

## On the Cold-Drawing of Plastics

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### INTRODUCTION

The cold-drawing of plastics is often characterized by two features, the shape of the drawing test specimen and the shape of the stress-strain (or load-extension) curve in tension. With a constant rate of elongation, the test specimen stretches uniformly to several per cent strain, at which strain a constriction, or "neck," forms in the specimen. With further elongation, the shoulders of the neck travel toward the ends of the specimen until travel is inhibited in the enlarged portions of the usual dumbbell-shaped specimen. Further elongation causes the neck to stretch uniformly until fracture occurs. Concurrent with the changes in the shape of the test specimen, the load rises rapidly on a load-extension curve, reaching a maximum (which corresponds to the yield stress) at a few per cent strain. With the formation of the neck, the load drops to a slightly smaller value at which it remains relatively constant while the shoulders of the neck travel toward the ends. When the shoulders reach the ends, the load rises again until fracture occurs at a load somewhat larger than the previous maximum. This seemingly peculiar phenomenon is actually observed with virtually all polymers, in a temperature range extending downward by several tens of degrees from the glass temperature  $T_g$  (for amorphous polymers) or the melting temperature,  $T_m$  (for crystalline polymers).

Three mechanisms have been proposed to explain the phenomenon of cold-drawing. Two of the proposed mechanisms have related cold-drawing to the glass temperature.<sup>1-4</sup> The other mechanism is based on the idea of biased segmental motion under the influence of a large shear stress.<sup>5</sup> Our work on Lexan<sup>®</sup> polycarbonate, a polymer that exhibits cold-drawing more than 150°C. below its glass temperature, suggests that the latter mechanism is correct: that cold-drawing is due to biased segmental motion.

### MECHANISM OF COLD-DRAWING

Müller<sup>1</sup> and Jäckel,<sup>2</sup> thinking that the molecular rearrangements necessary for cold-drawing could not occur below the glass temperature, described cold-drawing as resulting from an increase in local temperature above the ambient. Marshall and Thompson<sup>3</sup> have also used this explanation and have shown that after the formation of a neck at a constant elonga-

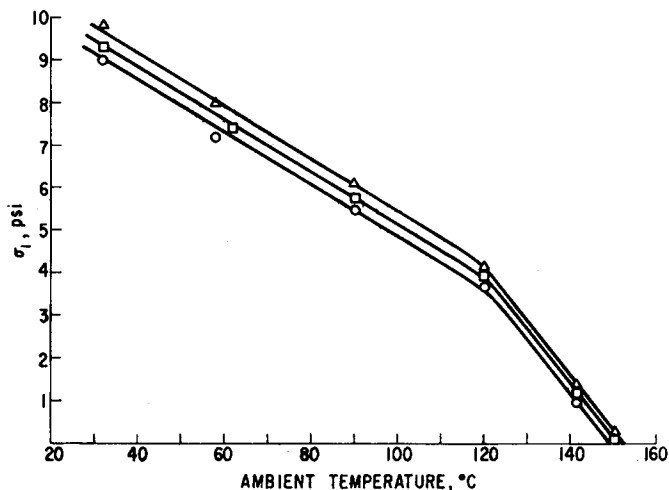


Fig. 1. Yield stress of Lexan films versus ambient temperature. Strain rates, in./min.: (○) 0.020; (□) 0.050; (△) 0.100.

tion rate a rather large amount of heat could be conducted along the test specimen just ahead of the shoulder. Indeed, the value of the load during the minimum plateau in the load-extension curve is largely determined by this heat conduction. For example, we find with Lexan, at an elongation of 0.020 in./min., that in air at room temperature the stress drops from around 9000 psi at the maximum to around 8000 psi at the minimum plateau; with the sample in contact with a water bath, we find that the stress only drops to 8800 psi at the minimum plateau. These decreases in stress can be related roughly to a temperature rise by comparing the stress decrease with the plot of yield stress versus temperature for Lexan, shown in Figure 1, by assuming that the fall in stress from the maximum to the minimum plateau is due solely to a temperature rise. Such an assumption is not altogether justified, however, because of the orientational effects. With it, however, we find that when the sample is in air or is in contact with water its temperature rises about 17 and 3.5°C. respectively. But these temperature rises occur *after* yielding and because of yielding; they do not appear to initiate yielding. Thus, with Lexan, which exhibits an elongation of roughly 65% on necking in the (ambient) temperature range of 25 to 90°C., we estimate from the work input on propagating the neck at 8000 psi a maximum temperature rise of 23°C. This compares fairly well with the estimated 17°C. rise for Lexan drawn in air, and it suggests that at the load maximum in the stress-strain curve the temperature of the specimen is fairly close to the ambient. In general, then, we believe that the temperature rise results from yielding rather than that yielding results from a temperature rise.

On the other hand, Vincent,<sup>4</sup> in experiments on polyethylene, explains cold-drawing by assuming that the softening temperature is *lowered* by

strain, the temperature rise being relatively insignificant. Recently, O'Reilly<sup>6</sup> carefully measured the change in the glass temperature with pressure, of polyvinyl acetate and Lexan, by measuring the dielectric loss. He found  $dT_g/dp$  to be 1.5°C. per 1000 psi for polyvinyl acetate and 3.0°C. per 1000 psi for Lexan. Relating tensile stress to a negative pressure, then, O'Reilly's measurements predict that a lowering of  $T_g$  does occur in tension. The data in Figure 1 show the yield stress values of four mil-thick cast films of Lexan in air at various temperatures and at the constant elongation rates of 0.020, 0.050, and 0.100 in./min. (The shapes of these curves, including the changes in slope at 120°C., are similar to curves obtained by Lazurkin<sup>7</sup> with other polymers. The abrupt change in slope is not yet completely understood, however.) The slope of curves up to about 120°C. is 16.5°C. per 1000 psi, while above 120°C. the slope is 7°C. per 1000 psi. In comparing our results with O'Reilly's, we see that ours are somewhat larger (although we do not expect that O'Reilly's change in  $T_g$  with pressure will necessarily apply throughout the tensile stress region, we expect his change to be correct, at least, for small tensile stresses; i.e., we do not expect a discontinuous change in slope at zero pressure). Furthermore, only a fraction of the tensile stress corresponds to pressure. But there is a more fundamental reason why we do not believe that cold-drawing is due to a decrease of  $T_g$  in tension. Yielding of the type observed in cold-drawing is also observed in simple shear and in compression (for the yielding of polystyrene, for example, in compression, see reference 8). Such phenomena are not explained by the tension lowering of the  $T_g$  mechanism.

Lazurkin and Fogel'son<sup>6</sup> pointed out some time ago that molecular backbone motion was not necessarily prohibited below the glass temperature. They showed, as evidence of this, that with both plasticized and unplasticized polymethyl methacrylate and with polystyrene the relation between the yield rate  $v_y$ , and the tensile stress  $\sigma_1$  has the form:

$$\ln v_y = a + b\sigma_1 \quad (1)$$

where  $v_y$  is taken to be the elongation rate at the stress maximum. Assuming, then, that  $v_y$  is proportional to the shear strain rate  $\dot{\gamma}$ , one obtains an equation that looks like the high stress limit of Eyring's<sup>9</sup> equation:

$$\dot{\gamma} = (1/b\eta) \sinh b'\sigma_1 \quad (2)$$

where  $\eta$  is the shear viscosity. Equation (2) was derived on the assumption that segmental motion in the absence of an applied force is governed by a symmetrical potential function, which virtually prohibits motion below the glass temperature, but under the influence of an applied force, the potential function becomes unsymmetrical, thus tending to allow segmental motion in the direction of the force.

The curves shown in Figure 2, which were obtained from stress relaxation measurements, show that Lexan also obeys eq. (1). The data in Figure 2 were obtained with thin films in contact with a water bath at 0 and 25°C.

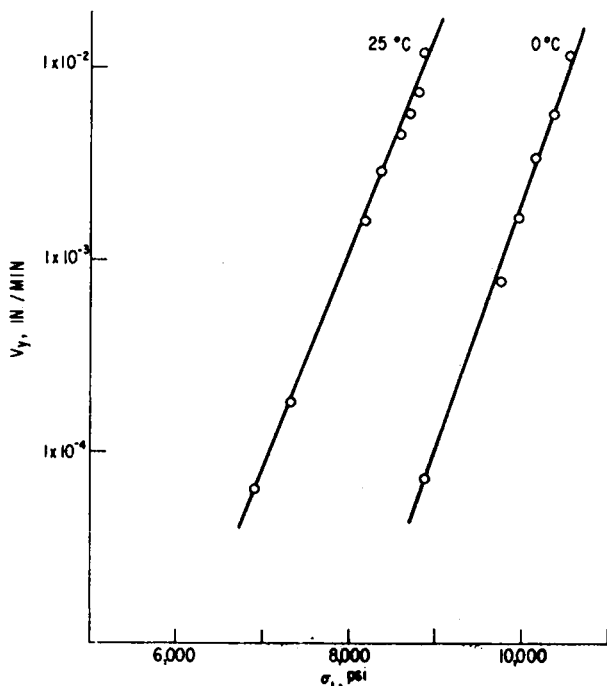


Fig. 2. Yield velocity versus conventional tensile stress for Lexan films.

before neck formation occurred. The rate of yielding,  $v_y$ , was related to the stress rate  $\dot{\sigma}_1$  by the equation for a series-connected spring and dashpot:

$$\dot{\epsilon} = \dot{\sigma}_1/E + v_y \quad (3)$$

where  $\dot{\epsilon}$  is the rate of elongation (which was zero for our stress relaxation measurements) and  $E$  corresponds to Young's modulus and is here assumed to be a constant.

To see that Eyring's theory is applicable to the cold drawing of Lexan, we rewrite eq. (2) in what corresponds to Eyring's original form:

$$\dot{\gamma} = (2kT/a\eta) \sinh \{a\xi S/2kT\} \approx (kT/a\eta) \exp \{a\xi S/2kT\} \quad (4)$$

where  $a$  can be taken to be the segmental volume although it really contains a jump distance,  $\xi$  is a stress concentration factor,  $k$  is the Boltzmann constant, and  $S$  is the shear stress. The product  $a\xi$  can be evaluated from the data in Figure 2 by taking the ratio of  $\dot{\gamma}$  at two stresses and assuming that shear stress is equal to one-half the tensile stress. From the curves at 0° and 25°C. we find that  $a\xi$  is  $6.44 \times 10^{-21}$  and  $6.24 \times 10^{-21}$  cc. respectively. Although we expect that the stress concentration factor  $\xi$  may decrease with rising temperature, we do not believe that the precision of the experiments warrants such a distinction here, and we thus assume the average value  $a\xi = 6.34 \times 10^{-21}$  cc. We now wish to consider the reasonableness of this value for  $a\xi$ .

First, we note that at 8000 psi tensile stress the energy for moving the segment over the potential barrier is  $a\xi S/2 = 12.6$  kcal./mole. This energy is roughly one-quarter the energy of a C—C single bond. Therefore, the energy for motion is not excessively high, but we might expect some broken bonds to result from the cold-drawing of Lexan at room temperature. Secondly, we see that, in assuming the molecular segment to be about 5 Å. on a side, the stress concentration  $\xi$  is about 50. We do not believe that this value for  $\xi$  is necessarily excessive for the following reasons: We might expect for a glassy polymer that the frozen-in voids would effectively reduce the area of contact across a shear plane between the segments by a factor of 2 to 5. More important, however, yielding in polymers probably takes place in a wormlike manner analogously to yielding in crystals; i.e., yielding in polymers is probably similar to the movement of a dislocation through a crystal. This type of motion allows a very high local stress to exist although the average stress is relatively small. At least, then, the value for  $a\xi$  that was inferred from our data does not seem unreasonable.

As a test of eq. (4) we wish to evaluate from it the viscosity coefficient  $\eta$  at various temperatures. For this purpose, we need a value for  $\dot{\gamma}$ . Unfortunately,  $\dot{\gamma}$  is not very well defined in a tensile test because of necking. We propose to define  $\dot{\gamma}$  as the product of the ratio of the drawn length to the undrawn length  $l/l_0$  (which is 1.65 in Lexan) and  $\sqrt{2}/2$ , where  $\sqrt{2}$  arises from the fact that shearing occurs at an angle of about  $45^\circ$  to the direction of tensile stress and 2 arises from the two propagating shoulders, divided by the time required,  $\Delta t$ , for the shoulder of the neck to pass through a point on the test specimen:

$$\dot{\gamma} = (\sqrt{2}/2) (l/l_0) (1/\Delta t) \quad (5)$$

Drawing Lexan at the elongation rate of 0.05 in./min., eq. (5) gives about  $0.03 \text{ sec.}^{-1}$  for the value of  $\dot{\gamma}$ . Using this value of  $\dot{\gamma}$  and assuming that  $a\xi = 6.34 \times 10^{-21}$  cc. and that the segmental volume is  $125 \text{ \AA.}^3$  we find from eq. (4) and the yield stress-temperature data at  $\dot{\epsilon} = 0.05$  in./min. given in Figure 1 that  $\eta = 5 \times 10^{20}$  poise at  $30^\circ$  and  $\eta = 10^{11}$  poise at the glass temperature ( $143^\circ\text{C.}$ ). These values for  $\eta$  may be a little large, however. First, if the segmental volume is taken to be  $625 \text{ \AA.}^3$  for example, then at 30 and  $143^\circ\text{C.}$   $\eta$  is  $10^{20}$  poise and  $2 \times 10^{10}$  poise respectively. Second, if  $\xi$  decreases to *one* at  $143^\circ\text{C.}$ , the viscosity is calculated to be about  $10^9$  poise; the calculation here is rather insensitive to the value for  $a$  (cf. eq. (4)):

$$\eta \approx S/\dot{\gamma} \quad (6)$$

Although the glass temperature has been defined<sup>10</sup> as that temperature at which the viscosity reaches the value  $10^{14.6}$  poise, we do not believe that our calculated value is necessarily too low. For example, Fox and Flory<sup>11</sup> found shear viscosities at the glass temperature of the order of  $10^{11}$  poise for polystyrene of molecular weights up to 50,000. Moreover, Davies and Jones<sup>12</sup> have pointed out that the *volume viscosity* is a better measure of the

glass temperature than is the shear viscosity (the volume viscosity is mathematically defined by Davies and Jones from entropy production considerations). We suggest, then, that cold-drawing is indeed explicable in terms of Eyring's model, although, quantitatively, the model needs refinement, as has been noted by Lazurkin and Fogel'son.<sup>5</sup> We note, for example, that the series model of a spring and an Eyring dashpot implied by eq. (3), although probably adequate for the stress regions involved in Figure 2, is not entirely adequate because the drawn plastic will return slightly on reducing the stress and will return to its original macroscopic shape on heating. Furthermore, the Eyring dashpot does not have a polymer orientation dependence, as is necessary to describe the draw ratio, for example.

### COLD-DRAWING AND THE GLASS TEMPERATURE

In accepting the mechanism of cold-drawing proposed by Lazurkin and Fogel'son in favor of that involving the lowering of the glass temperature with strain, we have not yet come to grips with the role played by the glass temperature in yielding. In the sense that the temperature dependence of viscosity can be written as

$$\eta = \text{const} \times \exp \{U/kT\} \quad (7)$$

so that eq. (4) can be written in the form

$$\dot{\gamma} = \text{const} \times \exp \{-(2U - a\xi S)/2kT\} \quad (8)$$

the stress might be interpreted as lowering the viscosity and hence the glass temperature. We wish to point out, however, that the segmental motion described by the high stress approximation of eq. (4) is virtually all in one direction and is hardly the slightly biased, random motion required for an adequate definition of a temperature. Moreover, we suggest that the glass temperature used by O'Reilly in his glass temperature-pressure measurements is relatively independent of the shear stress. If we describe pressure, as it enters into cold drawing, as the normal compressive stress  $\sigma$  across a shear plane, then the effective temperature of yielding can be described as:

$$T_{\text{eff}} = T + \sigma (dT_g/dp) \quad (9)$$

where  $\sigma$  is approximately related to the tensile stress  $\sigma_1$  by  $\sigma = -\sigma_1/2$ . By using eq. (9) in connection with data on the change in yield stress with temperature, the change in the shear stress required for yielding at a fixed elongation rate can be determined under various stress configurations. For example, with Lexan, using the slope of the curve below 120°C. in Figure 1, expressed in terms of the normal stress, and O'Reilly's value for  $dT_g/dp$ , we obtain:

$$S_{\dot{\epsilon}} = g(T) - (\sigma_1/2)(1000 \text{ psi}/33^\circ) (3^\circ/1000 \text{ psi}) = g(T) - 0.046\sigma_1 \quad (10)$$

where  $g(T)$  is some function of temperature. Since  $S = 1/2\sigma_1$ , we have:

$$\begin{aligned} \text{In tension:} \quad \sigma_y &= g(T)/0.546 \\ \text{In simple shear:} \quad S_y &= g(T) \\ \text{In compression:} \quad \sigma_y &= g(T)/0.454 \end{aligned} \quad (11)$$

With injected-molded samples of Lexan at about 25°C. and  $\dot{\epsilon} = 0.05$  in./min. we predict, assuming the measured yield stress in simple shear of about 5000 psi, that  $g(T = 25^\circ)$  is 5000 psi,  $\sigma_y$  in tension is 9200 psi, and  $\sigma_y$  in compression is 11,000 psi. These values compare fairly well with the measured values of 8800 psi in tension and 11,000 psi in compression. Since O'Reilly's use of the glass temperature is consistent with the WLF equation,<sup>13</sup> the glass temperature as used above may be considered generally consistent with other uses.

### CONCERNING NECK FORMATION

At very small elongation rates, some polymers yield homogeneously rather than form the constriction or neck, although high-density polyethylene, for example, is an exception and seems to form constrictions even at extremely slow elongation rates.<sup>14</sup> A homogeneous strain at small elongation rates has been interpreted in terms of the near isothermal conditions of the experiment; on this basis it has been argued that necking is a result of heat generation. We wish to point out that the homogeneous strain can also be accounted for on the basis of the slow elongation rates, irrespective of the temperature rise. We view the necking phenomenon in tension as being related to relative values of the shear rate at two different points, which in turn are related to the shear stress at these points. Let us consider two different points along the specimen with effective cross-sectional areas  $A'$  and  $A''$ , where  $A'$  differs from  $A''$  slightly, say by a small imperfection. The ratio of the shear strain rates at these points with a tensile force  $F$  applied to the specimen is, from eq. (4),

$$\begin{aligned} \dot{\gamma}'/\dot{\gamma}'' &= \{\exp\{b(F/A')\}\}/\{\exp\{b(F/A'')\}\} \\ &= \exp\{bF(1/A' - 1/A'')\} \\ &= \exp\{F \times \text{const}\} \end{aligned} \quad (12)$$

Therefore, the ratio of the strain rates is a function of the applied stress and thus a function of the elongation rate. At very small strain rates, eq. (12) approaches 1, and except for peculiar orientation effects as seem to occur, for instance, in high density polyethylene<sup>14</sup> the specimen is expected to exhibit homogeneous extension.

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### Synopsis

The characteristics of the cold-drawing of Lexan polycarbonate are compared with the several proposed mechanisms of cold-drawing. It is concluded that the mechanism of Lazurkin and Fogel'son, involving biased segmental motion, is correct. It is indicated that this mechanism easily explains the neck formation, and it is suggested how the glass temperature enters into cold drawing.

### Résumé

Les caractéristiques de l'étirement à froid du polycarbonate Lexan sont comparées aux nombreux mécanismes proposés pour l'étirement à froid. On en conclut que le mécanisme de Lazurkin et Fogel'son, qui suppose des mouvements de segments, est valide. On montre que ce mécanisme explique aisément la formation de craquelure; on présente une interprétation quant à la température de transition vitreuse en rapport avec l'étirement à froid.

### Zusammenfassung

Das Verhalten des Polykarbonates Lexan bei der Kaltverstreckung wird mit den verschiedenen, für das kalte Fliessen vorgeschlagenen Mechanismen verglichen. Der Mechanismus von Lazurkin und Fogel'son, der auf einer geneigten Segmentbewegung beruht, wird als der korrekte Mechanismus betrachtet. Dieser Mechanismus kann leicht die Bildung von Einschnürungen erklären; die Beziehung der Glasumwandlungstemperatur zum kalten Fliessen wird erläutert.

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