

Temperature Dependence of Tensile Properties of Polycarbonate Films

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Synopsis

The tensile properties of bisphenol A polycarbonate films were measured as a function of temperature from +25 to -180°C . The tensile properties at a given temperature were determined from the measured true stress-true strain behavior of the polycarbonate films by means of a photographic strain recording technique. The temperature dependence of the following tensile properties is presented: the yield stress, the fracture stress, the strain to yield, the cold-drawing strain, the fracture strain, and the strain-hardening rate.

I. INTRODUCTION

The tensile behavior of many polymers below their glass transition temperatures is superficially analogous to that of polycrystalline body-centered cubic materials, such as mild steel. The load-extension curves of many polymers show a rapid increase in load to an initial maximum value at a few per cent uniform extension. This maximum (the yield load) is followed by a drop in load to a smaller value which occurs simultaneously with the formation of a local constriction, or neck, in the gauge section of the tensile specimen. With continued extension, the load remains nearly constant at this value as the neck propagates to the shoulders at the ends of the gauge section. Further extension occurs uniformly and is accompanied by a gradual increase in load until fracture.

Important advances have been made in relating mechanical properties to structure in metals. However, because of the relatively recent recognition of the importance of polymers as engineering materials, limited progress has been made in understanding their mechanical behavior. Systematic studies which accurately characterize the mechanical properties of polymers are an essential first step of the understanding process. This paper presents a study of this type in which the tensile properties of bisphenol A polycarbonate were measured as a function of temperature from room temperature to -180°C . Bisphenol A polycarbonate (as Lexan, General Electric Company), is an amorphous, linear polymer of the polycarbonate family. The tensile properties of interest at a given temperature were determined from the measured true stress-true strain behavior of the polycarbonate by means of a photographic strain recording technique.

The tensile properties measured were: the yield stress, the fracture stress, the strain to yield, the yield point or cold-drawing strain, the fracture strain, and the strain-hardening rate.

II. EXPERIMENTAL METHODS

A. Preparation of Specimens

Tensile specimens were prepared from 4 mil thick, transparent, solvent-cast films of polycarbonate. The 1 dl./g. intrinsic viscosity film exhibited a uniform birefringence of 1.47×10^{-3} , indicating about 4% molecular orientation. Care was taken during specimen preparation to insure that this built-in molecular orientation was parallel to the tension axis in all specimens.

Specimens were cut with a dumbbell-shaped template (Fig. 1). A razor blade cutter (Fig. 2) was used in order to minimize edge distortion and produce tensile specimens with uniformly smooth edges. To prevent dirt particles from becoming embedded in the soft plastic film during specimen preparation, it was necessary to clean the film thoroughly and then to carry out the film mounting and cutting procedures in a distilled water bath.

Each specimen was then placed in a fixture fitted with a nickel evaporation mask through which rows of circular holes, 11 mils in diameter, had been photoetched. Selenium was then vacuum-evaporated through the nickel mask to produce a pattern of circular selenium spots on the specimen (see Fig. 5).

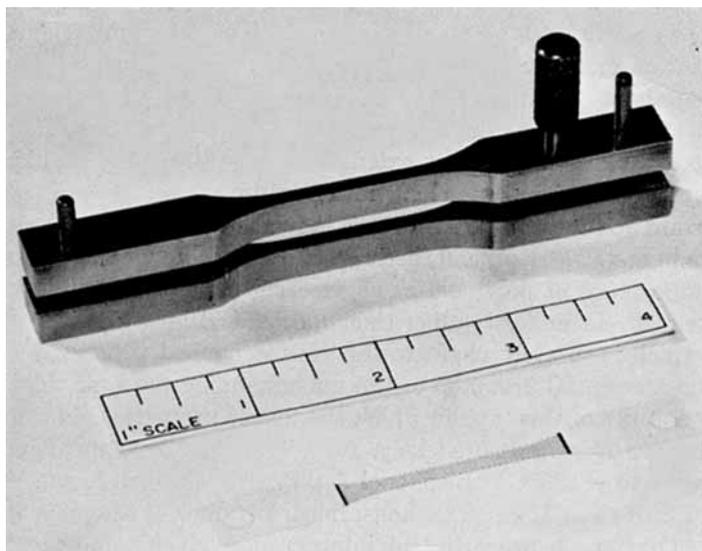


Fig. 1. Specimen template and tensile specimen of Lexan film. Rows of circular selenium spots have been evaporated on the specimen gauge section.

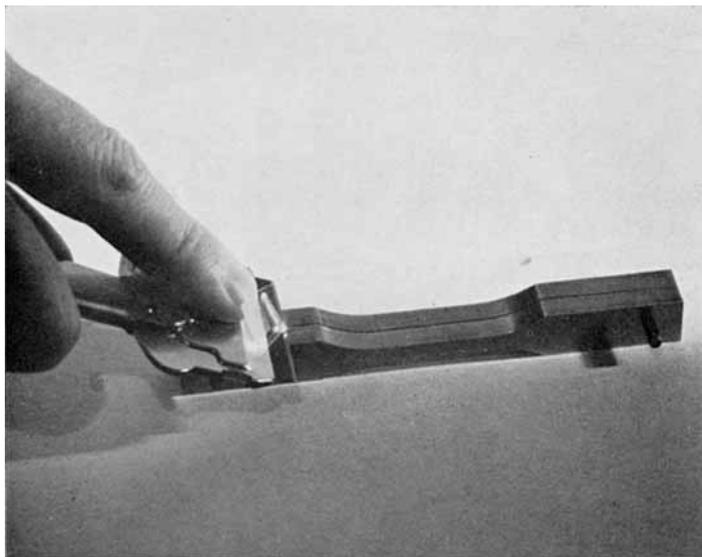


Fig. 2. The cutting operation used for forming tensile specimens from polycarbonate film. This operation is ordinarily carried out in a water bath.

B. Testing Procedure

The film specimens were pulled in tension in an Instron tensile machine with the use of the tensile rig shown in Figure 3. (The tensile rig was a modification of a rig loaned to this project by J. P. Berry of the G. E. Research Laboratory.) After careful alignment of the specimens, tests were conducted at a crosshead speed of 0.2 in./min.

To attain low temperatures, the tensile rig was enclosed in a Styrofoam chamber. Specimens were then cooled by feeding cold nitrogen gas into the chamber, a cooling system similar in principle to that of Wessel¹ being used. The cold gas entered the chamber through perforated copper coils located at A and B of Figure 3. Thermocouples (C, Fig. 3) indicated that the temperatures along the specimen were uniform and varied only $\pm 2-3^{\circ}\text{C}$. at a given test temperature setting.

C. Determination of True Stress and True Strain

Unless specifically stated to the contrary, the stress and strain values of this paper are reported as true stress and true strain. True stress, σ , is defined as the load applied to the specimen divided by the cross-sectional area of the specimen at that load. The true strain, δ , derives from the basic definition of strain, i.e., the fractional increase in length, dl/l . Here, l is the specimen length immediately preceding the incremental extension, dl . The true strain is found mathematically by summing these increments of strain:

$$\delta = \int_{l_0}^l dl/l = \ln (l/l_0)$$

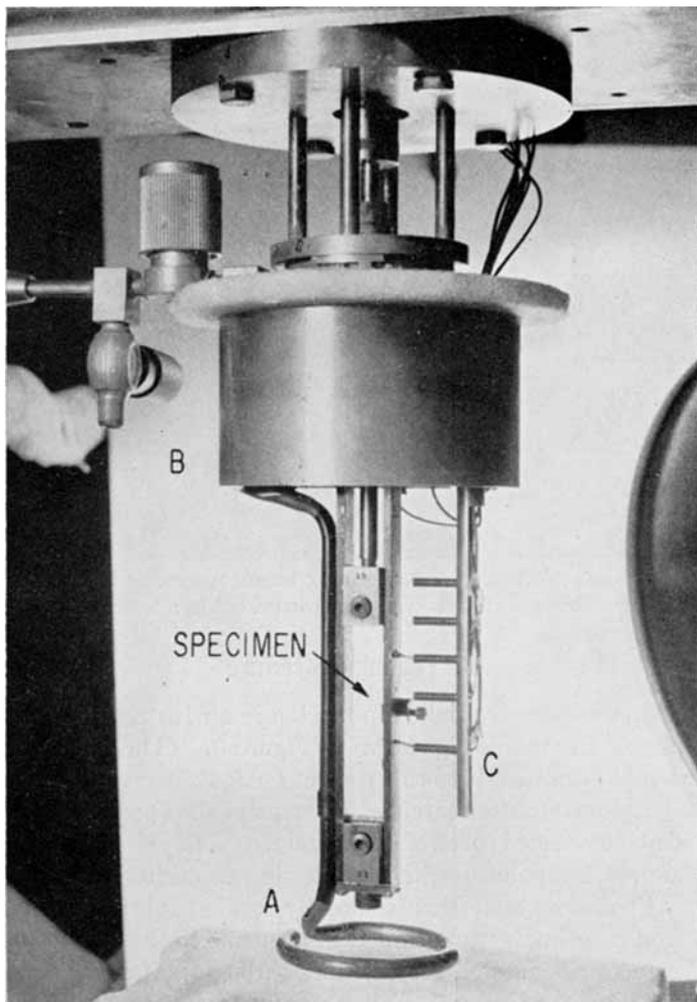


Fig. 3. Tensile rig used for testing polycarbonate tensile specimens. The rig is mounted on the bottom of the crosshead of an Instron tensile machine.

The more familiar engineering stress S and strain ϵ differ from the true or instantaneous stress and strain in that the engineering values are based on the original rather than the instantaneous specimen dimensions. The true and engineering values of stress and strain are related as follows:

$$\delta = \ln(1 + \epsilon)$$

and

$$\sigma = S(1 + \epsilon)$$

assuming constancy of volume.

A schematic drawing of the true stress-true strain curve for the polycarbonate is shown in Figure 4. Up to stresses equal to two-thirds the

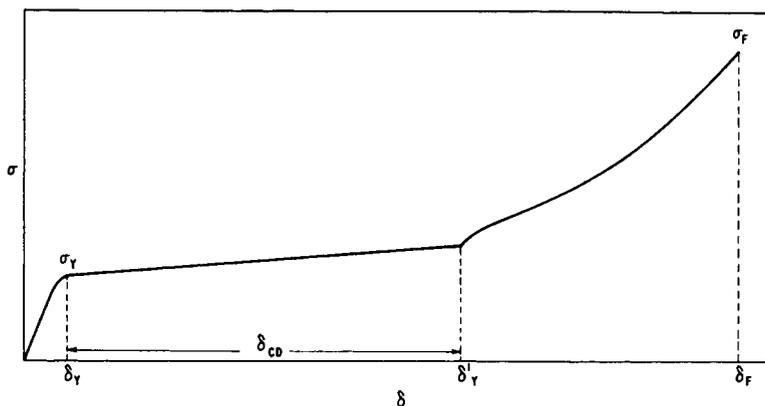


Fig. 4. Schematic representation of true tensile stress σ vs. true tensile strain δ , showing the stress and strain properties measured in this investigation: the yield stress, σ_Y , the fracture stress, σ_F , the strain to yield δ_Y , the cold-drawing strain δ_{CD} , and the fracture strain δ_F .

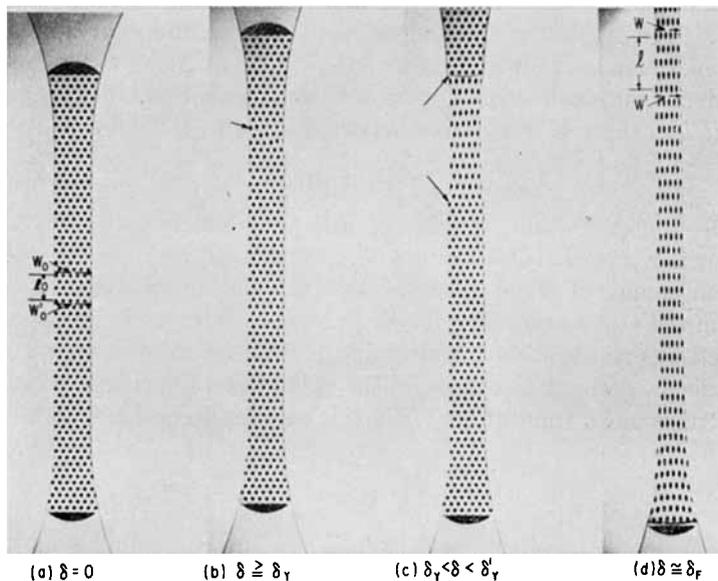


Fig. 5. Typical changes in specimen shape for the indicated strains at temperatures as low as -130°C .: (a) and (d) show the variation in gauge dimensions from zero strain to a strain near fracture; (b) shows the first stages of neck formation (see arrow) just beyond the strain to yield; (c) shows the fully developed neck (see arrows) propagating down the specimen.

yield stress, strains were too small to be measured accurately. During the portion of the curve from $\delta_Y + \delta'_Y$, neck formation is occurring in the specimen. Reliable strain measurements could not be made in this region, but the stress showed a steady increase in value.

The true stress and true strain tensile properties measured at each test temperature are also indicated in Figure 4. The properties shown are σ_Y , the yield stress (i.e., the stress at the first maximum load value as shown on the load versus extension curve); σ_F , the fracture stress; δ_Y , the strain to yield (i.e., the strain at σ_Y); $\delta_{CD} = \delta_{Y'} - \delta_Y$, the cold drawing or yield point strain (i.e., the strain which occurs during the formation and propagation of the neck to the specimen shoulders); and δ_F , the strain at fracture. One measured property not indicated in Figure 4 is the true lateral strain, δ_L , or the strain (in the width direction) normal to the tension axis.

True stress and true strain values were calculated from photographs taken of the polycarbonate specimen as it was pulled. Photographs of typical specimen behavior during a tensile test are shown with the corresponding strain values in Figure 5. Changes in specimen dimensions were measured from the photographs by using a comparator at 20 \times magnification.

Measurement of True Strain. True strains were determined from changes in the dimensions of the original gauge section as straining progressed. The original gauge dimensions, l_0 and w_0 , and their changes with increasing strain are shown in Figure 5 ($l_0 \cong 0.08$ in., $w_0 \cong w_0' = 0.125$ in.). For a given gauge extension, l , strains in the tensile direction were given by $\delta = \ln(l/l_0)$. Lateral strains were reported as

$$\delta_L = (\delta_1 + \delta_2)/2$$

where $\delta_1 = \ln(w/w_0)$ and $\delta_2 = \ln(w'/w_0')$. Tensile and lateral strains are known with a precision of ± 2 and $\pm 3\%$, respectively.

Measurement of True Stress. The calculation of true stress was based on the assumption that for all practical purposes the volume of the specimen was constant during straining. (Density measurements showed no significant permanent change in the volume of the polycarbonate, even after strains near fracture.) With this assumption, the true stress, σ , was given by

$$\sigma = P/A = Pl/Al = Pl/V = Pl/V_0$$

where P is load, l is gauge length at load P , V_0 is the original volume of the gauge section, V is the instantaneous volume, and A is the area. Reported true stress values are known with a precision of from $\pm 9\%$ at room temperature to $\pm 5\%$ at -180°C .

III. RESULTS AND DISCUSSION

A. Temperature Dependence of Yield Properties

Yield Strength Properties. The variation of the yield stress, σ_Y , with temperature is shown in Figure 6. Because no drop in stress is seen in the true stress-true strain tensile curve (see Fig. 4), values for the upper and lower yield stress were determined from engineering stress-strain curves.

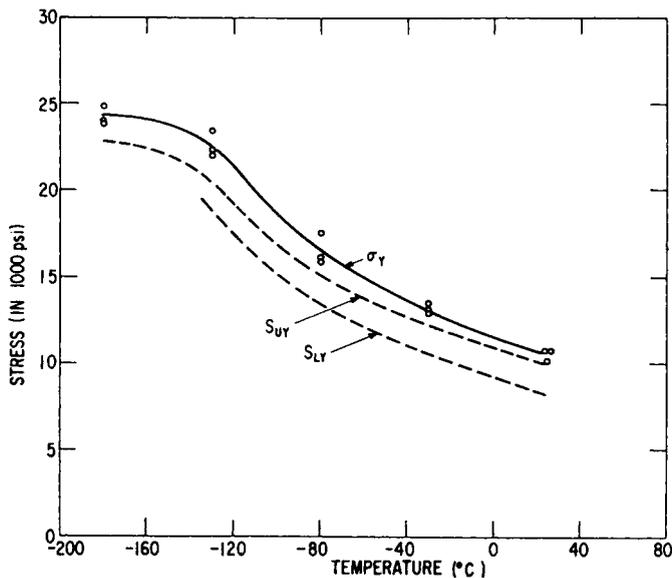


Fig. 6. The true yield stress σ_Y , the engineering upper yield stress S_{UY} , and lower yield stress S_{LY} vs. temperature for Lexan film.

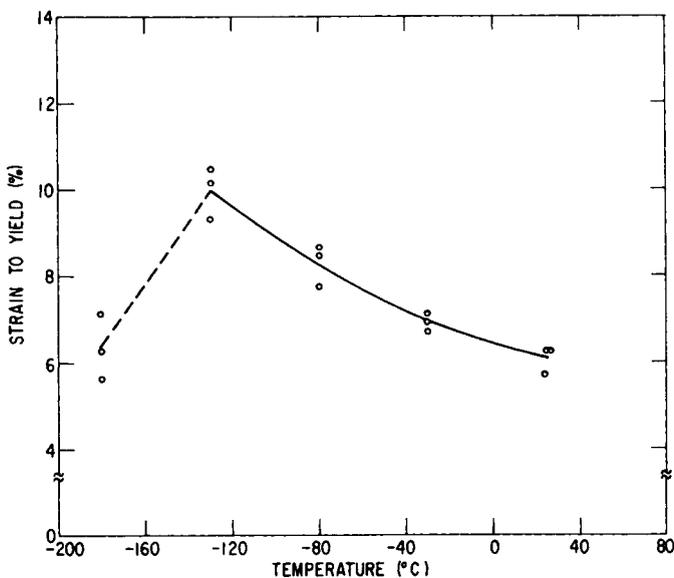


Fig. 7. The strain to yield δ_Y plotted as a function of temperature for polycarbonate film.

The engineering upper, S_{UY} , and lower, S_{LY} , yield stresses are plotted as dashed lines in Figure 6. An irregular drop in load at -180°C . precluded the determination of S_{LY} in all specimens but one. The three curves exhibit a gradual nonlinear increase of yield stress with decreasing temperature.

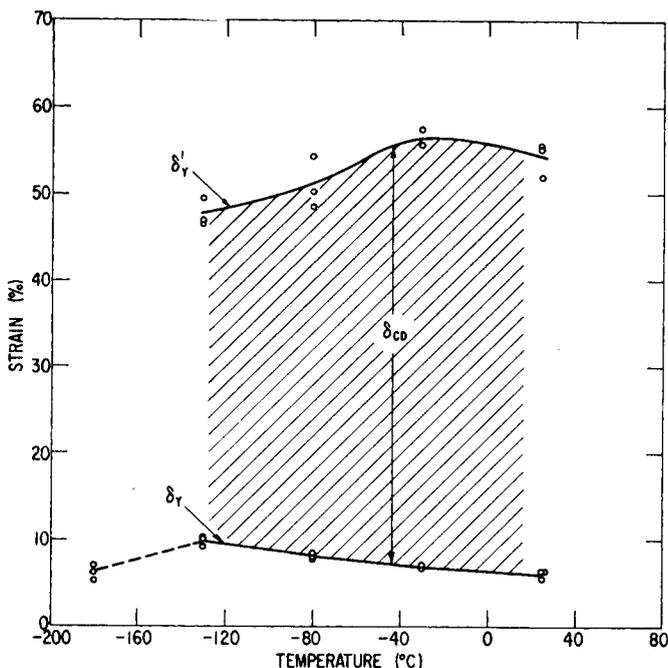


Fig. 8. Dependence of the cold-drawing strain δ_{CD} on temperature for polycarbonate film. The cold-drawing strain at a given temperature is $\delta_{CD} = \delta'_Y - \delta_Y$.

At temperatures from $+120^\circ\text{C}$. to room temperature, Robertson² found a linear increase of S_{UY} with temperature of ~ 60 psi/ $^\circ\text{C}$. for Lexan. The slope of the S_{UY} curve of Figure 6 is ~ 40 psi/ $^\circ\text{C}$. just below room temperature.

The pronounced change in the slope of σ_Y and S_{UY} between -130°C . and -180°C . is noteworthy. Data presented and discussed below suggest that a transition from ductile to nearly brittle behavior is occurring in this temperature range. Two of the specimens tested at -180°C . fractured shortly after the yield stress was reached. One fractured during the load drop, and the second fractured just after the minimum load was reached. The third specimen formed a neck in an irregular manner and its development was interrupted by fracture before cold drawing was complete.

As shown in Figure 6, the lower yield stress curve is nearly parallel to the upper yield stress curve down to -30°C . and then very slowly rises relative to S_{UY} at lower temperatures. Because S_{UY} and S_{LY} differ by less than 2000 psi at all test temperatures, the error involved in calculating the drop in stress, $\Delta S = S_{UY} - S_{LY}$ is large. A gradual decrease in ΔS , however, is indicated below -30°C . by the slow rise of S_{LY} relative to S_{UY} . This trend is continued in the only specimen showing an unequivocal drop in load at -180°C . ($S_{LY} = 20,900$ psi). (This specimen did not exhibit an observable neck.) An indirect measure of the drop in stress at a given temperature is given by the cold-drawing strain discussed below.

Yield Deformation Properties. The temperature dependence of the strain to yield δ_Y is shown in Figure 7. The increase of δ_Y with decreasing temperature is markedly reversed between -130 and -180°C . This change is another indication of a change in deformation mechanism, leading to the transition to more brittle behavior.

Both $\delta_{Y'}$ (see Fig. 4) and δ_Y are plotted versus temperature in Figure 8. Values of the cold-drawing strain, $\delta_{CD} = \delta_{Y'} - \delta_Y$, lie in the hatched area. No values of δ_{CD} are shown at -180°C . because necks did not fully develop

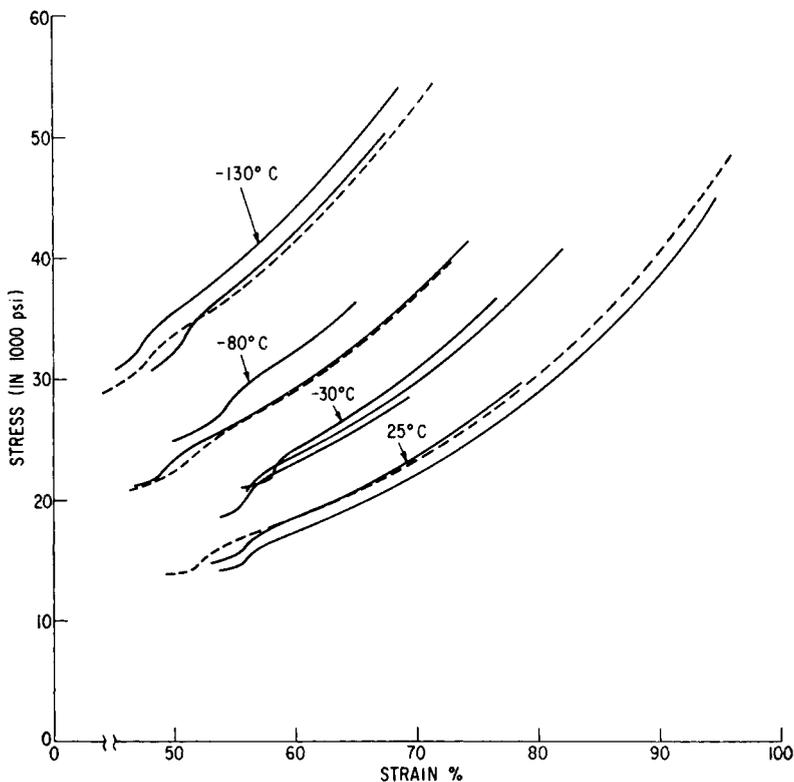


Fig. 9. The strain-hardening behavior of polycarbonate film as a function of temperature. The broken lines are used for purposes of clarity where two curves are nearly coincident.

at that temperature. In the one instance where a neck was clearly forming at -180°C ., accurate determination of the strain due to necking alone was not possible. Because of this the total strain occurring in the specimen (although local) was reported as a fracture strain.

The cold drawing strain is actually composed of two parts: strain due to the passing of the neck over a given gauge region and a much smaller strain (in the present work a few %) due to the continuation of straining in this region as the neck completes its propagation to the specimen shoulders. It should be noted that the latter part of δ_{CD} is a sample property in that it

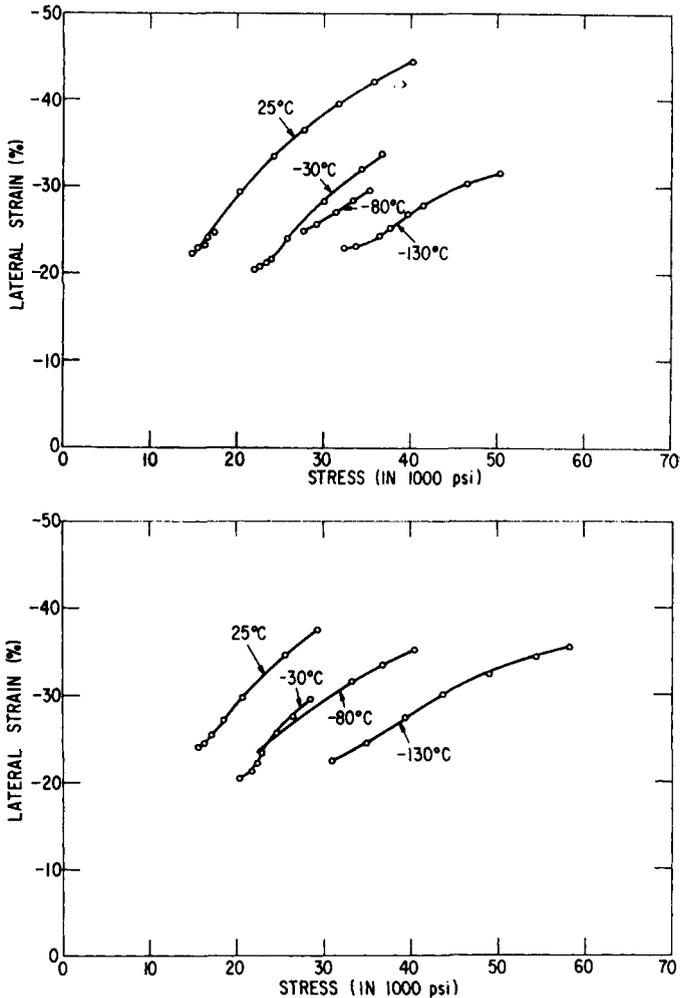


Fig. 10. Plots of (a) the dependence of lateral strain δ_L on applied stress for Lexan film at different temperatures; (b) variation of lateral strain δ_L , but for a different set of Lexan film specimens.

depends on the length of the specimen gauge section. Miklowitz³ found similar behavior in nylon.

The specimens having the highest values of δ_Y' at each temperature exhibited only one neck during straining. In all other specimens two and occasionally three necks formed some time during the propagation of the original neck to the specimen shoulders. The largest δ_Y' values occur with one neck because increasing the number of necks decreases the local strain rate and, as has been shown by Miklowitz³ in nylon, the cold-drawing strain decreases with decreasing strain rate. A curve of δ_Y' drawn through the largest values would thus give the most accurate values of the strain associated with the formation and propagation of a single neck.

As discussed above, δ_{CD} can be considered an indirect measure of the drop in stress. The decreasing values of δ_{CD} below -30°C . are, therefore, surprising in the light of the behavior of other ductile polymers. It has generally been found for other polymers that the drop in stress increases with decreasing temperature. The possibility of some liquid nitrogen spray coming into contact with the specimen at -130°C . may account for a small part of the observed decrease in the drop in stress at that temperature.

B. Temperature Dependence of Post-Yield Properties

Strain-Hardening Properties. Immediately following the arrest of neck propagation at $\delta_{Y'}$, straining becomes uniform over the entire gauge section of the specimen. Concurrently, the stress rises rapidly for a few per cent strain. The rise in stress signals the beginning of the strain-hardening

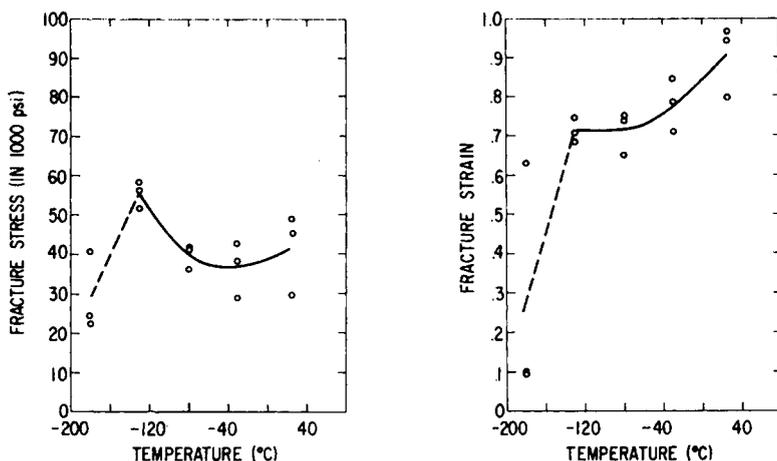


Fig. 11. Plots of (a) fracture stress σ_F and (b) fracture strain, δ_F , vs. temperature for polycarbonate film.

region of the stress-strain curve. After the initially rapid stress increase, the stress continues to rise, at a rate dependent on temperature, until fracture occurs. The rate at which stress increases with strain, $d\sigma/d\delta$, in this region, is commonly called the strain hardening rate* in metallurgical investigations.

The strain-hardening behavior of polycarbonate specimens is shown as a function of temperature in Figure 9. Three specimens were tested at each temperature.

In contrast to metals, the curvature in the strain-hardening region is convex upward. Further, necking observed in metals just prior to fracture

* The term strain hardening is used by analogy with metals which exhibit a pronounced increase of stress with strain which immediately follows the end of the yield point elongation and continues until fracture.

is absent in the polycarbonate which deforms uniformly from the beginning of the strain hardening region until fracture. This behavior is of particular importance in cold-forming operations such as stamping and drawing where uniform deformation is essential.

The strain-hardening rate increases with strain at a given temperature and increases nonlinearly with decreasing temperature for a given strain. Data at -180°C . are absent again because fracture occurred before the strain-hardening region was reached.

The lateral strains in the width direction which occur during strain hardening are shown as a function of temperature in Figures 10*a* and 10*b*.

Fracture Properties. The distinguishing features of brittle fracture in polymers are uniform deformation ($<5\%$) to the breaking point where catastrophic failure occurs by rapid crack propagation. No obvious permanent deformation is seen in the broken halves of the specimen.

Considering the characteristics of brittle fracture, the polycarbonate film fractures ductily even as low as -180°C . However, as has been suggested in the discussions above, the conspicuous change in the tensile properties between -130 and -180°C . is indicative of a transition from ductile to brittle behavior. Truly brittle behavior, as defined above, probably does not lie far below -180°C . It should be remembered here that the ductile-to-brittle transition depends, among other things, on the strain rate and temperature (see Vincent⁴). Both of these variables must be described in order to talk meaningfully of a fracture transition. The temperature range in which the transition occurs would be shifted upward for an increase in strain rate.

The fracture stress and fracture strain are plotted as a function of temperature in Figures 11*a* and 11*b*, respectively. Data points of both graphs show a good deal of scatter at the higher temperatures. The curves of each figure are constructed through the average values of the data at each temperature. Also, ultimate properties are ordinarily determined at a given temperature for a larger sampling than the three specimens used in the present tests. These points should be kept in mind when evaluating the significance of the curves presented in Figures 11*a* and 11*b*, especially the rise in the fracture stress curve between -30°C . and room temperature.

IV. SUMMARY

The tensile properties of polycarbonate film measured as a function of temperature down to -130°C . exhibit the following behavior.

(1) There was a nonlinear increase with decreasing temperature for the yield stress σ_Y , the strain to yield δ_Y , and the rate of strain hardening $d\sigma/d\delta$.

(2) The cold-drawing strain did not display a fixed trend, as it increased slightly between room temperature and -30°C . and decreased below this temperature.

(3) Scatter in the fracture stress and fracture strain data suggests the need for further tests to more definitely establish the temperature dependence of these properties.

The behavior of all properties measured at -180°C . indicated that for an initial strain rate of ~ 0.2 in./min, a transition from ductile to brittle behavior was taking place between -130 and -180°C .

The author is indebted to D. G. LeGrand, J. M. O'Reilly, J. P. Berry, and R. E. Robertson for many helpful discussions.

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Résumé

Les propriétés mécaniques réelles en tension des films de polycarbonate de bisphénol ont été mesurées en fonction de la température de $+25^{\circ}\text{C}$ à -180°C . Les propriétés mécaniques à une température donnée ont été déterminées à partir de mesures de tension-elongation vraies effectuées sur des films de polycarbonate en utilisant une technique photographique d'enregistrement de la déformation. On présente la dépendance vis à vis de la température des propriétés mécaniques suivantes: La tension à la limite d'élasticité, la tension de rupture, l'élongation à la limite d'élasticité, l'élongation pour l'étirement à froid, l'élongation de rupture et la vitesse de durcissement par élongation.

Zusammenfassung

Die wahren Zugeigenschaften von Bisphenol-A-polycarbonat-Filmen wurden in Abhängigkeit von der Temperatur zwischen $+25^{\circ}\text{C}$ und -180°C bestimmt. Die Zugeigenschaften bei einer bestimmten Temperatur wurden aus dem unter Verwendung einer photographischen Methode zur Dehnungsaufzeichnung bestimmten Zusammenhang zwischen wahrer Spannung und wahrer Dehnung der Polycarbonatfilme erhalten. Die Temperatur-abhängigkeit folgender Zugeigenschaften wird beschrieben: Reiss-spannung, Bruchspannung, Reissdehnung, Kaltreckungsverformung, Bruchdehnung und Dehnungshärtungsgeschwindigkeit.

Received August 28, 1963