Fracture Surface Work Measurements on Glassy Polymers by a Cleavage Technique.   II.   Effects of Crosslinking and Preorientation

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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 at 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 effect of crosslinking has been studied by measuring the surface work of crosslinked forms of Plexiglas and highly crosslinked thermosetting polymers. The surface work decreases as the degree of crosslinking in Plexiglas increases. Colors are absent on the fracture surface of the highly crosslinked Plexiglas, and the surface is mirror-smooth. The effect of crosslinking is to inhibit viscous flow or plastic deformation at the tip of the crack. The surface work of polyester and epoxy resins have been measured and found to be a factor of 10 smaller than the linear polymers, but still remain much higher than the theoretical estimates. Preorienting Plexiglas or polystyrene reduces the surface work of a crack propagating parallel to the orientation and increases the surface work of a crack normal to the orientation. The colors on the fracture surfaces of preoriented Plexiglas samples either disappear or change to colors of shorter wavelengths if the crack is propagated parallel to the orientation. This is a good indication that orientation occurs at the tip of a crack and is responsible for the appearance of colors on Plexiglas fracture surfaces. The surface work of 150% hot-stretched polystyrene is 7000 erg/cm.^{2}, and the fracture surface is mirror-smooth. This surface work is greater by only a factor of 10 than the theoretical estimate and suggests that only a small amount of molecular motion has taken place.

INTRODUCTION

The fracture surface work of a glassy polymer is simply defined as the energy required to cause crack propagation; however, this has also been called "surface tension,[1] "surface energy,"[2] "tearing energy,"[3] and is also related to G_c, critical strain energy release rate.[4]   Methods have recently been developed to measure, this quantity accurately for glassy polymers by a cleavage technique.[5-7]   It has been shown that the measured surface work of a glassy polymer is much greater than the calculated value and

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that this value is also a function of temperature.[7-9] The current theory to explain the above results is that the viscous flow or plastic deformation occurring in advance of the propagating crack results in molecular orientation at the fracture surface, especially in poly(methyl methacrylate); furthermore, polymers such as polystyrene are subjected to crazing at the crack tip, causing even higher values of fracture surface work. In order further to clarify these theories we have investigated the influence of certain molecular parameters, crosslinking and preorientation, on the resulting surface work of the polymers.

EFFECT OF CROSSLINKING ON THE FRACTURE SURFACE WORK

Background

The introduction of chemical crosslinks into a linear polymer increases many of the physical properties, such as elastic modulus, heat distortion temperature, solvent resistance, and glass transition temperature. The effect on tensile strength is not so clearly defined, except when the crosslink density becomes too great and causes a reduction in tensile strength because of embrittlement. The crosslinks transform the linear chain structure into a three dimensional network which reduces the chain mobility and greatly limits viscous flow. Since viscous flow, or plastic deformation, is thought to occur at the tip of a propagating crack in a glassy polymer, crosslinking the polymer should reduce the surface work. Berry has confirmed this by preparing a crosslinked Plexiglas using 10% ethylene glycol dimethacrylate as a cross-linking agent. He used the tensile strength versus flaw size experiment to measure surface work and found it to be only 4.5×10^4 erg/cm.[2] compared to 1.2×10^5 erg/cm.[2] for a conventional Plexiglas; he also reported that no colors were evident on the fracture surface.[8]

We thought it would be profitable to make additional measurements using the more accurate cleavage technique. A chemically crosslinked Plexiglas (Polymer K) was supplied to us by Rohm and Haas Co. The crosslink density is probably as high as can be feasibly achieved with Plexiglas. In order to establish the effect of crosslinking further, it was suggested that we measure the surface work of Plexiglas 55 which is described as being lightly crosslinked and therefore intermediate to that of the normal Plexiglas (Plexiglas II) and the highly crosslinked Plexiglas. The light crosslinking in Plexiglas 55 is thought to be due to hydrogen bonding occurring between the polymer chains, resulting in better crazing resistance and solvent resistance.

Investigations of the Crosslinked Forms of Plexiglas

The experimental procedure used to determine surface work for these polymers is identical to that already described and is a function only of whether the crack propagates continuously or in a stick-slip fashion.[7] The plot of data used to determine the surface work of the crosslinked
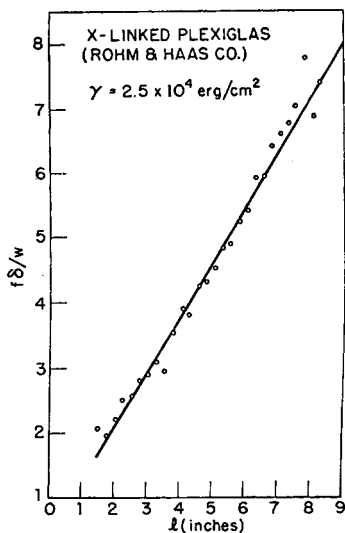
Fig. 1. Graph used to determine the value of γ from the relation $f\delta/w = 4\gamma l/n$ (slope of line $= 4\gamma/n$).
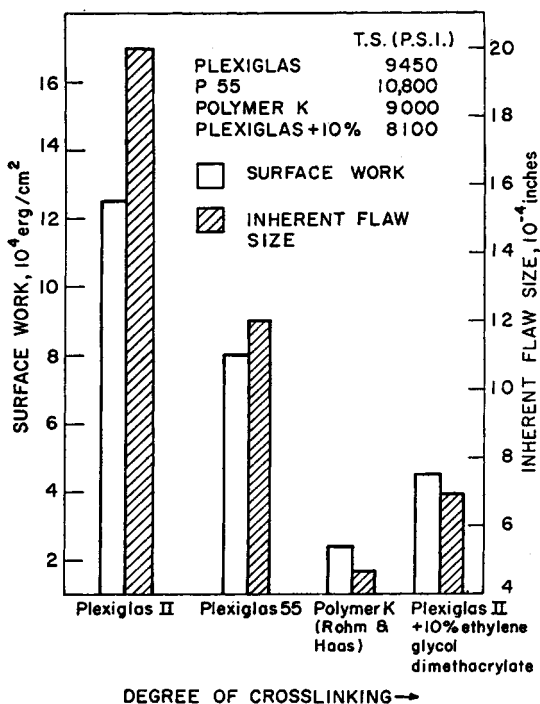

Fig. 2. Effect of crosslinking on the surface work and inherent flaw size of Plexiglas.

Plexiglas is shown in Figure 1, and it can be seen that the experimental scatter is very small.

Figure 2 shows the results of the surface work and flaw size measurements on the various forms of Plexiglas. The results are presented as a bar graph, with no quantitative significance to the axis, representing the degree of crosslinking since the absolute degree of crosslinking is not known for these polymers. Berry's measurements have also been included in the graph and are represented as the most highly crosslinked polymer. However, there is some question as to whether Berry's polymer is more highly crosslinked than Polymer K; therefore, not much significance should be placed on the relative positions given Polymer K and Berry's polymer in Figure 2. The surface work of Polymer K is reduced by almost a factor of 10 from that of Plexiglas II. The value measured for Plexiglas 55 lies almost halfway between these two values. From the results shown in Figure 2 one can conclude that increasing the degree of crosslinking restricts viscous flow or plastic deformation in the vicinity of the crack, causing a reduction in the measured surface work.

The inherent flaw size also decreases with increasing degree of crosslinking. If the flaw size represents the crazing behavior of a polymer, then Polymer K should be the most craze-resistant of the polymers tested and Plexiglas 55 should be more craze-resistant than Plexiglas II. This relationship has been found to be true in the actual performance of these materials.

The fracture surface appearance of Plexiglas 55 is nearly the same as that previously described for Plexiglas II.[7] The degree of roughness is almost identical, and the colors on the surface are the same and bear the same relationship to the topography of the surface. The mode of crack propagation is also the same for the two polymers. The fracture surface of Polymer K is much different than the surfaces of the above-mentioned polymers. It is completely featureless and mirror-smooth, with complete absence of colors. The crack propagation remains continuous, and therefore the crack velocity is low. This fracture surface is similar to that obtained on Plexiglas II at elevated temperatures, except for the absence of colors in the present case. The appearance of a mirror-smooth fracture surface at low crack velocities is an indication that a smaller amount of molecular motion is occurring ahead of the crack and therefore the resistance to crack propagation is reduced. This is shown quantitatively by a decrease in the surface work. The disappearance of colors indicates that the thickness of the oriented layer is not large enough to interfere with visible light or that the viscous flow did not manifest itself in orientation. The modes of crack propagation and fracture surface appearances are summarized in Table I.

The measured surface work is not only useful as a guide to the amount of molecular motion, but can be used to interpret the tensile strength. For instance, as shown in Figure 2, the tensile strength of Plexiglas 55 is greater than the strength of Plexiglas II. The crack toughness of Plexiglas 55 is smaller, as the surface work is about 50% less than that for Plexiglas II.

The reason for the increased tensile strength [refer to the Griffith equation, $\sigma = (2E\gamma/\pi c)^{1/2}$] must then be attributed to a greater than 50% reduction in flaw size of the material. The change in elastic modulus is small compared to the changes in surface work and flaw size. The reduction in strength shown for Polymer K is due primarily to a great reduction in crack toughness, or surface work, and the reduction in flaw size coupled with the increase in modulus is not sufficient to make up for the loss in crack toughness.

The temperature dependence of surface work has been measured for Plexiglas 55 and Polymer K and is shown in Figure 4. In addition, the

TABLE I
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
Polyesters	20	Discontinuous propagation	Mirror-smooth
Crosslinked Plexiglas II	20	Continuous tearing	Mirror-smooth, no colors
Oriented Plexiglas 55 (parallel)	20	Continuous tearing	Mirror-smooth, no colors
Hot-stretched polystyrene (150%)	20	Continuous tearing	Mirror-smooth, no colors
Hot-stretched Plexiglas (100%)	20	Continuous tearing	Mirror-smooth, violet colors

flaw size variation for Plexiglas 55 is also shown. The temperature behavior of Plexiglas 55 is different from that previously observed for Plexiglas II,[7] as a maximum in the surface work occurs at approximately 50°C. At temperatures greater than 50°C., the decrease in surface work is similar to that previously observed for Plexiglas II and can be explained by the ease of orienting molecules at these temperatures. However, below 50°C. the surface work decreases with decreasing temperature implying that the amount of orientation or viscous flow is decreasing. Although the surface work of Plexiglas II did not show a maximum over the same temperature range as used for Plexiglas 55, it was speculated that a maximum might occur at a temperature lower than used in our tests. The shape of the

curve for Plexiglas II would then be similar to that for Plexiglas 55, although the temperature scale would be shifted.

The flaw size for Plexiglas 55 at room temperature is smaller than the flaw size for Plexiglas II. The flaw size increases with increasing temperature, similar to that of polystyrene. At a temperature of about 70°C. the flaw size of Plexiglas 55 becomes larger than that of Plexiglas II; therefore at elevated temperatures this polymer would no longer be more craze-resistant than normal Plexiglas, providing the analogy between flaw size and crazing behavior is valid. The variation in the appearance of the fracture surface is similar to that already discussed for Plexiglas II. Crack propagation remained continuous over the temperature range studied.
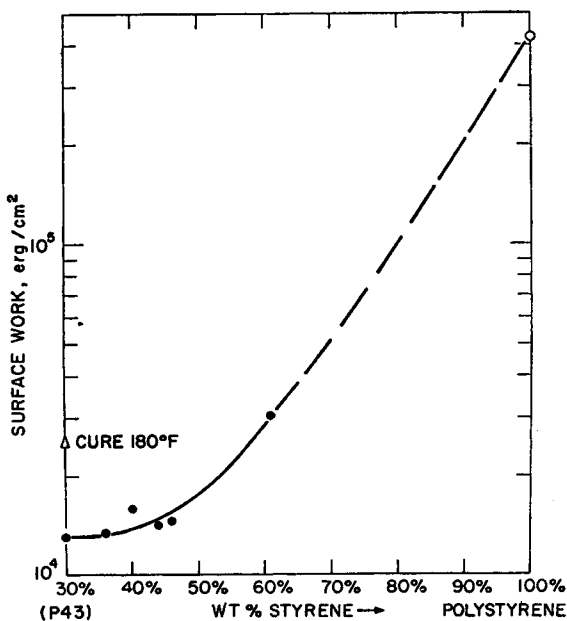

Fig. 3. Variation of surface work with the amount of styrene added to a polyester (Paraplex 43) resin.

The variation of the surface work of Polymer K is also shown in Figure 3, though only two points are available due to a limited amount of material. The surface works measured at 20 and 60°C. were almost identical and almost an order of magnitude smaller than those measured for Plexiglas II. The fact that no variation was measured between these temperatures might be due to the presence of a maximum or minimum in the variation between these two temperatures. If there is no variation with temperature, it may result from restricted chain mobility due to the crosslinking of the polymer molecules. Neither the fracture surface nor the mode of crack propagation, which was continuous, differed at the two temperatures.

Investigation of Thermosetting Polymers

In order to learn more about the effect of crosslinking, especially the relation between the measured surface work and the theoretical surface energy of a crosslinked polymer, we have investigated thermosetting polymers which can be considered highly crosslinked. One of the questions which we sought to answer was how small was the measured surface work of these crosslinked polymers, since the crosslinking should substantially reduce the amount of molecular flow which occurs in the vicinity of the crack. In our investigations we used a polyester resin supplied by Rohm and Haas (Paraplex 43) and an epoxy resin supplied by Shell Chemical Co. (Epon 828). One of the primary reasons for using these polymers was the ease with which they could be cast into flat sheets.

TABLE II
Data Used to Determine Surface Work of an Epoxy Resin[a]

Crack length l, in.	Force f, lb.	Deflection δ, in.	Crack width w, in.	f/δ	$f\delta/w$
1.95	7.13	0.022	0.185	322	0.85
2.21	6.29	0.030	0.181	210	1.04
2.85	5.43	0.042	0.185	130	1.23
3.55	4.52	0.062	0.192	73	1.46
4.48	3.72	0.094	0.189	39.4	1.86
5.75	2.96	0.149	0.185	19.8	2.38
7.35	2.51	0.204	0.192	9.8	3.32
1.58	6.75	0.015	0.142	458	0.70
1.82	6.50	0.019	0.138	346	0.82
2.17	5.94	0.025	0.150	236	0.96
2.64	4.99	0.034	0.150	148	1.13
3.24	4.25	0.047	0.157	90	1.28
4.02	3.62	0.069	0.154	52	1.63
5.13	2.86	0.100	0.154	28.4	1.87
6.45	2.51	0.175	0.169	14.4	2.59
8.86	1.86	0.303	0.157	6.2	3.59

[a] Material: epoxy (two specimens with data combined); test temperature: 23°C.; specimen thickness: $1/4$ in. Results: $n = 2.54$; $\gamma = (4.3 \pm 0.03) \times 10^4$ ergs./cm.^{2}.

The mold used to cast both $1/4$ in. and $1/8$ in. sheets of these materials consisted of two sheets of plate glass approximately 15 in. square. Along the perimeter of the glass was placed either $1/4$ or $1/8$ in. soft rubber, and the glass plates were held together with spring clips. The rubber was soft enough to allow for the shrinkage of the resin which occurs during curing. The curing agents used for the polyester resin were $1 1/2\%$ MEK peroxide and 0.2% cobalt naphthenate. The epoxy resin was cured with 10% diethylenetriamine. The resin was left in the mold for 24 hr.; the sheets were then removed from the mold and post-cured at a temperature of 240°F.

Results of measurements made on the epoxy resin can be found in Table II. The crack propagation mode was discontinuous, and the length of the crack jumps sometimes exceeded 1 in. This means only a limited number of data points can be taken on a single specimen. Table II shows the data taken for two separate specimens from the same casting. The data for the two specimens has been combined to determine one value of the surface work. The value of the surface work from these measurements is $(4.3 \pm 0.03) \times 10^4$ erg/cm.[2] The error is very small, considering the combination of data which had to be made. Although the surface work is reduced from the values observed for noncrosslinked glassy polymers, it is still a factor of one hundred greater than the theoretical value for a glassy polymer (450
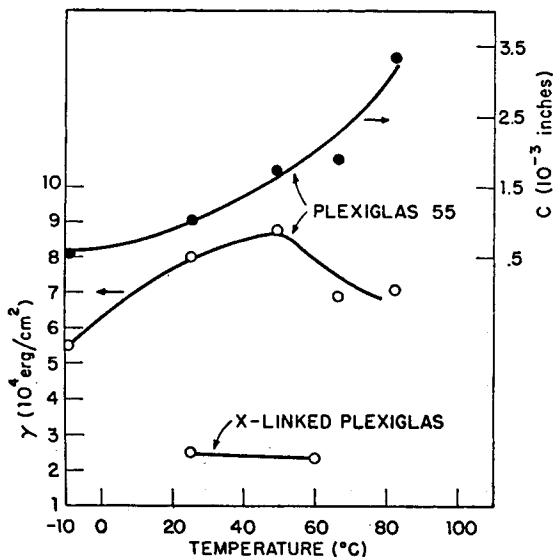

Fig. 4. Variation in the surface work and inherent flaw size with temperature or Plexiglas 55 and a crosslink Plexiglas.

erg/cm.[2]). This indicates that even for this highly crosslinked polymer a large amount of viscous deformation, or plastic deformation, may occur ahead of a growing crack. The fracture surface of the epoxy resin was mirror-smooth, which could have been due to the high crack velocity or to a comparatively small amount of molecular motion in front of the crack.

The polyester resin was studied in more detail than the epoxy resin. The polyester resin (P43) as prepared contains 30% styrene which forms the crosslinks between the polyester chains during the curing of the resin. In order to determine the effect of the styrene on the surface work, we added increasing amounts of styrene monomer to the P43 resin and measured the surface work of the resulting polymer. The results can be seen in Figure 4. If the increased styrene resulted in more crosslinks, the surface work should be reduced; however, if the added styrene monomer increased the length

TABLE III
Inherent Flaw Size for Polyester–Styrene Mixtures

Material	Strength, psi	Elastic modulus, psi	Flaw size, in.
P43[a]	7,619[b]	610,000	0.46×10^{-3}
P43	7,327[b]	550,000	0.52×10^{-3}
	9,000[c]	550,000	0.34×10^{-3}
	17,500[d]	550,000	$0.9 \ \times 10^{-4}$
P43 + 36% styrene	6,166[b]	625,000	0.79×10^{-3}
P43 + 41% styrene	5,708[b]	570,000	0.94×10^{-3}
P43 + 44% styrene	4,130[b]	625,000	$1.9 \ \times 10^{-3}$

[a] Subjected to vacuum before casting.
[b] Flexural strength (two-point loading).
[c] Tensile strength.
[d] Flexural strength (one-point loading).

of the styrene link or merely polymerized within the polyester gel, the effect of the surface work would be less predictable.

It can be seen that increasing the styrene content of the resin increased the measured surface work. The increase was insignificant until the polyester–styrene mixture reached 50% by weight of styrene. The maximum styrene content which could be used was about 61%, since excess shrinkage during curing caused the castings to crack while in the mold. The increase in surface work above 50% styrene content indicates that the styrene did not further crosslink the resin. Either the length of the styrene link must have increased or free polystyrene existed as a second phase. This may have caused the crack to pass through an environment of polystyrene in addition to the polyester molecules. The polystyrene, which is able to flow more readily than the polyester, could have acted to increase the surface work. The curve in Figure 4 has been shown extrapolated to the surface work value of pure polystyrene which remains much greater than any of the measured values for the mixtures. The effect of curing temperature is also indicated in Figure 4 for a P43 sample. The lower temperature cure resulted in a higher measured surface work.

The inherent flaw size of these polyester–styrene blends has also been calculated as shown in Table III. The flaw sizes of these materials are only one-tenth to one-hundredth of the values for the noncrosslinked amorphous polymers. It can be seen that the flaw size increases substantially with increasing styrene content. The variation in flaw size is much greater than the variation in surface work as a result of increasing the styrene content.

As shown in Table I the mode of crack propagation for the thermosetting polymers is discontinuous propagation. The fracture surface was mirror-smooth and usually featureless, except at the points where the crack stopped and then started again (Figs. 5 and 6). At these points a cleavage step is present which represents a change in elevation as the crack began to propagate. Note that the fracture front or cleavage step is not perpendicular

to the edges of the specimen but rather leads at the outside edges.   This is an indication that the velocity of the crack is faster at the outside edges of the specimen.   The fine cracking which occurs on the surface is caused by
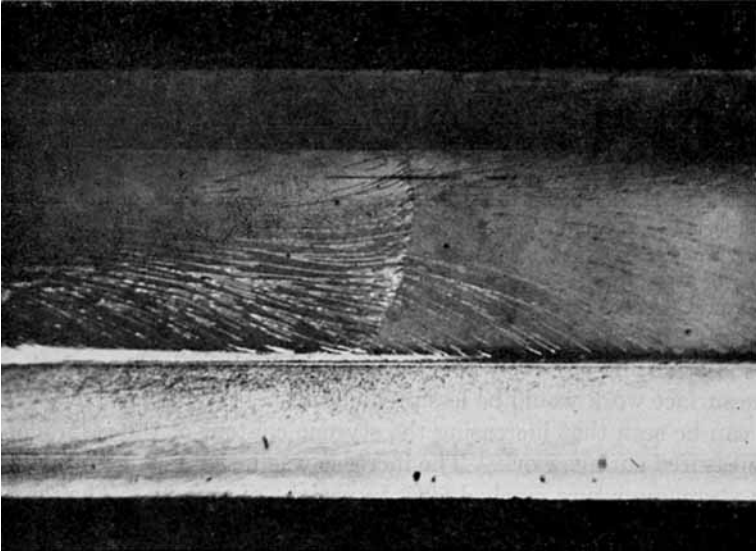

Fig. 5. Cleavage fracture surface of a polyester casting with 61% styrene.   Note where the crack stopped and then started forming a cleavage step.   Crack propagated from right to left (13.5×).
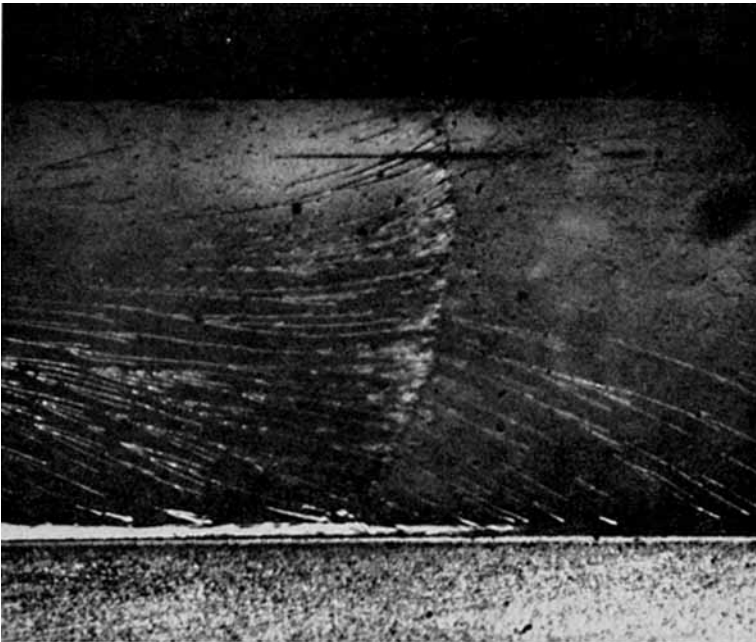

Fig. 6. Detail of cleavage step shown in Fig. 5 (27×).

the addition of the styrene. The fracture surface of the P43 resin alone does not show these fine cracks and is almost featureless.

The results for the crosslinked polymers indicate that the surface work of a polymer decreases as the degree of crosslinking increases. The surface work of a crosslinked polymer may be a factor of ten smaller than that for a noncrosslinked polymer; however, the surface work of a crosslinked polymer is still 100 times greater than the theoretical value, which indicates that a substantial amount of viscous flow or plastic deformation may still occur in the vicinity of a propagating crack. The fracture surfaces of crosslinked polymers are mirror-smooth, and the fracture surface of a highly crosslinked Plexiglas has been shown to be colorless, which indicates a reduction in the thickness of the oriented layer.

EFFECT OF PREORIENTATION ON THE SURFACE WORK

Background

Preorienting a glassy amorphous polymer can be accomplished by stretching the polymer at a temperature above the glass transition temperature and then rapidly chilling it to the glassy state while holding the stretched length fixed. The resultant structure remains uniaxially oriented and highly anisotropic in the glassy state, and its physical properties are significantly changed by the orientation; the tensile strength and modulus of elasticity are increased in the direction of orientation but are decreased in the direction normal to it. The index of refraction also differs in the two perpendicular directions and this resulting birefringence is often used as a measure of the degree of orientation. Another measure of orientation which has been proposed by Irwin is the K value of a polymer.[4] This is related to the surface work of the material and is measured in a tension test using a specimen with a central notch. The value of K has been shown to depend on the stretching rate and temperature of orientation,[10] and has been measured principally for biaxially oriented materials in which case the crack propagates normal to the plane of the oriented structure.

Although there has been much interest in studying crack propagation in this fashion, normal to the direction of orientation, there has been little work in crack propagation studies parallel to the orientation. Since orientation is believed to occur locally on the fracture surfaces of Plexiglas and polystyrene it appeared highly interesting to measure the surface work of a uniaxially oriented polymer when cracked in planes parallel to the direction of prior orientation. If orientation occurs at the fracture surface, then the surface work should decrease as the polymer preorientation increases; furthermore, one would expect the colors on the fracture surfaces of Plexiglas to disappear when the crack is propagated parallel to the orientation. Although we can measure the surface work of these polymers, the values have significance only when we know the theoretical value for the polymer. The theoretical value of 450 erg/cm.[2], which has been previously calculated, is based on the assumption that the polymer molecules

are originally oriented normal to the crack; fracture occurs by separation of the primary valence bonds of the carbon–carbon polymer chain. The calculated value of surface energy is only slightly affected by temperature and crosslinking, but orienting polymer molecules parallel to the direction of crack growth will reduce the calculated value. We will see later that the reduction in the experimentally measured surface work will make any reduction in the calculated surface work seem insignificant.

Studies on Multiaxially Oriented Sheets of Plexiglas

The first type of material studied to evaluate the effect of orientation on surface work was a sheet of stretched Plexiglas 55, commercially available (Swedlow, Inc.). The oriented sheets are described as being multiaxially stretched, and the particular ones we received were hot-stretched 65% in all directions. The sheet used for the surface work measurements was $5/8$ in. thick and is pictured in Figure 7. The specimens labeled 0°, 45°, and 90° show the effect of a crack propagating through oriented chains, and the specimens are oriented similarly to the specimens used to determine the K value for the material. Fortunately, the sheet was thick enough to allow us to also propagate a crack parallel to the planes of orientation, as indicated in Figure 7.

Only three data points could be taken for each specimen, as crack propagation was discontinuous and the crack jumps were extremely large. The surface work values are shown in Figure 7 and they are greater by at least a factor of 6 than those for unoriented Plexiglas 55. The reason the values shown for 0° and 90° are different could be a result of experimental error since only three points were taken on each specimen. Another reason for the difference could be due to nonuniform orientation during the stretching process. The surface work at 45° to the orientation axes was the smallest

MULTIAXIALLY STRETCHED (65 %) PLEXIGLAS 55

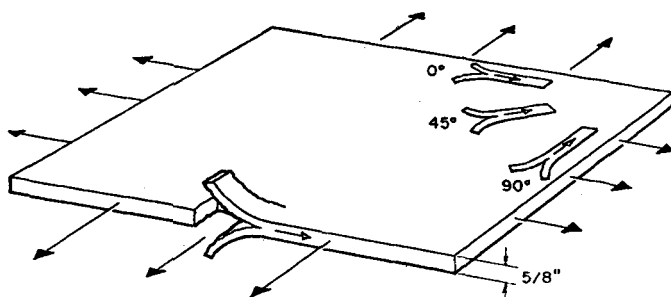| STRETCHED P55	SURFACE WORK (erg/cm^2)
0°	6.5×10^5
45°	5.8×10^5
90°	7.8×10^5
II	1.65×10^4

Fig. 7. Location of cleavage specimens taken from oriented Plexiglas sheet.
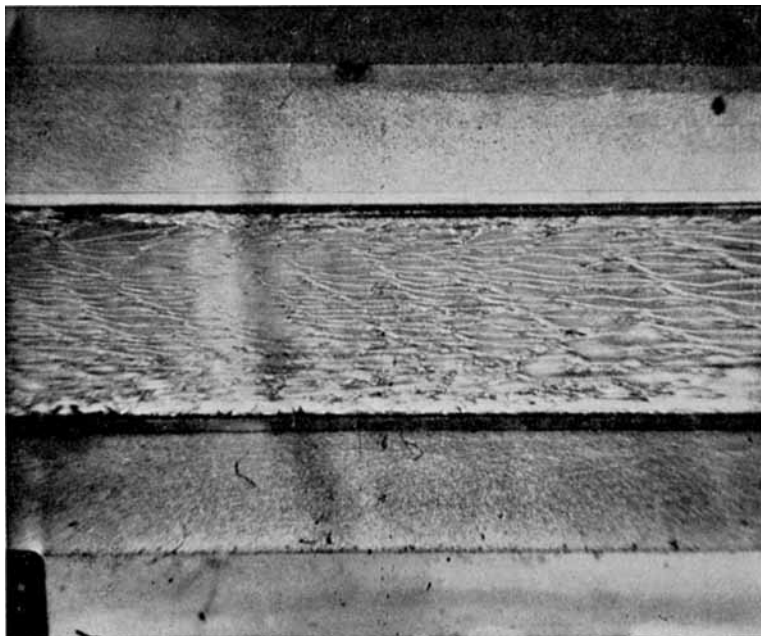
Fig. 8. Cleavage fracture surface of oriented Plexiglas. Fast crack growth region and crack propagated from left to right (7×).

of the values, and could indicate that the orientation was the least in this direction.

Fracture surfaces for these specimens can be seen in Figures 8 and 9 which represent regions of fast crack growth. In contrast to the other polymers studied, the region of fast crack growth is not mirror-smooth. The surface is finely divided by subcracks which indicate the difficulty the crack encountered in trying to pass through the oriented chains. Therefore, it appears that the surface work even at high crack velocities remains high. The occurrence of large crack jumps represents a large release of strain energy which is stored in the specimen before the unstable crack growth. The excess strain energy is stored in the specimen because of the difficulty the crack has in starting to move through the oriented chains. Green and red colors were seen on the fracture surface and they appeared the same on mating surfaces. However, the roughness of the surface made them appear irregular.

In addition to the above surface work measurements, the surface work was also measured parallel to the orientation planes. The surface work is reduced to a value of 1.65×10^4 erg/cm.^{2}, less than 20% of the surface work for unoriented Plexiglas 55. This value would be smaller if the sheet had been stretched more than 65%. As pointed out earlier, the theoretical value of the surface work will also be reduced, but the reduction will be small compared to the experimental reduction. It was observed after the test that these specimens did not return to their original shape. Each half

Fig. 9. Details of fast crack growth region shown in Fig. 8 (27×).

of the specimen had a concave curvature which resulted in a residual deflection when the two halves were placed together. This was caused by residual stresses present in the specimen before testing. By cleaving the specimen the residual stress was relieved and a permanent deformation resulted. By measuri. g the residual curvature the measured surface work can be corrected to a true measured value.[11] The true measured value is greater than the experimentally measured value because the addition of a residual strain energy release besides the normal strain energy release is not considered in the original theory. The correction is small, and the corrected value of the surface work is approximately 1.90×10^4 erg/cm.^{2}

The fracture surface was mirror-smooth, and the crack propagation was continuous. There were no colors present on the fracture surfaces which indicate that the thickness of the oriented film has become very small or that no orientation is present. We feel that this is excellent evidence for the postulated occurrence of orientation at the fracture surface in Plexiglas. In other words, the crack could not produce as much orientation as usual, since the orientation of the chains before the test was more nearly parallel to the direction of crack growth.

Studies on Uniaxially Stretched Plexiglas and Polystyrene

In order to measure the surface work of a crack propagating parallel to the orientation as a function of the degree of orientation, we developed a procedure for uniaxially hot stretching of both Plexiglas and polystyrene.
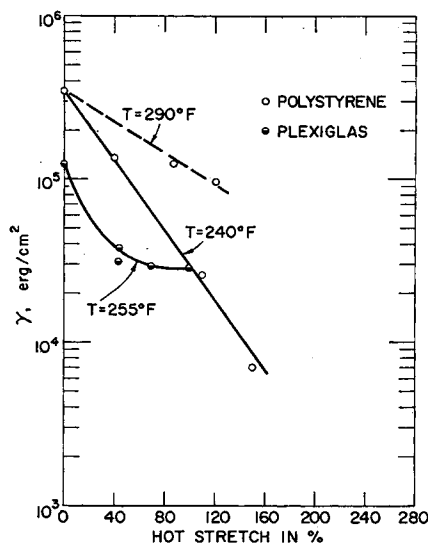
Fig. 10. Effect of preorientation on the surface work of polystyrene and Plexiglas.

A hydraulic testing machine was used to stretch the material and a heating chamber, capable of reaching 350°F. was placed in the machine. Rectangular bars of $1/8$ and $1/4$ in. thickness were stretched, the initial thickness depending on the degree of orientation which was to be achieved. The thicker bars were used for the higher degree of orientation so that the final thickness would be convenient for machining cleavage specimens. The width of the bars was 2 in., and the lengths varied from 4 to 7 in., depending on the degree of stretch required. A rectangular cross section was used for the stretching as this required the least amount of machining after stretching. The only machining necessary was to make the edges of the stretched bar parallel and to cut off the ends of the specimens near the gripping area where nonuniform stretching might have occurred.

In order to select a stretching temperature one has to choose between ease of orientation and the amount of relaxation which might occur while the polymer is above its glass transition temperature. Bailey has shown that a good temperature for stretching polystyrene is about 220°F.; at this temperature, the birefringence remains proportional to the per cent of hot stretch.[12] We have used two different stretching temperatures for polystyrene, 240 and 290°F. The stretching temperature used for Plexiglas II was 255°F. The stretching rate used for polystyrene and Plexiglas was approximately $3^{1}/_{2}$ in./min.

The results of the surface work measurements can be seen in Figure 10. The surface work has been plotted as a function of the per cent hot stretch which is defined as the per cent increase in length of the stretched specimen. Although it might have been better to use birefringence as a measure of the orientation, it is thought that for stretching temperatures of 240 and 255°F.

the birefringence is proportional to the per cent hot stretch. We observed that the birefringence in the cleavage specimen was uniform along the length of the specimen although it varied across the width. This indicates that the orientation was uniform along the entire crack length.

Polystyrene, stretched 150% at 240°F., has a surface work 100 times smaller than unoriented polystyrene if a crack is propagated parallel to the direction of orientation. The surface work of polystyrene at 150% hot stretching is only 7000 erg/cm.^{2}, which is the lowest surface work we have measured for a polymer. The value of 7000 erg/cm.^{2} is of the same order of magnitude as that measured for metallic crystals, and is only a factor of 10 greater than the theoretical value of surface work for a polymer. If the curve shown in Figure 10 for polystyrene stretched at 240°F. was extended to higher degrees of orientation, it would probably not continue as a straight line but would begin to level off similar to the curve for Plexiglas. A curve is also shown for polystyrene stretched at 290°F., and the surface works are higher than for the specimens stretched at 240°F. This results from increased relaxation at the higher temperature and the degree of orientation would therefore be less for any per cent hot stretch.

The crack propagation for oriented polystyrene remained continuous at all orientations. The fracture surfaces remained rough until 150% hot stretching (240°F.); at this orientation the surface was mirror-smooth and featureless. This was the first time a smooth fracture surface had been produced with polystyrene. The very small measured surface work, which corresponds to a small degree of molecular flow at the tip of the crack, results in a smooth fracture surface. Colors appeared on the fracture surface of the specimen which had been stretched 40% at 240°F. This was the only polystyrene specimen on which the colors appeared. Although the colors appeared the same on both surfaces, the surfaces were quite rough, and the colors could not be related to specific topographic features. When microscopic observations were made it appeared that the colors formed rings around hundreds of tiny nuclei on the surface. The microscopic appearance resembled a Newton's ring effect which could be a result of submicroscopic cracking below the surface.

The results obtained for Plexiglas are also shown in Figure 10. The maximum degree of hot stretch was 100%, and higher degrees of stretch could not easily be achieved. The surface work decreased to 2.8 × 10^4 erg/cm.^{2} at 100% stretch, and this value could possibly be decreased further if the stretching had been performed at a lower temperature. The leveling off of the curve could represent a decreasing degree of orientation as the per cent hot stretch increased.

The fracture surface of the oriented Plexiglas changed from rough to mirror-smooth at about 40% hot stretch. Colors also changed from green and red to violet at approximately 70% orientation. The color was uniform along the entire length of surface and was the same on both of the fracture surfaces. The appearance of violet on the fracture surface could represent a decrease in the thickness of the oriented layer, since the wave-

length of violet light is at least 1000 A. less than that of green or red light. This means that the thickness of the oriented layer on each fracture surface is reduced by a few hundred Angstroms, providing the colors are the result of a first-order interference effect.

As a result of our measurements on oriented polymers it has been shown that the surface work decreases greatly as the orientation is increased if the crack is propagated parallel to the orientation. The colors on the fracture surface of oriented Plexiglas specimens either disappear or change to colors of shorter wavelengths, and the fracture surface changes from rough to mirror-smooth. These results lend additional support to the theory that orientation occurs in the vicinity of a crack propagation through a glassy amorphous polymer.

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Résumé

On a récemment émis l'hypothèse qu'un écoulement visqueux ou une déformation plastique se produisait au bord d'une fissure se propageant dans des polymères amorphes à l'état vitreux tel le Plexiglas et que ceci aboutissait à une orientation moléculaire de la surface de la fracture. L'apparition de coloration sur les surfaces des fractures fraîches du Plexiglas et le travail de surface extrèmement élevé qui a été mesurée et qui est ˙000 fois plus grand que l'énergie de surface théorique, en constituent les preuves. L'effet du pontage a été étudié en mesurant le travail de surface pour des formes pontées du Plexiglas et pour des polymères thermodurcissables fortement pontés. Le travail de surface diminue avec l'augmentation du degré de pontage dans le Plexiglas. Il n'y a pas de coloration à la surface de fracture du Plexiglas fortement ponté et cette surface est lisse comme un miroir. L'effet du pontage est d'empêcher l'écoulement visqueux ou la déformation plastique au bord de la fissure. Le travail de surface a été mesuré dans le cas des résines polyesters et époxy, et on a trouvé qu'il était inférieur d'un facteur 10 au travail de surface dans le cas des polymères linéaires mais qu'il demeurait néanmoins de loin supérieur aux estimations théoriques. Par préorientation du Plexiglas et du polystyrène,

on réduit le travail de surface pour une fissure qui se propage parallèlement à l'orientation et on l'augmente pour une fissure perpendiculaire à l'orientation. La coloration des surfaces de fracture des échantillons de Plexiglas préorientés disparaît ou bien est déplacée vers les longueurs d'onde plus courtes dans le cas où la cassure se propage parallèlement à l'orientation. Ceci indique bien que l'orientation se produit au bord d'une fissure et est responsable de l'apparition de couleurs sur les surfaces de fracture du Plexiglas. Le travail de surface pour du polystyrène étiré à chaud à 150% est de 7000 erg/cm² et la surface de fracture est lisse comme un miroir. Ce travail de surface est seulement supérieur d'un facteur 10 aux prévisions théoriques et fait supposer que quelques mouvements moléculaires seulement se sont produits.

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 an der frischen Bruchoberfläche von Plexiglas und die gemessene extrem hohe Oberflächenarbeit, die 1000 mal grösser ist als die theoretische Oberflächenenergie. Der Einfluss von Vernetzung wurde anhand von Messungen der Oberflächenarbeit von vernetztem Plexiglas und hochvernetzten wärmehärtenden Polymeren untersucht. Die Oberflächenarbeit nimmt mit zunehmendem Vernetzungsgrad im Plexiglas ab. An der Bruchoberfläche von hochvernetztem Plexiglas treten keine Farben auf, und die Oberfläche ist spiegelglatt. Die Vernetzung verhindert viskoses Fliessen oder plastische Deformation an der Spitze des Risses. Die Oberflächenarbeit von Polyester und Exopyharzen wurde gemessen und ergab sich zu um einen Faktor 10 kleiner als die der linearen Polymeren, ist jedoch noch viel höher als der theoretische Wert. Vororientierung von Plexiglas oder Polystyrol setzt die Oberflächenarbeit eines parallel zur Orientierungsrichtung wachsenden Risses herab und vergrössert die Oberflächenarbeit eines Risses normal zur Orientierungsrichtung. Die Farben an der Bruchoberfläche von vororientierten Plexiglasproben verschwinden oder ändern sich zu Farben kürzerer Wellenlänge, wenn der Bruch parallel zur Orientierung verläuft. Dies ist ein guter Beweis dafür, dass an der Spitze eines Risses Orientierung auftritt und für das Auftreten von Farben an Plexiglasbruchoberflächen verantwortlich ist. Die Oberflächenarbeit von zu 150 Prozent heiss-gestrecktem Polystyrol beträgt 7000 erg/cm², und die Bruchoberfläche ist spiegelglatt. Die Oberflächenarbeit ist nur um einen Faktor 10 grösser als der theoretische Wert und legt nahe, dass nur eine geringe Molekülbewegung stattgefunden hat.