. Boyer, *Polym. Eng. Sci.*, **8:3**, 161 (1964).
9. P. Heydemann and H. D. Guicking, *Kolloid-Z.*, **193**, 16 (1964).
10. J. M. Crisman, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci.*, **A2**, 5075 (1964).
11. J. Heijboer, *J. Polym. Sci.*, **C16**, 3755 (1968).
12. J. C. Woodbrey, J. E. Kurz, and M. Ohta, to be submitted to *J. Polym. Sci.* for publication.
13. F. P. Reding, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.*, Vol. 54, Issue 160, S56 (1961).
14. G. M. Bryant, *Text. Res. J.*, **31**, 399 (May 1961).
15. M. H. Litt and P. Koch, *Polymer Letters*, **5**, 251 (1967).
16. M. H. Litt and A. V. Tobolsky, *J. Macromol. Sci. Phys.*, **B1:3**, 433 (October 1967).
17. M. H. Litt, P. J. Koch, and A. V. Tobolsky, "Cold Flow of Glassy Polymers; III. Temperature Dependence of Yield Elongation in BPA Polycarbonate," *J. Macromol. Sci. Phys.*, **B1:3**, 587 (October 1967).
18. L. E. Nielsen, *Trans. Soc. Rheology*, **9:1**, 243 (1965).
19. S. Strella, *Appl. Polymer Symposia*, **7**, 165 (1968).
20. S. S. Sternstein, L. Ongchin, and A. Silverman, *Appl. Polymer Symposia*, **7**, 125 (1968).
21. R. E. Robertson, *Appl. Polymer Symposia*, **7**, 201 (1968).
22. R. Haldon and R. Simha, *J. Appl. Phys.*, **39**, 1890 (1968).

Received May 18, 1970