

Crazing, Yielding, and Fracture of Polymers. I. Ductile Brittle Transition in Polycarbonate

D. G. LEGRAND, *General Electric Research and
Development Center, Schenectady, New York*

Synopsis

Most thermoplastics far below their glass transition give a brittle fracture when deformed in uniaxial tension. Bisphenol-A polycarbonates are an exception and deform in a ductile manner. However, it has been observed in Izod impact studies of notched samples that the mode of failure changes from a ductile to a brittle fracture on annealing samples below T_g . It has been found that, when notched samples are stressed, a Griffith type flaw is formed under the notch. The criterion for the ductile brittle transition is evaluated in terms of σ_G (the stress required to propagate the Griffith flaw), and σ_y , the yield stress for the polymer. It has been found that the density and yield stress for samples annealed at various temperatures are dependent upon previous thermal history and in particular on the molecular weight. On the basis of these measurements, it is concluded that many of the so-called anomalous effects observed with polycarbonate can be explained.

INTRODUCTION

Most glassy thermoplastics fail in an apparently brittle manner when tested in uniaxial tension. However, these same materials exhibit plastic deformation or cold flow in either shear or uniaxial compression. Evidence presented by Berry¹⁻³ indicates that in both polystyrene and poly(methyl methacrylate) a submicroscopic flaw exists which satisfies the Griffith criterion for fracture, while evidence by Andrews and Whitney⁴ indicates cold flow or plastic deformation in shear and compression. Recent observations indicate that in brittle fracture not only macromolecular plastic flow but also crazing takes place in the fracture surface.^{5,6} Such observations suggest that all failure processes occur as a result of plastic failure and that the mechanism of failure rather than the mode of failure be examined. This led us to inquire as to why polycarbonate should show high notched Izod impact strength under condition of a ductile-type failure and a low value after annealing at temperatures below its T_g as well as a brittle-type fracture surface.

Many different experiments have been performed to learn the mechanism that brings about this transformation. We have, for example, measured the dynamic modulus and loss factor for samples aged from 100-125°C and found no significant change.⁷ Similar studies on the other physical properties yielded no marked variation. Recent work by Stuart⁸ indicates that

changes occur in the shear modulus. In this report we present data which establish (1) an empirical relationship between the induction time for embrittlement and the annealing temperature, the molecular weight, notch sensitivity, and molding condition; (2) new techniques of observation; (3) the initiation mechanism for flaw formation and its relation to the brittle-ductile transition for notched samples; (4) an empirical relationship with respect to the recovery of ductility.

It is further shown that when the stress or energy required to yield is greater than the energy or stress required to fracture, brittle behavior is observed. Since the energy per unit volume is much greater in the case of brittle fracture than that of ductile failure, this indicates that the major contributor to the energy in brittle fracture is not the flow but the dilation of the fracture surfaces.⁹ This latter point is proved by the absence of void scattering in ductile failure.

EXPERIMENTAL

Samples

Samples of Lexan polycarbonate of various molecular weights were obtained in the form of Izod impact bars, tensile bars, compression-molded and extruded sheets through the courtesy of Dr. K. B. Goldblum, Plastics Department, General Electric Company.

All samples were heat aged at various temperatures in both a vacuum and an air oven. The temperature was controlled to within $\pm 1^\circ\text{C}$.

Density Measurements

Two techniques were used to measure the change in density on annealing at various temperatures: (1) hydrostatic weighing in a silicone oil bath, and (2) dilatometers (obtained from Dr. F. P. Price). Both techniques gave similar results.

X-Ray Measurements

Wide-angle x-ray diffraction scans were obtained with a GE XRD-5 diffractometer. Low-angle x-ray scattering measurements were obtained using both a standard pinhole evacuated camera and a slit Kratky camera.

Sample Notching

Samples were notched with a standard Izod notcher. Notched samples were deformed in any of four ways: (1) tensile deformation, (2) Izod impact, (3) three-point bending, (4) cleavage.

Most of the results to be presented were obtained in three-point bending on an Instron machine.

G Tensile Yield Stress

Tensile yield stress measurements were made using the dogbone samples on the Instron machine. Due to imperfections in the mold (4 samples/

shot) it was found that it was necessary to compare samples coming from the same part of the mold. This was easily carried out since the bars were numbered 1 through 4.

RESULTS

In order to acquaint the reader with Izod impact data on heat-aged samples, we present the results shown in Figure 1. These data were obtained on samples with an intrinsic viscosity of 0.52, annealed at 120°C for the time indicated, and tested at room temperature. These data are in good agreement with those of other investigators. The effects of changing molecular weight and temperature are shown in Figures 2 and 3. With this evidence we initially started to look for evidence of crystallization using

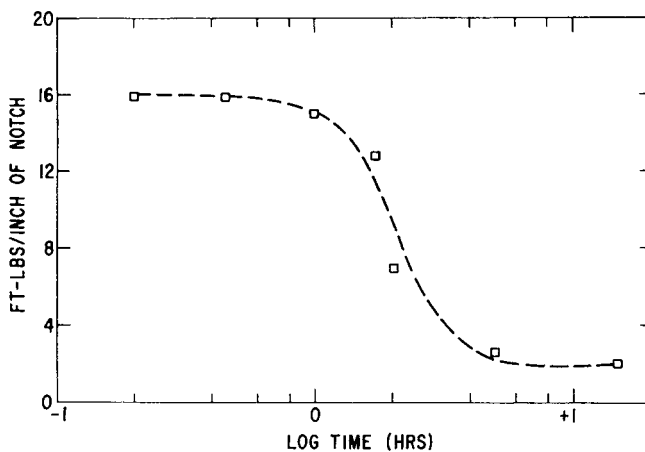


Fig. 1. Izod impact data as function of annealing time. $T = 120^{\circ}\text{C}$.

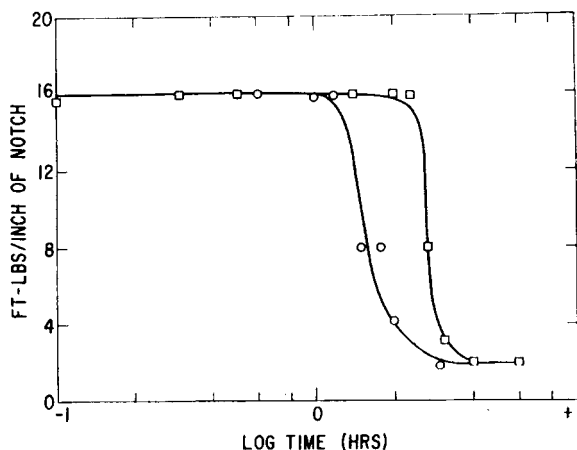


Fig. 2. Effect of molecular weight on Izod impact data. \square $[\eta] = 0.58$; \circ $[\eta] = 0.50$.

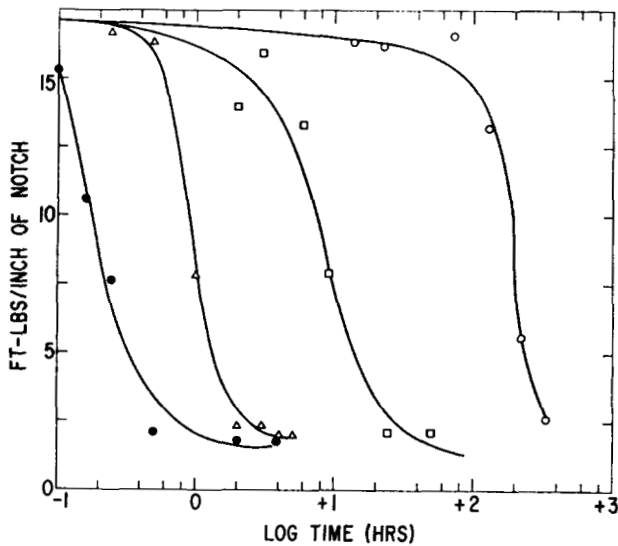


Fig. 3. Effect of annealing temperature on Izod impact data. \circ) 100; \square) 115; \triangle) 125; \bullet) 130; $[\eta] = 0.58$.

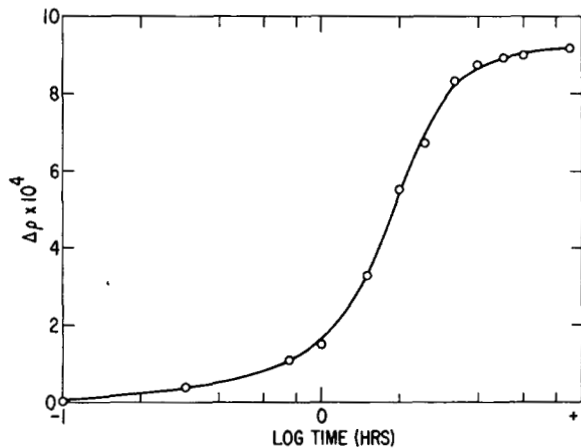


Fig. 4. Density as function of annealing time at temperature. $t = 120^\circ\text{C}$; $[\eta] = 0.62$.

x-ray diffraction. While negative evidence with respect to crystallization was obtained, positive evidence for a small change in density was observed between unannealed and annealed samples. This led to the measurement of density as a function of annealing time at temperature. Results are presented in Figures 4, 5, and 6. At this point it was postulated that voids either being nucleated or aggregating might be the mechanism of change. Low-angle x-ray scattering measurements were carried out. No positive evidence for any changes was found.

It was then decided to determine if any difference existed in the stress field surrounding the notch in unannealed and annealed samples. This was

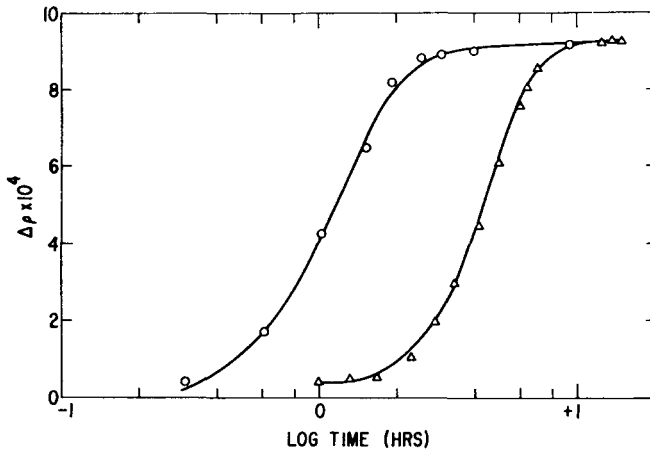


Fig. 5. Density as function of annealing time at temperature. ○) $[\eta] = 0.50$ at 110°C ;
 Δ) $[\eta] = 0.62$.

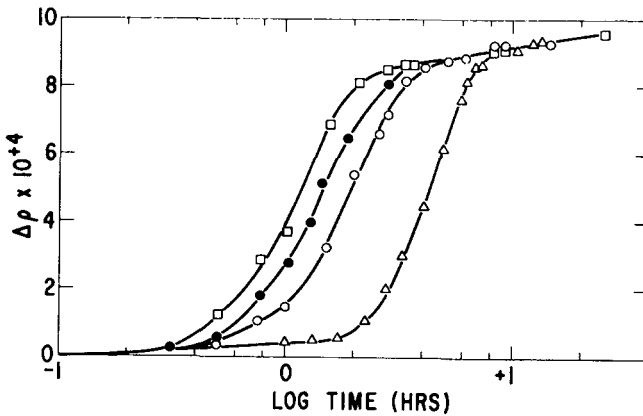


Fig. 6. Density as function of annealing time at temperature. □) 125°C ; ●) 122°C ;
 ○) 120°C ; Δ) 110°C . $[\eta] = 0.62$.

initially done in a polariscope. However, it was decided that a more detailed observation of the area surrounding the notch was necessary.

In the course of these observations with a polarizing microscope, it was observed that a flaw, similar to the schematic shown in Figure 7, was generated when the sample was deformed in three-point bending. The point of inception of this flaw was found to be approximately $160 \pm 10 \mu$ below the tip of the notch. It was subsequently found that a flaw of this type was generated in notched samples of unannealed BPA polycarbonate, poly(methyl methacrylate), polystyrene, PPO, and polyethylene. In the case of polycarbonate it was found that the flaw did one of two things, depending upon the history of the sample. In the case of brittle-type failure, the flaw increased in size as the stress was increased until it was

very near the surface boundary of the sample, at which time catastrophic failure of the sample took place. For unannealed samples (ductile-type failure) the flaw grew until it was approximately 0.01 cm² and then the walls of the bar yielded inward, causing the flaw to change from a two-dimensional to a three-dimensional void (see Figures 7b and 7c). Subsequent observations on notched samples broken in tensile deformation and by Izod impact indicated similar results.

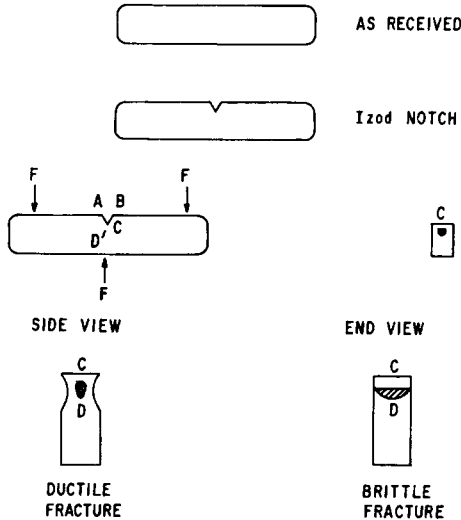


Fig. 7. Flaw formation.

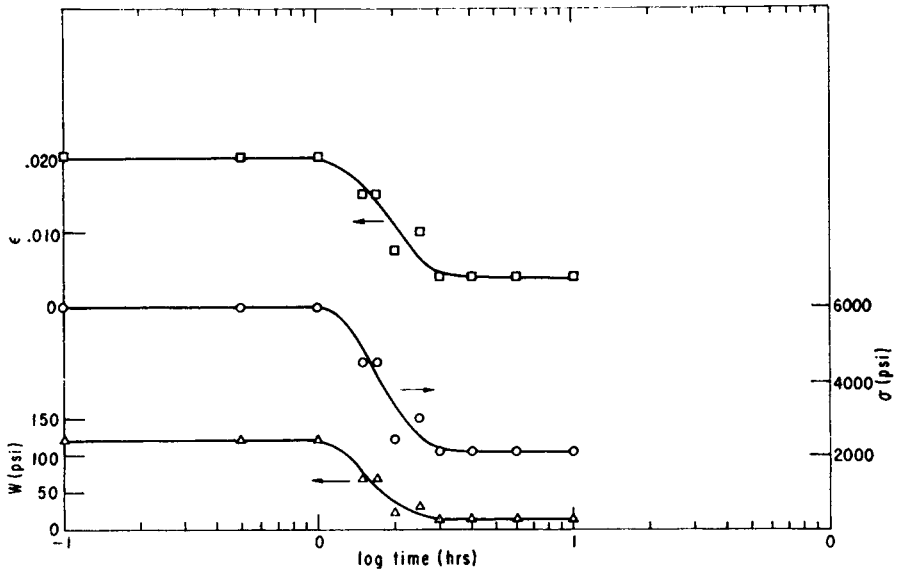


Fig. 8. Work, stress, and strain to break. Rate = .25"/min; T = 120°C; $\eta_i = 50$. (○) σ (psi); (□) ϵ ; (△) W (psi).

Further work, using the three-point bending technique, was carried out on annealed samples to determine the stress, strain, and work to break as a function of annealing time. These results are shown in Figure 8. The value of the energy to break is somewhat misleading since it represents the total over the entire deformed volume. If one measures the volume deformed in a ductile break, it is of the order of 0.08 cc, while in a brittle break it is of the order of 3.6×10^{-4} cc. Using the work-to-break values in Figure 8 and the volume of the deformed material, then the energy to break brittle is approximately 10,000 times greater than that for ductile failure.

TABLE I

Sample	Temp.	Fracture	Surface
Notched unannealed	25°C	ductile	uncrazed
Notched unannealed	Liquid N ₂ -180°C	brittle	crazed
Notched annealed*	25°C	brittle	crazed
Notched annealed*	Liquid N ₂ -180°C	brittle	crazed
Cold drawn notch	25°C	brittle	uncrazed
Cold drawn notch	-180°C	brittle	uncrazed

* Annealed at 125°C.

This calculation led us to examine the nature of the failure surfaces of samples broken under a variety of conditions, using low x-ray scattering. These results are presented in Table I.

Since it was observed that a critical stress and time was necessary for the formation of the flaw, we adopted the theory of Fisher¹⁰ for the nucleation of cracks in glass in a stress field. His analysis leads to the following equation:

$$r^* = \frac{\pi \gamma E}{2(1 - \nu)\sigma^2} \quad (1)$$

where r^* is a critical-size crack which is stable, σ is the stress, E is Young's modulus, and ν is Poisson's ratio. From measurements of the flaw size and the stress, γ , the surface energy term, is found to be approximately 300 ± 100 ergs/cm². This value is much lower than expected from Berry's work.^{1,2} However, examination of the flaw region indicated a noncrazing fracture mechanism similar to cold-drawn fracture phenomena. We then determined the surface energy for fracture of a cold-drawn sample and found this to be of the same order of magnitude.

Electron micrographs were obtained from the surface of the material in the flaw area and were found to be structureless at magnifications of 50,000. This is in marked contrast to the normal fracture surfaces and supports our hypothesis that this flaw is formed by a cohesive failure of the material at this point.

Criterion for a Ductile-Brittle Transition

The presence of a notch has an important effect on fracture behavior. This occurs because:

- (1) The notch acts as a stress magnifier.
- (2) The notch changes the applied stress system at the notch from a uniaxial to a biaxial or triaxial one prior to yielding, depending upon the dimensions of the sample near the notch. Further, the maximum shear stress is reduced, while the maximum normal stress remains unchanged. This is partially verified by the fact that all samples (annealed and unannealed) flow ductily in pure shear.
- (3) The notch enhances the rate of strain near the notch.

Since the observed flaw must be generated via one or all of the mechanisms in the previous statements, we proposed that the criterion for the brittle-ductile transition was based on magnitude of the stress necessary for the growth of the flaw versus the stress necessary to cause yielding. Using the Griffith equation,¹⁻³

$$\sigma_g = \sqrt{\frac{E\gamma}{c}} \quad (2)$$

where E is Young's modulus in dynes/cm², γ is surface energy in ergs/cm², and c is the size of the flaw in cm.

Then when

$$\sigma_g > \sigma_y \quad (3)$$

where σ_y is the yielding stress, ductile failure will take place, while when

$$\sigma_y > \sigma_g, \quad (4)$$

brittle failure will take place.

Using this criterion, we annealed samples for various lengths of time and examined their behavior with respect to temperature. These results are listed in Table II.

With this apparent support of our criterion we examined the effect of heat aging on yield stress of two different molecular species. The data obtained are shown in Figures 9 and 10. Note that the samples compared

TABLE II

Time of aging of 125°C, hr	Test temp., °C				
	-178	-78	0	20	40
0	B ^a	D ^b	D	D	D
1	B	B	D	D	D
2	B	B	B	D	D
3	B	B	B	B	D
4	B	B	B	B	B

^a B = Brittle.

^b D = Ductile.

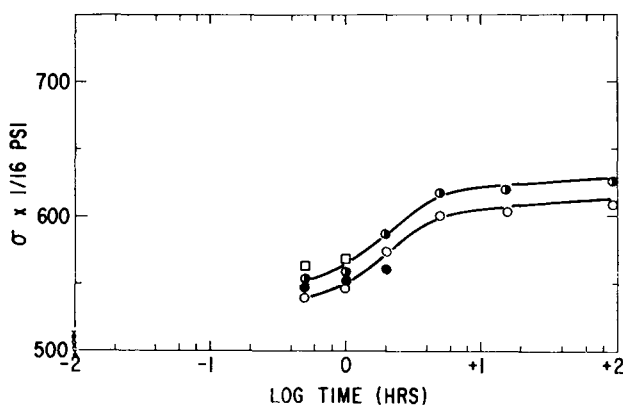


Fig. 9. Yield stress as function of time. $T = 125^{\circ}\text{C}$; $[\eta] = 0.58$. Sample #: 1) \circ ; 2) \bullet ; 3) \bullet ; 4) \square . Untreated samples— \times .

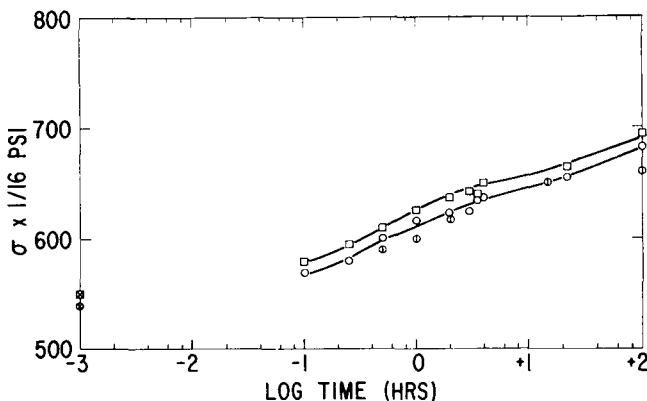


Fig. 10. Yield stress as a function of time. $T = 125^{\circ}\text{C}$; $[\eta] = 0.50$. Sample : 1) \odot ; 2) \circ ; 3) \square . Untreated samples: \otimes , \boxtimes .

are from the same part of the mold. Using these data in conjunction with three-point bending data, it was found that the critical point for brittle failure occurred at a yield stress of 9,600 psi and 10,000 psi for molecular weights of 2.6×10^4 and 3.27×10^4 , respectively. Using eq. (1) and a flaw size of 0.1 cm, $E\gamma$ is found to be 4.70×10^{16} and 5.11×10^{16} ergs/cm², respectively. Following Berry,¹¹ $\gamma_{\infty} = 3.35 \times 10^6$ ergs/cm² and critical molecular weight is 7,500. This critical molecular weight is approximately that found by Golden et al.¹² in irradiation studies. An alternate value for γ was determined using the Berry-type cleavage experiment yielding similar values.³ Comparing this to the value found for the formation of the flaw, i.e., 300 ± 100 ergs/cm², we see an extremely large difference. However, the surface structure, where the larger value of γ is obtained, is crazed. If we use the value of the specific surface area in the craze layer, the volume of crazed material, and γ flaw, we find that craze formation in

fracture represents 70–80% of γ total in a brittle fracture. This would imply that without crazing, polymers would be very weak materials.

Effect of Molecular Weight and Annealing Temperature on the Ductile-Brittle (D-B) Time

Since the variation in yield stress and density were difficult to measure on an absolute basis, it was decided to use the D-B transition point as a measure of the relaxation process involved. Thus, the time at which the transition occurred was measured as a function of both molecular weight and intrinsic viscosity of the starting material and the annealing temperature. The results of this study are presented in Figures 11 and 12. By utilizing the following empirical equation,

$$\log \tau_B = A \log [\eta_i] + \frac{F^\ddagger}{RT} + \log C \quad (5)$$

or

$$\log \tau_B = K \log [M_w] + \frac{F^\ddagger}{RT} + \log C \quad (6)$$

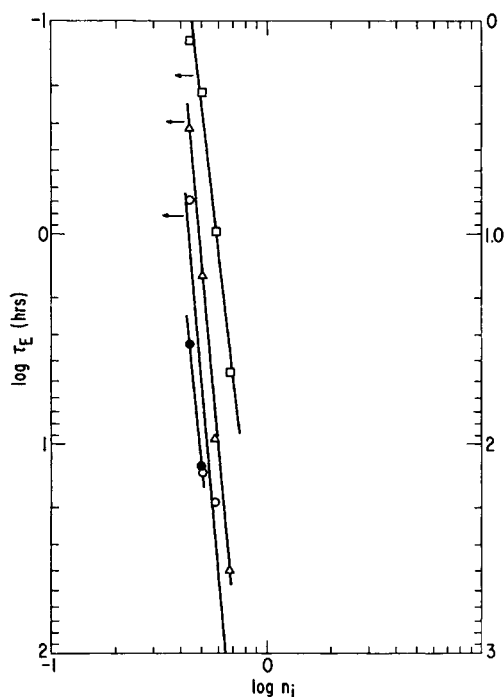


Fig. 11. T_E versus intrinsic viscosity. $\log \tau_E$ versus $\log \eta_i$. \circ) 100°C; Δ) 115°C; \square) 125°C; \bullet) 40°C.

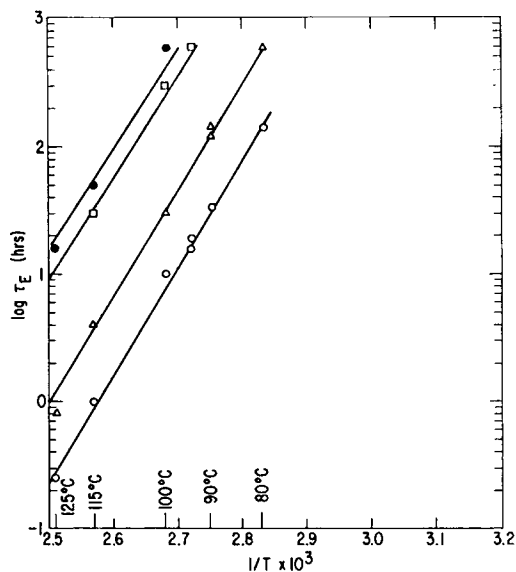


Fig. 12. T_E versus annealing temperature. η : \circ) 0.44; Δ) 0.50; \square) 0.58; \bullet) 0.68.

where K is a constant, M_w is the molecular weight, R is the gas constant, T is the temperature, F^\ddagger is the activation energy, and C is another constant similar to one used by Tobolsky and Murakami¹³ for maximum terminal relaxation time of polystyrene, in conjunction with the data in Figures 11 and 12 the constants were evaluated to be: $A = 10.0 \pm 0.5$, $K \cong 5.34$, $\log_{10} C = -16.1$, and $F^\ddagger = 35.2$ kcal/mole.

By heating annealed (brittle) samples above their T_g , it was found that ductility could be recovered. It was further found that the density and yield stress recovered approximately to their initial values, i.e., prior to their embrittlement. By carrying out experiments similar to those described in previous paragraphs and utilizing the following equation,

$$\log \tau_R = K_v \log M_w + \log C + \frac{F^\ddagger}{RT} \quad (7)$$

$$= A_v \log [n_i] + \log C + \frac{F^\ddagger}{RT} \quad (8)$$

where τ_R is the time at some temperature t above the T_g necessary to recover ductility, it was found that $K_v \cong 3.2$, $A_v \cong 6$, $C \cong -20.8$, and $F^\ddagger = 35.2$ kcal/mole.

It should be pointed out that work on branched polymers indicated that the same basic equations apply, and the τ 's appear to be a function of the number-average rather than the weight-average molecular weight. However, it may be that the processing history has an effect on this interpretation. It is worth noting that for sheet-extruded material, τ_E , was found to

have a small directional dependence, which was related to the extrusion axis (see next paragraph).

Effect of Molding Pressure

Since it was observed that compression-molded samples give different results from injection-molded samples, it was decided to investigate the effect of molding pressure in order to see how τ_E was affected. In order to carry out these experiments, two different materials with intrinsic viscosities of 0.5 and 0.62, respectively, were chosen, since they would allow the greatest variation in molding pressure without significantly altering the molding temperature. The results of this work are shown in Figure 13. The dashed line represents the normal pressure line for molding standard samples. By comparing the $\ln \tau_E$ -pressure data for the 0.50 material in Figure 13 to $\ln \tau_E$ -temperature data in Figure 12, the value of $\Delta T/\Delta P$ is found to be $0.047^\circ\text{C}/\text{atm}$, which is close to that reported by O'Reilly,¹⁴ i.e., $0.044^\circ\text{C}/\text{atm}$ for the effect of pressure on T_g . Assuming this effect to be independent of molecular weight, the upper line in Figure 13 was drawn by using the data point for a sample molded under standard pressure condition and the same slope as the 0.50 material. The 0.62 material was then molded at 1500 psi and τ_E evaluated. The fact that this point falls right on the line is probably fortuitous, but certainly indicates that molding pressure is an important variable.

We have not pursued this effect to any greater detail because of the extreme difficulty in preparing samples of this type and because we were

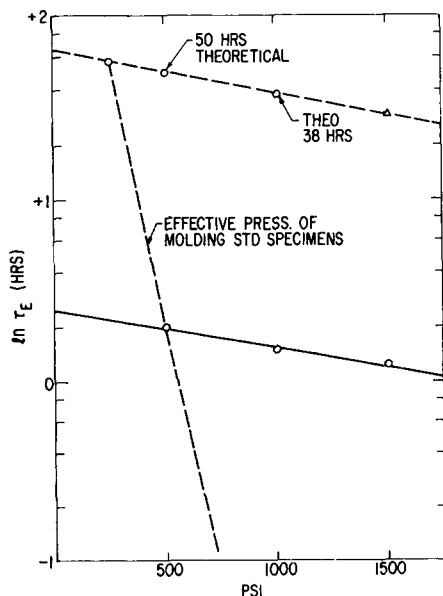


Fig. 13. Effect of molding pressure on T_E . ○) 0.50; △) 0.62.

unable to examine samples with a larger difference in molecular weight without changing the molding temperature.

DISCUSSION

It is our opinion that all glassy materials should undergo a yielding, or flow, which is dependent on an internal state parameter, s , of the system. The reason that most materials do not is due to the intervention of fracture or crazing. Under some conditions fracture can be prevented by lowering the yield stress below the critical stress for fracture. For example, Andrews and Whitney¹⁵ and Andrews and Kimmel¹⁶ have reported work on the effect of preorientation and/or quenching on the yielding behavior of polystyrene and poly(methyl methacrylate). In our work we have found that prestressing of annealed polycarbonate lowers the yield stress and gives rise to ductile rather than brittle fracture for notched samples. It is our hypothesis that annealing below the glass transition, quenching, small amounts of preorientation, prestraining, or various combinations of these induce small but very significant changes in structure. Quenching and

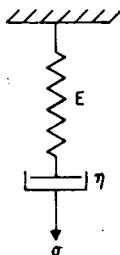


Fig. 14. Maxwell element.

annealing are known to produce rarefaction or densification in many organic glasses. Since Poisson's ratio for glassy materials is approximately 0.30–0.35, a 3% strain will produce a change in volume of 0.009 cc/cc. Removal of the stress will allow a partial recovery of some of this change, but a permanent change may be produced.¹⁷ The magnitude of this permanent change should be dependent on the straining time, the time at strain, and the subsequent time left in the unstressed condition.

We believe the preorientation does not affect the yield stress directly, but in some way affects the packing density. Since yielding in polymeric systems represents a plastic type of deformation, where chains or segments of chains slip by one another as well as drag one another, we propose that equations normally used for bulk viscosity may be applicable. We assume initially the following simplified model, involving a single Maxwell system (see Figure 14). The equation for this system is

$$\dot{\sigma} + \frac{\sigma}{\tau} = E\dot{\epsilon} \quad (9)$$

where σ is the stress, E is modulus of elastic element, η is viscosity of viscous element, τ is relaxation time and equals η/E , and $\dot{\epsilon}$ is the strain rate.

In a constant rate of strain experiment, $\dot{\epsilon}$ equals a constant, K , and at the yield point $\dot{\sigma}$ goes to zero. This occurs at $\sigma/\tau = E\dot{\epsilon}$ and thus

$$\sigma_y = \eta K t \quad (10)$$

at the yield point. This point is determined by K and η , the viscosity.

One could at this point employ the relationship derived by Bueche¹⁸ for bulk viscosity, i.e.,

$$\eta = \rho \frac{N k T}{6\delta^2} \left(\frac{R^2}{M} \right) N^* \exp \left[\frac{B^* v^*}{v_f} \right] \quad (11)$$

and therefore

$$\frac{\sigma}{\dot{\epsilon}} = \rho \frac{N k T}{6\delta^2} \left(\frac{R^2}{M} \right) N^* \exp \left[\frac{B^* v^*}{v_f} \right] \quad (12)$$

where $\sigma/\dot{\epsilon}$ has replaced the viscosity, or

$$\frac{\sigma}{\dot{\epsilon}} = B \exp [B^* v^*/v_f], \quad (13)$$

where B is equal to the factors in front of the exponential, η is Bueche's equation, σ_y is the stress at yield, $\dot{\epsilon}$ is the rate of strain, ρ is the density, k is the Boltzmann factor, and T is the temperature in degrees Kelvin.

If one measures the yield stress at two different temperatures, T_1 and T_2 , then

$$\frac{\sigma_1}{\sigma_2} = \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} \exp \left[B^* v^* \left(\frac{1}{v_{f_1}} - \frac{1}{v_{f_2}} \right) \right]. \quad (14)$$

Taking the logarithm of eq. (14), we have

$$\log \frac{\sigma_1}{\sigma_2} = \log \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} + B^* v^* \left(\frac{1}{v_{f_1}} - \frac{1}{v_{f_2}} \right) \quad (15)$$

Following Bueche, we can substitute

$$v_{f_2} = v_{f_1} + \alpha v_1 (T_2 - T_1) \quad (16)$$

into eq. 15 and obtain

$$\log \frac{\sigma_1}{\sigma_2} - \log \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{B^* v^*}{v_{f_1}} \left[\frac{T_2 - T_1}{(v_{f_1}/\alpha v_1) + (T_2 - T_1)} \right] \quad (17)$$

If, instead, measurements are made at constant temperature, where time-dependent changes in free volume occur,

$$v_f(t) = v_{f_0} \pm (1 - e^{-t/\tau}) (v_{f_0} - v_{f_\infty}) \quad (18)$$

where the \pm sign is used to indicate that either an increase or decrease may occur depending upon previous history, substitution of this into equation 15 leads to

$$\log \frac{v_1}{v_2} - \log \frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{B^* v^*}{v_{f_0}} \left[\frac{\pm (1 - e^{-t/\tau_n}) (v_{f_0} - v_{f_\infty})}{v_{f_0} \pm 1 - e^{-t/\tau_n} (v_{f_0} - v_{f_\infty})} \right], \quad (19)$$

which indicates that if the free volume increases, then the yield stress at constant rate of strain and temperature should decrease, while a decrease in free volume should lead to an increase.

Finally, for measurements where free volume changes at temperatures T_1 and T_2 are both time dependent, a more complex expression is required involving two time-dependent as well as temperature-dependent terms.

We believe that the effect concerning the nonlinear behavior of embrittlement times is caused by this, and that it may also explain the falling off of the yield stress in this temperature range as noted by Robertson¹⁹ and Goldblum.²⁰ In fact, if one uses the outlined theory, the yield stress obtained at constant strain rate, for samples aged 24 hr at test temperatures prior to testing, will give the results of Goldblum, who aged over night.

The phenomena would be expected to also reflect themselves in creep measurements below the glass transition. One would expect that the creep rate, instead of increasing as a function of temperature, would level off around the same temperature interval where the yield stress does. Preliminary creep measurements in this laboratory indicate this to occur.

Since current thinking concerning free volume theories is at least questionable, we present an alternate theory for yielding of polymeric-type materials, i.e., associated liquids as well as high polymers. We draw freely on the thoughts and theories of Adam and Gibbs,²¹ Goldstein,²² Robertson,²³ and Eyring²⁴ in our formulation.

Thermodynamics of Ordering

Our model of the glassy state for such materials assumes that the configurational entropy is not zero but has some small but finite value and that two states are available for segments in the polymer molecule. We subdivide each of our polymer chains into m_i segments and let n_{iA} be the number in state A and n_{iB} the number in state B. We let E_i be the energy in changing from state A to B.

The contribution to the entropy arising from these alternate states is therefore

$$S_{Ai} = k \left[n_{iB} \log 2 + \log \left(\frac{m_i!}{n_{iA}! n_{iB}!} \right) \right] \quad (20)$$

which gives via Stirling's approximation

$$S_A = k [n_{iB} \log 2 + m_i \log m_i - (m_i - n_{iB}) \log (m_i - n_{iB}) - n_{iB} \log n_{iB}] \quad (21)$$

If we neglect initially any changes in volume and in vibrational frequency as a result of a segment changing from A to B, this will represent the only term in the entropy, which depends on n_{iB} .

The change in internal energy due to changing n_{iB} segments from state A to B will be $n_{iB}E_i$. Thus, the free energy of the i 'th chain will be

$$F_i = n_{iB} \epsilon_i - k T [n_{iB} \log 2 + m_i \log m_i - (m_i - n_{iB}) \log (m_i - n_{iB}) - n_{iB} \log n_{iB}] \quad (22)$$

In order to correct for changes in the internal energy as a result of volume changes, we let

$$\epsilon_i = \epsilon_{i0} - \phi (v - v_0) \quad (23)$$

where ϕ is a constant, v is volume at temperature T , and v_0 is volume at temperature $T = 0$. Following Frenkel,²⁵ the volume may be written as

$$\frac{v - v_0}{v_0} = BT - \frac{P}{K} \quad (24)$$

where B is coefficient of volume expansion, P is pressure, and K coefficient of compressibility.

Therefore, the free energy, F_i , may be rewritten as

$$F_i = n_{iB} [\epsilon_{i0} + \phi v_0 (P/K - B/T)] - k T [n_{iB} \log 2 + m_i \log m_i - (m_i - n_{iB}) \log (m_i - n_{iB}) - (n_{iB} \log n_{iB})] \quad (25)$$

The probability, P_{iB} , that in the i 'th chain a given segment will be in the state B is n_{iB}/m_i , which can be found by assuming a condition for thermal equilibrium, i.e.,

$$\frac{dF}{dn_{iB}} = 0 \quad (26)$$

which gives

$$P_{iB} = \frac{1}{1 + 1/2 \exp\{[\epsilon_{i0} + \phi v_0 (P/K - BT)]/k T\}} \quad (27)$$

Alternately, P_{iB} may be interpreted as representing the fraction of segments which may rearrange, which is then similar to the work of Adam and Gibbs.²¹

While the above treatment is applicable at temperatures above T_g , it seems reasonable that at temperatures below T_g

$$P_{iB T < T_g} = \frac{1}{1 + 1/2 \exp\{[\epsilon_{i0} + \phi v_0 (P/K - BT)]/k T_g\}} \quad (28)$$

Thus the difference between the number of segments in the B conformation for thermodynamic equilibrium and for the glassy polymer at $T < T_g$ is given by

$$n_B - n_{B T_g} = n [P_{iB} - P_{iB T < T_g}] \quad (29)$$

which we denote by x . Similarly,

$$n_A - n_{AT\epsilon} = -x \quad (30)$$

and

$$n = n_A + n_B \quad (31)$$

Assuming a cooperative transition, which is described by the equation

$$A^T + B^{T\epsilon} \frac{K_1}{K_2} B^T + A^{T\epsilon} \quad (32)$$

this can be rewritten, in terms of eqs. (30), (31), and (32).

$$\frac{d[x/n]}{dt} = K_1 \left[\frac{n_A}{n} - \frac{x}{n} \right] \left[\frac{n_B}{n} + \frac{x}{n} \right] - K_2 \left[\frac{x}{n} \right]^2. \quad (33)$$

If we let

$$\frac{n_A}{n} = \beta \text{ and } \frac{n_B}{n} = 1 - \beta, \quad (34)$$

then eq. (33) can be rewritten as

$$\frac{d[x/n]}{dt} = K_1 \left[\beta (1 - \beta) - \frac{x}{n} + \left(\frac{x}{n} \right)^2 \right] - K_2 \left(\frac{x}{n} \right)^2 \quad (35)$$

At equilibrium

$$\frac{d[x/n]}{dt} = 0 \quad (36)$$

and therefore

$$\frac{K_1}{K_2} = K = \frac{x^2/n^2}{(1 - \beta) - \frac{x}{n} + \left(\frac{x}{n} \right)^2} \quad (37)$$

The variable x/n , in terms of the Bragg-Williams order, parameter S , becomes

$$\frac{x}{n} = (1 - X) \beta (1 - \beta) \quad (38)$$

therefore eq. (37) becomes

$$K = \frac{\beta (1 - \beta) (1 - S)^2}{S + \beta (1 - \beta) (1 - S)^2} \quad (39)$$

or

$$K^{-1} = \frac{S}{\beta (1 - \beta) (1 - S)^2} + 1 \quad (40)$$

which is identified by Bragg and Williams as eV/RT . They assume that $V = V_0S$. From our kinetic argument and conventional rate theory, K is derived as follows: Let the potential barrier in going from $A \rightarrow B$ be denoted by U and the energy difference between A and B by V . Then

$$K_1 = \nu_1 e^{-(U+V)/RT} \quad (41)$$

and

$$K_2 = \nu_2 e^{-U/RT} \quad (42)$$

and therefore

$$K = \frac{K_1}{K_2} = \frac{\nu_1}{\nu_2} e^{-V/RT} \quad (43)$$

If we assume that $\nu_1 = \nu_2$ and $V = V_0S$, then the kinetic theory reduces to the equilibrium theory of Bragg and Williams. Clearly, the assumption that $\nu_1 = \nu_2$ amounts to assuming that the entropy of activation in either direction is equivalent and, therefore, amounts to neglecting differences in entropy arising from a change in the vibrational spectrum. Assuming for the moment that $\nu_1 = \nu_2 = \nu$ and letting $V = V_0S$, we find that

$$\frac{dS}{dt} = \nu e^{-U/RT} [\beta (1 - \beta) (1 - S)^2 - e^{-V_0S} + [S + \beta (1 - \beta) (1 - S)^2]] \quad (44)$$

The basic difference between this equation and others is the dependence of the second exponential on S , which states that the energy of the transformation depends on the extent of the transformation. Thus, in a polymer chain composed of both A and B conformations, the rate of change of $A \rightarrow B$ will be either increased or decreased by the amount of conversion. This equation is a mixed algebraic and exponential expression which can be best handled by computer calculations.

It should be mentioned that the quantity X could be interpreted in several ways, i.e., the number of flexed bonds, the number of free volume packets, or the z parameter from irreversible thermodynamics.

In order to get a first-order approximation, we expand eq. (44) in a Taylor's series about the equilibrium value of $S = \bar{S}$, which yields a solution of the following form:

$$\frac{(1 - S/1 - \bar{S}) + \lambda}{1 + \lambda} = \frac{\coth}{\tanh} (\alpha t + B) \quad (45)$$

For $\lambda \ll 1$,

$$\frac{1 - S}{1 - \bar{S}} = \frac{\coth}{\tanh} (\alpha t + B) \quad (46)$$

Now, assuming that either the yield stress or the density variation is linearly related to S , we obtain

$$\sigma_y = \sigma_{y_0} + C(1 - S) \quad (47)$$

and

$$\frac{\sigma_y - \sigma_{y_0}}{\bar{\sigma}_y - \sigma_{y_0}} = \frac{\coth}{\tanh} (\alpha t + B). \quad (48)$$

Since σ_y is assumed to be linearly related to S , which is related to x by eq. (38), the variation in σ_y would be a direct measurement of the change in N_{AT_g} and N_{BT_g} . Evaluation of these parameters is in progress and will be presented elsewhere. Until such time as these calculations have been performed and verified by other experiments, Bueche's theory should be used.

The author is indebted to Mr. R. Rissman for some of the measurements, in particular the density, and to Mr. L. Osika for the high-angle x-ray measurements. Thanks are extended to Drs. K. Goldblum, F. P. Price, and H. Rogers for their comments concerning this work.

References

1. J. P. Berry, *J. Polym. Sci.*, **50**, 107 (1961).
2. J. P. Berry, *J. Polym. Sci.*, **50**, 313 (1961).
3. J. P. Berry, *Mod. Aspects Vitreous State*, **2**, 114 (1962).
4. R. D. Andrews and W. Whitney, *Study of the Phenomenon of Cold Drawing in High Polymers*, Textile Div. Rept. #TD-123-64, MIT, Cambridge, Mass., May 1964.
5. J. A. Sauer, S. Moving, and C. C. Hsiao, *J. Appl. Phys.*, **20**, 507 (1949).
6. R. P. Kambour, *J. Polym. Sci. A-2*, **4**, 17, 349 (1966).
7. D. G. LeGrand and P. F. Erhardt, *J. Appl. Poly. Sci.* (in press).
8. H. H. Stuart, private communication.
9. D. G. LeGrand (in preparation).
10. J. Fisher, *J. Appl. Phys.*, **19**, 1062 (1948).
11. J. P. Berry, *J. Polym. Sci. A-2*, 4069 (1964).
12. J. H. Golden, B. L. Hammant, and Y. Hazell, *J. Polym. Sci. A-2*, 4787 (1964).
13. A. V. Tobolsky and K. Murakami, Rept. to QMC, Cont. DA-19-129-QM-1306, Oct. 1959.
14. J. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962).
15. R. D. Andrews and W. Whitney, *J. Appl. Phys.*, to be published.
16. R. D. Andrews and R. M. Kimmel, *J. Appl. Phys.*, to be published.
17. W. Whitney, *Yielding Behavior of Glassy Amorphous Polymers*, Sc.D. Thesis, MIT, Cambridge, Mass., Nov. 18, 1964.
18. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962.
19. R. E. Robertson, *J. Chem. Phys.*, **44**, 3950 (1966).
20. K. B. Goldblum, *J. Appl. Polym. Sci.*, **8**, 111 (1964).
21. G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **43**, 139 (1965).
22. M. Goldstein, *Polymer Letters*, **4**, 87 (1966).
23. R. E. Robertson, *J. Appl. Polym. Sci.*, **1**, 443 (1963).
24. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
25. J. Frenkel, *Kinetic Theory of Liquids*, Darier Publ., New York, 1955.

Received March 20, 1969

Revised May 21, 1969