

Fracture Surface Work Measurements on Glassy Polymers by a Cleavage Technique.

I. Effects of Temperature

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Synopsis

It has recently been postulated that viscous flow or plastic deformation occurs near the tip of an advancing crack in glassy amorphous polymers such as Plexiglas, and this results in molecular orientation of the fracture surface. The evidence for this has been the appearance of colors on fresh fracture surfaces of Plexiglas and the extremely high measured surface work which is 1000 times greater than the theoretical surface energy. The surface energy of a solid is defined as the amount of energy required to create unit area of surface in the material by separating two planes each of half a unit area in extent, and the measured surface work of a polymer may also include any irreversible work which occurred during the fracture process. In the present investigation a cleavage test has been employed to measure the surface work of glassy polymers and to measure the effects of temperature on the surface work. A reproducible procedure has been developed to measure the surface work of cracks which propagate continuously and for cracks which propagate in a stick-slip fashion. The measured surface work of Plexiglas II is 1.2×10^2 erg/cm.², and the value for a typical polystyrene is 4×10^5 erg/cm.², compared to a theoretical estimate of 450 erg/cm.². The surface work varies with temperature over the range of -40 to 80°C . The surface work of Plexiglas II and polystyrene decrease with increasing temperature. Colors have been seen on the Plexiglas fracture surfaces over the entire temperature range, and the fracture surface changes from rough to mirror-smooth at elevated temperatures. The inherent flaw size of the polymers, from Griffith's equation, also varies with temperature and is thought to be related to the crazing behavior of the polymer. At 23°C . the flaw size for polystyrene is 0.05 in. and for Plexiglas II, 0.002 in.

INTRODUCTION

A satisfactory explanation of brittle strength phenomena was first proposed by Griffith in 1920,¹ partly based on the earlier work of Inglis,² who had analyzed the elastic stress distribution around an elliptical hole in a stressed plate, utilizing the classical methods of elasticity. Griffith assumed that the discrepancy between theoretically estimated and experimentally observed values of tensile strength was due to the presence of very small cracks or flaws around which a stress concentration arose when the

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solid was loaded. He made use of Inglis' calculation by regarding these cracks as very flat elliptical holes, further postulating that the crack would lengthen and cause gross fracture if, for a small increase of its length, the release in elastic strain energy became equal to the energy required to form new surfaces, that is, if

$$d(W_e - W_s)/dc = 0$$

This analysis leads to Griffith's well known expression:

$$\sigma = (2\gamma E/\pi c)^{1/2}$$

where σ is tensile strength, γ is surface energy, E is Young's modulus, and $2c$ is the length of a surface crack.

This equation assumes that the thickness of the plate is small compared to the crack length, or more precisely, that a state of plane stress obtains, while for a thick plate (plane strain), the equation is modified somewhat:

$$\sigma = [2E\gamma/\pi c(1 - \nu^2)]^{1/2}$$

where ν is the Poisson's ratio of the material. Griffith verified his theory by producing microscopic flaws in glass tubes which were subsequently burst with internal pressure.

Orowan^{3,4} and Irwin⁵⁻⁸ later applied the Griffith criterion to brittle fracture of ship steel. Orowan measured the Griffith surface energy by inserting fine cracks into the solid body and measuring the resulting tensile strength as a function of flaw size.

The surface energy so found was 10^6 erg/cm.², which compares to a theoretical estimate of 10^8 erg/cm.² based only on the reversible work necessary to separate two atomic planes of the metal. This large discrepancy is explained by the formation of a plastically deformed layer of material near the tip of the crack which absorbs a large amount of irreversible work during the crack propagation; in order to account for this factor, Griffith's equation is modified:

$$\sigma = [2E(\gamma + p)/\pi c]^{1/2}$$

where p is the work of plastic deformation. Orowan showed by means of x-ray diffraction studies that $p \gg \gamma$. Irwin employed a centrally notched sheet specimen of metal to determine a quantity, G_c , the critical strain energy release rate. This is equal to 2γ in Griffith's equation and is measured at the instant when a stable crack growing from the notch becomes unstable, propagates rapidly, and causes fracture of the sheet. Because of the additional work required to propagate a crack other than surface energy, it would be more appropriate to name this quantity "fracture surface work."

The Griffith theory has also been recently applied to polymers by Berry.⁹⁻¹³ By measuring the tensile strength of polystyrene and poly-(methyl methacrylate) as a function of flaw size, Berry found that the polymers obey Griffith's criterion, the tensile strength, varies as $(1/c)^{1/2}$.

The fracture surface work for Plexiglas was found to be 3×10^5 erg/cm.² and the value for polystyrene was 1.7×10^6 erg/cm.². The theoretical value of surface energy for glassy polymers was calculated to be 450 erg/cm.². This large discrepancy between the measured and calculated value is similar to the difference observed for ship steel (inorganic glass does not exhibit this discrepancy).

Berry proposed that this high value of the measured surface work was caused by viscous flow at the tip of the crack which results in polymer orientation.¹⁴ This orientation hypothesis was based on the prior observations that fresh fracture surfaces of Plexiglas exhibit bright colors.^{15,16} Color photographs can be seen in the papers by Higuchi¹⁵ and Wolock.¹⁷ The observed colors vary with the angle of incidence of the light, and therefore an interference phenomenon is assumed responsible for this color production which is due to the difference in index of refraction of the oriented layer and the bulk polymer. The relationship of the colors to the topographic features of tensile fracture surfaces have recently been studied in detail by Berry.¹⁸

FRACTURE SURFACE WORK DETERMINED BY CLEAVAGE METHODS

Obreimoff derived an expression relating the surface energy of a solid to variables which could be measured in a cleavage test.¹⁹ Obreimoff measured the surface energy of mica, and Orowan later extended his measurement.²⁰ Gilman has recently measured the surface energies of a large number of ionic and metallic crystals.²¹

TABLE I
Surface Energies Determined by Various Investigators

Investi- gators	Materials	Test method	Surface energy, erg/cm. ²
Benbow and Roesler ^{23,24}	PMMA ^a	Wedge splitting	4.9×10^5
	Polystyrene	Wedge splitting	2.5×10^6 (slow crack) 3.0×10^5 (fast crack)
Irwin and Kies ^{7,8}	PMMA ^b	Central notch	4.4×10^5
	Polyesters	Central notch	0.88×10^5
Svensson ²⁵	PMMA ^a	Wedge splitting	4.4×10^5
	Polystyrene	Wedge splitting	8.8×10^5
Berry ^{10,18}	PMMA ^b	Tensile test	3.0×10^5
	Polystyrene	Tensile test	1.7×10^6
	PMMA ^b	Cleavage test	1.4×10^5
	Polystyrene	Cleavage test	7.1×10^5
Present studies	PMMA ^b	Cleavage test	1.25×10^5
	Polystyrene ^c	Cleavage test	4.00×10^5
	Polyesters ^d	Cleavage test	1.2×10^4

^a Tradename: Perspex.

^b Tradename: Plexiglas II.

^c Tradename: Dow Styron 666.

^d Tradename: Paraplex P43.

In order to propagate a cleavage crack in an isotropic material, such as an amorphous glassy polymer, the crack has to be confined to its original plane; this is so, as the stress distribution at the tip of a cleavage crack has a tendency to turn the crack out of its original plane. Gilman and Guernsey have calculated the stress distribution from photoelastic measurements.²² Benbow and Roesler have confined the crack to a single plane by applying a compression force to the specimen; they then propagate the crack parallel to the compression force.^{23,24} They have measured the surface energies of Plexiglas and polystyrene using this method. Svensson has modified the apparatus of Benbow and Roesler and measured the variation of the surface energy of Plexiglas and polystyrene with temperature.²⁵ Their results are summarized in Table I.

Berry has reported another technique to confine crack propagation to a single plane in a cleavage test.²⁶ This is accomplished by slotting the sides of a specimen (0.006 in. wide slot) so that the crack will be geometrically confined to the section of minimum cross section area. It is thought that this method allows a more accurate determination of the surface work and allows the elimination of some critical assumptions used in the calculations of Benbow and Roesler.

EXPERIMENTAL PROCEDURE FOR MEASURING FRACTURE SURFACE WORK

The cleavage specimen suggested by Berry and modified by the present authors is shown in Figure 1. In this technique a crack is propagated along the median plane of a strip sample by forces applied at the free ends. Berry found that this method yields more accurate results than the tensile technique and therefore can be better used for comparative measurements. Other advantages include: (1) the surface work can be determined from

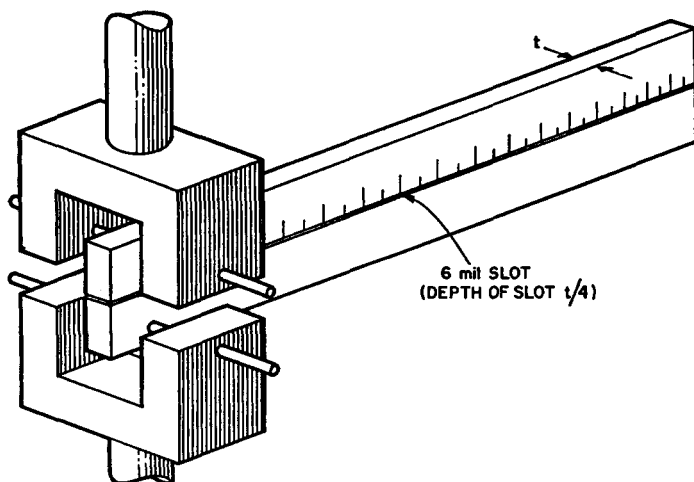


Fig. 1. Cleavage test specimen placed in loading arms.

measurements on one specimen; (2) the calculation of the surface work does not require a knowledge of the modulus of the material; (3) less time required. The 0.006 in. slot shown in Figure 1 confines the crack so it propagates through a specific volume in a stable manner. The necessity for confining the crack in an isotropic material has already been discussed. The slot requires careful machining and all cleavage specimens have been conditioned uniformly. A description of the preparation of a cleavage specimen can be found in the Appendix.

In order to determine the surface work from the cleavage experiment, one must relate it to experimentally measured quantities. Griffith's energy balance theorem ($-\partial U/\partial c = \partial S/\partial c$) has been applied to the cleavage test by assuming the specimen acts as two symmetrical cantilever beams. By making this assumption, one can relate the stored strain energy to the crack length, since

$$U = f\delta/2$$

where U is the strain energy, f is the applied force, and δ is the deflection; for a generalized beam,

$$f = a\delta/l^n \quad (1)$$

where

$$a = f(EI)$$

and l is the crack length and n is a constant.

The surface work is also simply related to the crack length. If the specimen arms acted as true cantilever beams, then $a = 3EI$ and $n = 3$ would be used in eq. (1). By applying Griffith's criterion eq. (2) is derived:²⁶

$$f\delta/w = 4\gamma l/n \quad (2)$$

where f is the applied force, δ is the deflection of one arm, w is the measured crack width, l is the crack length, n is an experimentally determined constant [from eq. (1)], and γ is surface work.

The force and deflection must be measured as a function of crack length in order to determine the surface work. It will be seen that the method required to make the above measurement is dependent on the mode of crack propagation.

All of the cleavage experiments were conducted in an Instron testing machine and the applied force and deflection were continuously recorded. As will be discussed shortly, a constant crosshead rate was used to cleave the specimen. Since the method used to measure the force and deflection at various crack lengths is dependent on the mode of crack propagation, we will first describe how the crack may move through the material. The first type of crack propagation can be considered as "continuous" tearing. The crack moves continuously through the specimen as the ends of the specimen are being separated; the rate of separation of the specimen ends controls the crack velocity, which remains reasonably constant over the

TABLE II
Mode of Crack Propagation and Fracture Surfaces for Materials Tested

Material	Temperature, °C.	Mode of crack propagation	Fracture surfaces
Plexiglas II	50	Continuous tearing	Mirror-smooth, green color
Plexiglas II	20	Continuous tearing	River patterns, colored green, red
Plexiglas II	-40	Discontinuous propagation	Mirror-smooth, no color
Polystyrene	49	Discontinuous propagation	Finely cracked surface without silvery appearance
Polystyrene	20	Continuous tearing	Finely cracked surface, silver appearance
Polystyrene	-20	Continuous tearing	Finely cracked surface, silver appearance

specimen length (approximately 3 in./min.) providing the rate of separation is constant. The second type of crack propagation is described as "discontinuous propagation" or "stick-slip" tearing. This is characterized by a continued increase in deflection at the ends of the specimen without a corresponding increase in crack length; then suddenly, the crack will jump to a new length. The crack velocity is very high and the jump seems to occur instantaneously. The crack does not continue to run through the entire specimen because the specimen is being unloaded as the crack velocity becomes much greater than the rate of machine separation. The length of the crack jump varies depending on the material being tested; moreover, it also varies in the material itself and crack jumps of 2 or 3 in. have sometimes been observed. Table II illustrates the type of crack propagation for the various materials tested.

Plexiglas, at room temperature, displays the first type of crack propagation, continuous tearing. As can be seen in Figure 1, calibration marks have been engraved on the specimen at $1/4$ in. intervals. The procedure used to measure the force and deflection at various crack lengths then depends on visual observation. The specimen ends are separated at a rate of 0.2 in./min., and as the crack front passes a calibration mark the observer presses a button on the testing machine which puts a mark on the recording of force and deflection. After the test is completed, the crack width is measured using a microscope.

In determining the optimum crosshead rate, several other crosshead rates were also tried. Crosshead rates less than 0.1 in./min. (for Plexiglas) led to more experimental scatter than higher crosshead rates especially at large crack lengths. This could be due to relaxation of the stress in the material due to the excessive time the force has to be applied to the specimen before the crack propagates completely through the specimen. Therefore the force measured at the beginning of the test will differ from the force at the end of the test, not only because of increased crack length but because of stress relaxation; therefore, a crosshead rate of 0.2 in./min. was selected for

TABLE III
Effect of Experimental Parameters on Surface Work

Material	Specimen thickness, in.	Crosshead rate, in./min.	Surface work, erg/in. ²
Plexiglas	0.250	0.1	1.20×10^6
Plexiglas	0.250	0.2	1.04×10^6
Plexiglas	0.250	0.2	1.20×10^6
Plexiglas	0.100	0.2	1.20×10^6
Plexiglas	0.100	0.1	1.12×10^6
Polystyrene	0.250	0.2	4.4×10^6
Polystyrene	0.125	0.2	4.3×10^6

tests which involved continuous crack propagation. The specimen size should not affect the value of surface work. Specimen thicknesses have ranged from 0.100 to 0.250 in. Results for different size specimens and different rates of crosshead separation can be seen in Table III.

The presence of the slot influences the measured value of the surface work by making crack propagation easier, especially near the edges of the slot. The high stresses near the slot edges cause the velocity of the crack to be higher at the edges than at the center. If the crack growth is changed by the presence of the slot, then the surface works we have measured will be smaller than the true values which might be measured without a slot. However, we feel this is a small effect, and the value of the surface work is not greatly distorted. Results indicate that the surface work remains the same if a 50 mil slot is used in a $1/4$ in. specimen rather than a 65 mil slot. However, the crack is more easily confined in a 65 mil slot.

The procedure used for the second type of crack propagation, discontinuous tearing must obviously be different than the preceding methods. The crack length is first measured by a traveling telescope which can be read to the nearest 0.001 cm. The length is measured from the nearest calibration mark. The ends of the specimen are then separated at a constant rate until the crack jumps. The force and deflection at the instant of the crack jump are noted. After the crack jumps, the crosshead motion is reversed, and the specimen is returned to its equilibrium position. After a short waiting period, the new crack length is measured, and the deflection is again increased; when the crack jumps, the force and deflection are again measured for this new crack length. This method is considered equivalent to the first method and both should give the same value of surface work if used on two identical specimens of the same material. The procedures described above are much different from the procedure developed by Berry.²⁶ Our procedure requires much less time, and yet the values obtained are similar to Berry's (Table I).

ANALYSIS OF DATA

The force, deflection, and crack width at each crack length are tabulated as shown in Table IV. In order to determine the surface work γ , two

TABLE IV
Data Used to Determine Surface Work*

Crack length l , in.	Force f , lb.	Deflection δ , in.	Crack width w , in.	f/δ	$f\delta/w$
1.65					
1.90					
2.15	12.9	0.029	0.141	445	2.65
2.40	11.7	0.034	0.141	340	2.85
2.65	10.5	0.041	0.141	256	3.05
2.90	9.7	0.048	0.141	204	3.27
3.15	8.8	0.054	0.134	163	3.54
3.40	8.1	0.063	0.134	130	3.78
3.65	7.3	0.067	0.141	110	3.46
3.90	6.9	0.077	0.150	90	3.54
4.15	6.73	0.089	0.150	76	3.97
4.40	6.50	0.101	0.154	64	4.26
4.65	6.37	0.116	0.146	54	5.08
4.90	6.24	0.131	0.157	47.4	5.27
5.15	5.76	0.142	0.150	40.6	5.45
5.40	5.22	0.148	0.141	35.2	5.50
5.65	4.92	0.157	0.146	31.2	5.31
5.90	4.77	0.174	0.154	27.4	5.39
6.15	4.59	0.189	0.150	24.4	5.77
6.40	4.38	0.203	0.141	21.6	6.30
6.65	4.19	0.218	0.150	19.2	6.07
6.90	4.05	0.232	0.150	17.4	6.26
7.15	3.88	0.249	0.154	15.6	6.28
7.40	3.77	0.268	0.150	14	6.73
7.65	3.63	0.287	0.154	12.6	6.76
7.90	3.59	0.312	0.146	11.6	7.61
8.15	3.57	0.339	0.154	10.6	7.86
8.40	3.42	0.356	0.154	9.6	7.90
8.65	3.29	0.374	0.157	8.8	7.82

* Material: Plexiglas II; test temperature: 23°C.; specimen thickness $1/4$ in. Results: $n = 2.86$; $\gamma = 1.04 \times 10^6$ ergs/cm.².

graphs have to be plotted for each specimen. The first graph determines the value of n from the relation:

$$f = a\delta/l^n$$

If one plots $\log f/\delta$ against $\log l$, the slope of the line will be equal to n . This is shown for three different polymers in Figure 2. The experimental scatter is negligible, and a precise determination of n can be made. This was true for every specimen tested. However, near each end of the specimen the experimental points usually do not fall along the straight line; this is due to the presence of shear deformations which have been neglected in the theory and also the decrease of the end rigidity. It is significant that the measured value of n is always less than 3, the value for a true cantilever beam.

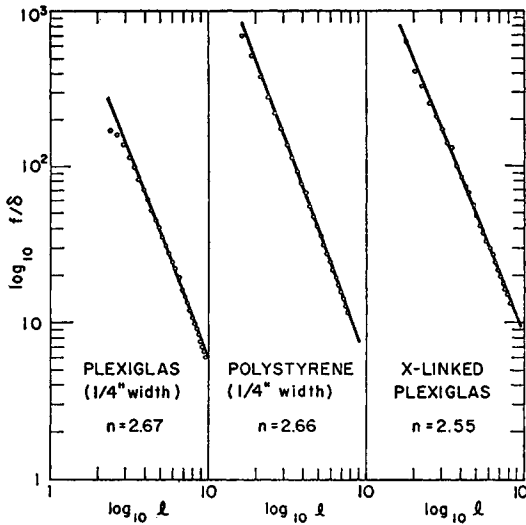


Fig. 2. Graphs used to determine the value of n from the relation $f = a\delta/l^n$.

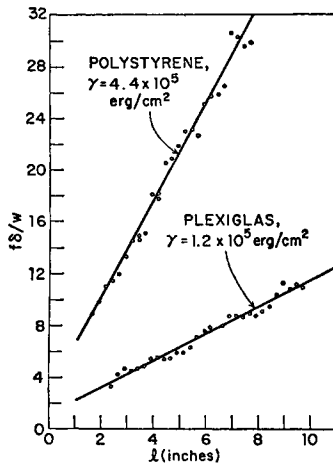


Fig. 3. Graph used to determine the value of γ from the relation, $f\delta/w = 4\gamma l/n$ (slope of line = $4\gamma/n$).

In the second graph, one plots the quantity $f\delta/w$ against the crack length l from the equation,

$$f\delta/w = 4\gamma l/n$$

and the slope of this plot will be equal to $4\gamma/n$, n having already been determined from the first plot. Figure 3 shows the results for polystyrene and Plexiglas. The experimental scatter is exceptionally low for each specimen, the standard deviations being less than 1% for the cases shown. The results are also very reproducible from specimens of the same material.²⁷

SURFACE WORK MEASUREMENTS ON PLEXIGLAS AND POLYSTYRENE

The results in Figure 3 show that the measured surface work of Plexiglas and polystyrene is at least a factor of 1000 times greater than the calculated value. The significance of this has already been adequately discussed by Berry.¹⁰⁻¹² He has postulated that the viscous flow which must occur at the tip of a propagating crack results in polymer orientation at the fracture surface. The colors which have been seen on the fracture surfaces of Plexiglas reinforce this theory because their appearance may be due to light interference between the fracture surface and the interface between the oriented material and the bulk polymer. In order for colors to be seen, assuming first-order interference occurs, the thickness of the oriented layer must be about $1/4$ of the wavelength of the visible light, which represents an oriented layer about 1500 Å. in thickness. The length of an average polymer chain in Plexiglas with a molecular weight 3,000,000 would be about 50,000 Å. The extended portion of the oriented layer represents only a small part of the total chain length.

Besides the above-mentioned results, one can also see in Figure 3 that the surface work of polystyrene is four times greater than that of Plexiglas. We usually associate a higher surface work with increased molecular motion at the tip of the propagating crack; however, in this case, the crack growth in polystyrene is also accompanied by crazing at the tip of the growing crack. The creation of these fine subsurface cracks, or craze flaws, requires additional work. This will be discussed in more detail when the appearance of the fracture surfaces are discussed.

Several other investigators have reported values for the surface work of poly(methyl methacrylate) and polystyrene (Table I). It can be seen that the values for polystyrene vary greatly among the investigators. The primary reason for this is the variability between commercially available polystyrenes and their method of fabrication. For instance, Benbow has shown the surface work and mode of crack propagation to be very dependent on molecular weight.²⁴ The surface work value for polystyrene is also dependent on the amount of crazing which occurs in front of the propagating cleavage crack; furthermore, this is dependent on the conditioning the specimen has received and the commercial type of polystyrene being tested.

There should be less such variability evident in Plexiglas, because of the casting method of sheet fabrication; further, the molecular weight should not be very different in the samples used by the various investigators. However, the values obtained by Benbow and Roesler and by Svensson are greater by a factor of 4 than those obtained by Berry and by the present investigation. In all cases a cleavage technique was used, although Benbow and Roesler did not use a slot to confine the crack. Although the presence of the slot could have caused our values to be too low, we feel this is not the primary cause for the difference between the surface work measurements. The real cause might be in the theoretical expressions used by Benbow and Roesler to determine the surface work, as they assume their

specimen behaves as two cantilever beams and they use the beam formulae to relate force to deflection.

EFFECT OF TEMPERATURE ON THE SURFACE WORK OF PLEXIGLAS AND POLYSTYRENE

Berry measured the variation in surface work over a temperature range from -200 to 50°C . using the tensile test technique.¹³ The results indicate that the surface work increases as the temperature is reduced from 50 to -200°C . In addition, the inherent flaw size varies with temperature, and a minimum occurs at about -25°C . Since these measurements were performed with tensile specimens, the values show considerable scatter and these values should not be considered precise especially at the liquid nitrogen temperature. However, the variation with temperature seems well established. Svensson has measured the variation of surface work with temperature for poly(methyl methacrylate) (Perspex) and polystyrene using the cleavage technique suggested by Benbow and Roesler.²⁵ The temperature range studied was 20 – 80°C . Their results indicate a maximum value in the surface work of Perspex at 60°C . and a maximum value for polystyrene at 70°C . However, the experimental scatter is high, and the exact shape of the curve for surface work versus temperature is not really evident. The data of Berry and Svensson only overlap in the narrow region of 20 – 50°C ., and the data in this range do not agree.

We have measured the temperature dependence of Plexiglas and polystyrene using the cleavage technique. The temperature range studied was -40 to 80°C . The cleavage tests were performed in an air-circulating chamber which was placed directly in the testing machine. The front of the chamber had a large area of glass and therefore the crack could easily be observed as it propagated through the specimens. The specimens were kept at the test temperature at least 45 min. before testing.

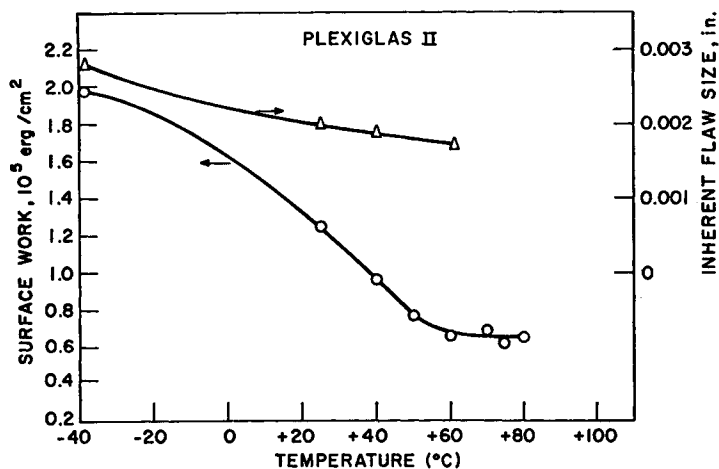


Fig. 4. Variation of the surface work and inherent flaw size of Plexiglas with temperature.

The results of measurements made on Plexiglas II are shown in Figure 4. The inherent flaw size was calculated from Griffith's equation with values of tensile strength and modulus taken from the literature.²⁸ It was thought that 80°C. should be the maximum temperature used as the ductility of the polymer increases rapidly above this temperature.

The variation of the surface work with temperature is well defined and agrees with the results found by Berry for Plexiglas. A decrease in temperature results in an increase of the surface work. However, in the range from 60 to 80°C. the surface work remains almost constant. Although the present results for surface work extend only to -40°C., Berry has shown the surface work continues to increase down to -200°C. The explanation for this is that increasing the temperature reduces the strength of the secondary bonding forces between molecules and allows them to flow easier. By the appearance of the colors on the fracture surface at elevated temperatures, which will be discussed in more detail later, there is no indication that the amount of orientation increases. The increased temperature serves only to reduce the work necessary to orient the molecules and, hence, a lower surface work is measured at elevated temperatures. The fact that the surface work continues to increase and that colors have been seen on the fracture surface even at liquid nitrogen temperatures, agrees with the theory that more work has to be expended as the temperature is lowered to achieve molecular orientation. However, it seems unreasonable that flow could still take place at -200°C., but the observed colors on cleavage specimens fractured at this temperature indicate an oriented layer of molecules is still present.¹³

In order to explain how viscous flow could occur at a temperature so far below the glass transition temperature of the polymer, the following theories have been expressed: (1) the extremely high localized stresses in front of the crack might cause the flow regardless of the low temperature;¹⁰ (2) the irreversible work is dissipated as heat energy which can raise the local temperature in front of the crack by 100°C. or greater;²⁹ (3) the glass transition temperature of a polymer is lowered by hydrostatic tension, thus, the local transition temperature in front of the crack would be reduced.

In addition to measuring the surface work as a function of temperature, the inherent flaw size has also been determined as a function of temperature over the range -40 to 60°C. The flaw size, as postulated by Griffith, is the length of the largest flaw existing in the material prior to fracture. Berry suggested that the crazing behavior of a polymer is related to the flaw size calculated from the Griffith equation. This means that the larger the calculated flaw size of a material, the greater would be the tendency for the material to craze. Figure 4 shows that the inherent flaw size increases slightly with decreasing temperature. Although the form of this curve does not agree with Berry's results on flaw size measurements, both sets of measurements indicate that the flaw size increases at low temperatures. This agrees with observations by Berry on tensile specimens of Plexiglas which crazed very badly at liquid nitrogen temperatures.

The temperature dependence of the surface work and the inherent flaw size of polystyrene can be seen in Figure 5. The polystyrene used in this study was supplied by the Dow Chemical Co. in the form of compression-molded sheets of Styron 666. Although the absolute values of the surface work are higher than those of Plexiglas, the curves are similar in shape.

The molecular mechanisms occurring in front of the crack for polystyrene are believed to be the same as those for Plexiglas. Moreover, quite extensive fine cracking occurs in front of the growing crack in polystyrene, and this has been found to be quite dependent on the type of polystyrene tested. The reduction in surface work with increasing temperature is a result of increased ease of molecular orientation. The slight increase in surface work from 50 to 70°C. might only be a result of experimental scatter.

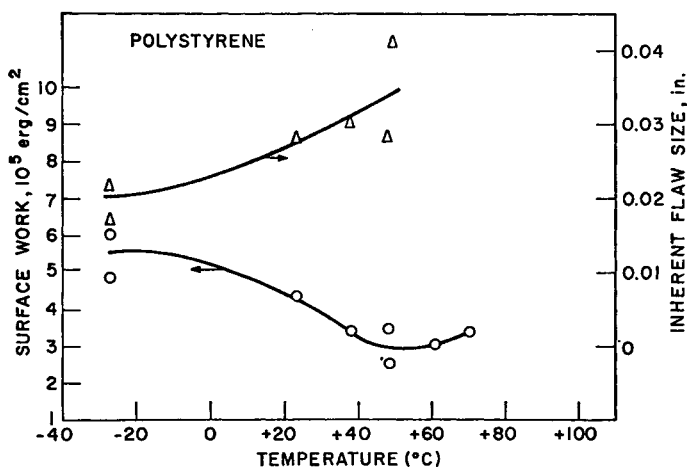


Fig. 5. Variation of the surface work and inherent flaw size of polystyrene with temperature.

The flaw size is also plotted as a function of temperature in Figure 5. It is seen to increase with increasing temperature from -27 to 50°C . This is opposite to the behavior measured for Plexiglas. The flaw size, $2c$, of polystyrene is approximately 0.05 in. at room temperature. This dimension approaches that of crazing flaws seen in polystyrene and therefore might actually represent the crazing behavior of polystyrene. Therefore crazing marks could be thought of as the Griffith flaws in the material which ultimately cause fracture. The curve in Figure 5 indicates the crazing resistance of polystyrene decreases with increasing temperature.

The crack propagation mode in polystyrene (Table II) is dependent on temperature. Contrary to Plexiglas, the crack propagation changes from continuous to discontinuous as the temperature is increased above 50°C . At -29°C . the propagation is still continuous, and the crack tears smoothly through the specimen. The molecular mechanisms causing a change in the mode of crack propagation are not yet clear.

SIGNIFICANCE OF THE FRACTURE SURFACE

The topography of tensile fracture surfaces of Plexiglas has been investigated in detail.^{15,17,18} The fracture surface of a cleavage sample and the appearance of colors on the surface have been described by Berry.¹⁴ In this investigation we have tried to relate the fracture surfaces to the mode of crack propagation and the measured value of surface work. The most important features of the fracture surface are the appearance of colors on the surface and the degree of roughness of the surface.

The appearance of colors is thought to be proof that an oriented layer of molecules is present at the fracture surface. The roughness of the fracture surface is dependent on the crack velocity, and in a tensile fracture the velocity can become great enough so that crack forking occurs which results in a very roughened surface. A velocity this high is never attained in the cleavage test, and the highest velocity reached in the cleavage test always resulted in a mirror-smooth surface. At the lower cleavage crack velocities which occur during continuous crack propagation, one material may have a roughened fracture surface while another type of material may have a mirror-smooth surface; in addition, the material with the less roughened surface has a lower surface work. Therefore it is believed that the degree of roughness of the fracture surface during slow controlled crack growth is an indication of the amount of molecular motion or viscous flow occurring in front of the propagating crack. Descriptions of the fracture surface for various polymers can be found in Table II.

Colors have been observed on Plexiglas II cleavage specimens. These colors remain constant over the entire length of the specimen but are confined to specific areas on the surface. Figures 6 and 7 show fracture sur-

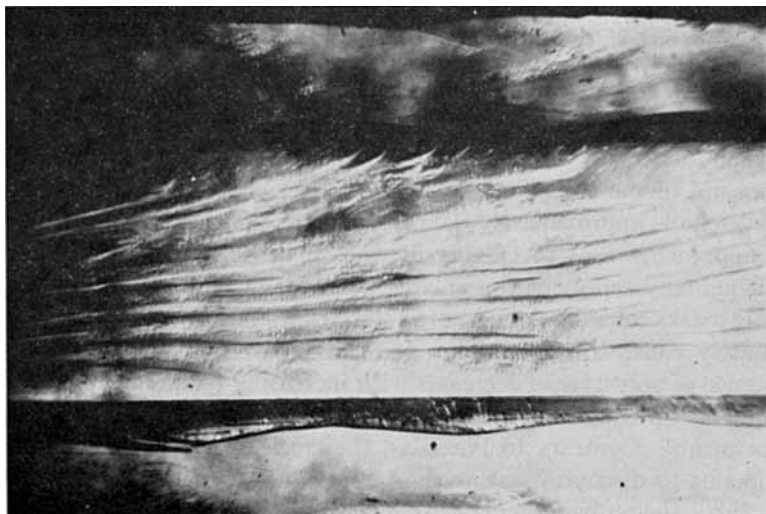


Fig. 6. Fracture surface of Plexiglas cleavage specimen. Crack propagated slowly from left to right (7 \times).



Fig. 7. Enlargement of fracture surface in Figure 6. The vertical striations represent crack hesitation points (27 \times).

faces for Plexiglas cleavage specimens. Figure 6 also shows the slotted sides and excess material which the crack picked up as it traveled partly out of the plane of the slot. This makes it necessary to measure the crack width at the end of the experiment rather than assuming the width is merely the unslotted area. The areas on the fracture surface which appear as ridges are usually colored green with some yellow, while the valleys are colored red mixed with yellow. On the opposite surface the colors are reversed; that is, the red areas on one surface are green on the mating surface. The patterns seen in Figures 6 and 7, sometimes called "river patterns," occur at low crack velocities and are associated with a high value of surface work. As the crack approaches the end of the specimen it becomes unstable because of the decreased end rigidity and propagates through the last $\frac{1}{2}$ in. with a high velocity. In this region the surface is also colored but mirror smooth; that is, there are no visible markings on the surface.

The fracture surfaces for polystyrene are much different than those of Plexiglas as can be seen in Figures 8-10. The polystyrene surfaces are not as organized as those of Plexiglas, and colors usually cannot be seen. The crazing and fine cracking accompanying the slow crack results in a very laminated surface which appears silvery when ordinarily viewed. Since the fracture surface is finely cracked, the colors might be made obscure. The odd foot-shaped patterns shown in Figure 8 occurred for only one type of polystyrene. These occurred along the entire crack length and are elevated above the surface. The walls of these patterns had to be formed by

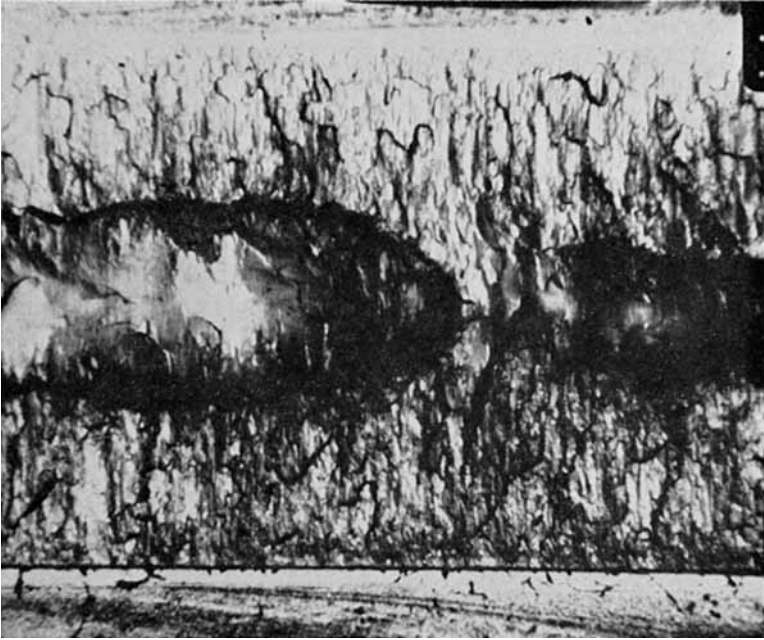


Fig. 8. Fracture surface of polystyrene cleavage specimen. Crack propagated slowly from left to right ($13.5\times$).



Fig. 9. Enlargement of fracture surface in Figure 8. The foot-shaped step is raised above the surface ($27\times$).

shear fractures. A high crack velocity in polystyrene results in a different type of surface, as may be seen in Figure 10. The surface is no longer laminated and does not appear silvery. However, it is still very rough, and also no colors are seen. The amount of crazing accompanying the crack seems to be reduced with increased crack velocities, as can be seen by the fracture surfaces. The reduction in crazing at high velocities would result in a lowering of the surface work. Therefore the surface work of a fast crack should be smaller than that of a slow crack. This agrees with experimental results found by Benbow.²⁴

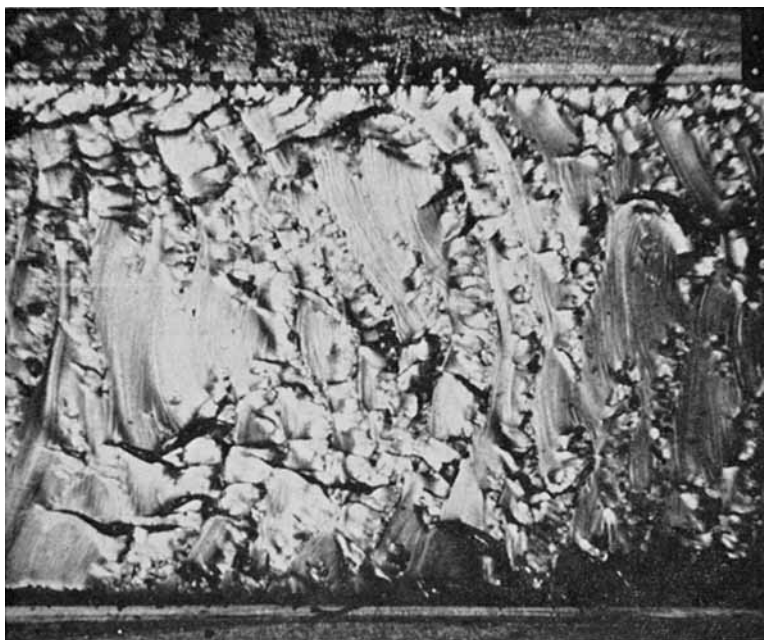


Fig. 10. Fracture surface of polystyrene cleavage specimen. Crack propagated with high velocity from left to right (13.5 \times).

It is interesting to note that as the test temperature increased the fracture surfaces of Plexiglas remained similar to those in Figures 6 and 7 until a temperature of 50°C. was reached. As can be seen in Table II, above 50°C. the fracture surface became mirror-smooth, with no distinguishable features. The mating fracture surfaces were both colored green uniformly along the entire crack length, and the crack propagation remained smooth and continuous. The uniformity of the color on both fracture surfaces is perhaps due to the absence of any topography on either fracture surface. Colors on the fracture surface indicate orientation still occurs at elevated temperatures, and the smooth surface at a low crack velocity indicates that orientation took place more easily; moreover, this means less resistance was offered to the crack propagation which is reflected by the lower

surface work. We might also be able to conclude that a fast crack has a lower surface work associated with it than a slow crack, as the fracture surface of a fast crack is smoother than that of a slow crack. We have now seen that both high crack velocities and elevated temperatures produce mirror-smooth fracture surfaces; in addition, for Plexiglas the surfaces remain colored under these conditions. The above conclusions are based on the assumption that a rougher fracture surface indicates increased molecular motion at the tip of a crack which results in a higher surface work.

At temperatures below -40°C . the crack propagates discontinuously, and the mirror-smooth surface is a result of high crack velocity. The fact that Table II reports no colors were seen on the fracture surface is perhaps a result of water condensation on the surface during the test. Benbow reports that water applied to the fracture surface will remove the colors.²⁴

In review it can be said that a smooth featureless fracture surface is due either to a high crack velocity or smaller amounts of molecular motion which is reflected by a lower value of surface work. Colors seem to be restricted to Plexiglas fracture surfaces, and the absence of colors does not necessarily mean an absence of molecular orientation at the fracture surface. Absence of colors could mean the oriented film is not thick enough to interfere with the light or that the surface roughness eliminates the colors.

APPENDIX

Preparation of Cleavage Samples

In cases where comparative measurements are being made, such as the surface work versus temperature for a given material, individual specimens are taken from the same sheet of material. The cleavage specimens have a length of approximately 10 in. and a width of 1.2 in. The specimens are first cut from the sheet in 2 in. wide strips and then milled so their edges are parallel. Although the final specimens are only 1.2 in. wide, the extra width allows extra height in positioning the specimen to cut the 6-mil slot. The slot is cut with a 0.006-in. screw slotting saw ($2\frac{1}{4}$ in. diameter, 60 teeth) placed in the Bridgeport milling machine. It was found desirable to rotate the saw blade at 325 rpm, and the specimen was fed past the blade at approximately 0.75 in./min. A soap solution was applied to the blade to reduce frictional wear and also to reduce the temperature in the specimen. With this technique the total depth of slot can be cut in one pass. The optimum slot depth was found to be one-quarter of the specimen thickness which resulted in a maximum cut of 0.065 in. for $\frac{1}{4}$ in. thick specimens. After the sides are slotted, a crack is machined at one end of the specimen by increasing the depth of the slots until they intersect. The resulting cut is called a "swallow-tail" cut, and the initial crack is machined to a length of about 1 in.

After the slotting operation is completed, the specimen is washed to remove all of the lubricant. Calibration marks are next engraved on the

specimen in a horizontal milling machine so that the crack length can be conveniently recorded during the test. The marks are placed every $1/4$ in. with an accuracy of ± 0.001 in. The specimens are next reduced in width from 2 in. to the final width, which in most cases was 1.2 in. Finally, $1/8$ in. holes are drilled to receive the loading pins. The holes are placed 0.1 in. from the end of the specimen and approximately 0.14 in. from top to bottom. After the machining is completed, the specimens are annealed according to manufacturers' recommendations.

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Résumé

On a admis récemment que l'écoulement visqueux ou la déformation plastique s'effectue près du sommet d'une fissure dans des polymères amorphes et vitreux tels que le Plexiglas, et ceci conduit à une orientation moléculaire à la surface de fracture. On en trouve la preuve dans l'apparition d'une couleur à la surface d'une fracture fraîche de Plexiglas et d'un travail de surface mesuré extrêmement élevé, qui est 1000 fois supérieur à l'énergie de surface théorique. L'énergie de surface d'un solide est défini comme la quantité d'énergie requise pour créer une surface unitaire dans le matériau par séparation de deux plans, chacun de la moitié d'une unité de surface et le travail de surface mesuré d'un polymère peut également comprendre tout travail irréversible qui s'effectue lors du processus de fracture. Dans les présentes recherches, on a utilisé un test de clivage pour mesurer le travail de surface d'un polymère vitreux et pour mesurer les effets de la température sur ce travail de surface. On a utilisé un moyen reproductible pour mesurer le travail de surface pour des fissures qui se propagent d'une manière continue et pour des fissures qui se propagent par ramification. Le travail de surface mesuré pour le Plexiglas II est 1.2×10^5 erg/cm² et la valeur pour un polystyrène typique est de 4×10^5 erg/cm² comparée aux estimations théoriques de 450 erg/cm². Le travail de surface varie dans le domaine de température de -40°C à 80°C . Le travail de surface du Plexiglas II et du polystyrène diminue avec une augmentation de la température. Des colorations ont été observées sur les surfaces de fractures pour l'ensemble du domaine de température et la surface de fracture passe de rugueuse à lisse par élévation de la température. D'après l'équation de Griffith, le côté interne fissuré des polymères varie aussi avec la température et on pense le relier au mauvais comportement du polymère. A 23°C , le côté fissuré du polystyrène est de 0.05 pouces et pour le Plexiglas II de 0.002 pouces.

Zusammenfassung

Kürzlich wurde postuliert, dass viskoses Fliessen oder plastische Deformation nahe der Spitze eines fortschreitenden Risses in glasig amorphen Polymeren, wie Plexiglas, auftritt; dies ergibt eine Molekülorientierung an der Bruchoberfläche. Ein Beweis dafür ist das Auftreten von Farben auf der frischen Bruchoberfläche von Plexiglas und die extrem hohe gemessene Oberflächenarbeit, die 1000 mal grösser ist als die theoretische Oberflächenenergie. Die Oberflächenenergie eines festen Körpers wird definiert als der zur Schaffung einer Einheitsoberfläche im Material durch Trennung von zwei Flächen, die jede das Ausmass einer halben Einheitsfläche haben, notwendige Energiebetrag; die gemessene Oberflächenarbeit eines Polymeren kann auch irreversible, während des Bruchprozesses auftretende Arbeit beinhalten. In der vorliegenden Untersuchung wurde ein Spaltbarkeitstest zur Messung der Oberflächenarbeit von glasigen Polymeren und der Temperatureinflüsse auf die Oberflächenarbeit verwendet. Ein reproduzierbares Verfahren zur Messung der Oberflächenarbeit von kontinuierlich oder stossweise wachsenden Rissen wurde entwickelt. Die gemessene Oberflächenarbeit von Plexiglas II beträgt $1,2 \times 10^5$ erg/cm², der Wert für ein typisches Polystyrol 4×10^5 erg/cm², im Vergleich zu einem theoretischen Schätzwert von 450 erg/cm². Die Oberflächenarbeit ändert sich mit der Temperatur über einen Bereich von -40°C bis 80°C . Die Oberflächenarbeit von Plexiglas II und Polystyrol nimmt mit zunehmender Temperatur ab. Farben konnten an Plexiglasbruchoberflächen über den ganzen Temperaturbereich beobachtet werden, und die Bruchoberfläche geht bei erhöhten Temperaturen von einer rauhen Beschaffenheit zu einer spiegelglatten über. Die spezifische Fehlstellengrösse der Polymeren nach der Gleichung von Griffith variiert ebenfalls mit der Temperatur, und scheint mit dem Rissverhalten der Polymeren zusammenzuhängen. Bei 23°C beträgt die Fehlstellengrösse für Polystyrol 0,05 in und für Plexiglas II 0,002 in.

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