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The effect of specimen size on the mechanical behaviour associated with crazing

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Since crazes generally nucleate at the surface it is expected that the size of the specimen, as described by the ratio of surface area to volume, should affect the mechanical behaviour of polymers which deform primarily by crazing. The stress relaxation curves and the stress–strain curves of PS, PMMA, PTFE, and PC were measured in liquid nitrogen for specimens of different size which were machined from the same rod. The predicted size effect was observed in that the smaller (6.4 mm diameter) specimens stress-relaxed faster and the stress to produce a given amount of craze deformation was lower than for the larger (12.7 mm diameter) specimens. The range of the tensile strength from 0 to ∞ size is also presented based on the stress to nucleate the first craze and on the tensile strength that is observed when no crazing occurs.

1. Introduction

The effect of specimen size on the mechanical behaviour of solids may manifest itself in two ways. (1) If the specimen fails by brittle fracture, its fracture stress depends on the largest pre-existing crack or notch in the specimen. If the specimen size is reduced, then the size of the largest crack that can occur is reduced; therefore, the fracture stress increases as the specimen size decreases. The large fracture stress of fine fibres is often attributed to this effect. (2) If the units of plastic deformation, such as dislocations, slip bands, or crazes, nucleate only at the surface and propagate inward from the surface, then the flow stress (the stress to produce a given strain) decreases as the cross-section area of the specimen decreases. Since crazes are generally nucleated at the surface of a polymer, the expected mechanical behaviour of crazed specimens is as follows: the larger the ratio of surface to volume in the specimen, (a) the lower the yield point, (b) the faster the creep rate for a given stress and, (c) the faster the rate of stress relaxtion.

The basis of the size effect during crazing comes from the basic equation for describing the rate of craze deformation. [1, 2, 3]

$$\dot{\epsilon}_c = \rho b \gamma \mathrm{d}A/\mathrm{d}t \tag{1}$$

ρ is the craze density (number of crazes per unit area of surface, b is the width of the craze, (the displacement which produces the strain) γ is the ratio of surface to volume of the specimen, and $\mathrm{d}A/\mathrm{d}t$ is the change in area of the craze with respect to time where area A is perpendicular to the displacement b. It was shown [3] that the yield point associated with crazing is a dynamic yield point, and that the stress–strain curve can be calculated when the stress and time dependence of the parameters in Equation 1 are known. The theory showed that the craze yield point increases with the strain rate, which is in agreement with experiments [4]. In a similar way the theory shows that the craze yield point would decrease as γ, the size parameter, increases. The equation for stress relaxation can also be calculated from Equation 1, and results of the calculation show that the rate of relaxation increases as γ increases.

The measurement of an intrinsic size effect requires the surface and bulk properties, which are connected with crazing, be identical for specimens of different size. If the surface or bulk properties are different, then a pseudo-size effect would be observed. Two surfaces can be considered identical if their surface density of crazes are the same. The velocity of the crazes depend on the bulk properties. If the bulk properties vary radially along the as-received rod, then a pseudo-size effect may be observed. In order to equilibrate the structure of the bulk, the as-received rods were annealed below T_g, the glass transition temperature.

In this paper a size effect was measured in four polymers; PC, PMMA, PS, and PTFE. The effect of shear flow was minimized by observing crazing at a low temperature, 78 K. Both stress-strain and stress relaxation tests were used. The expected size effect was observed in that the small diameter specimens deformed more readily than the large ones.

2. Experimental

2.1. Material

The four polymers were all stock commercial items. The starting rods were 19.1 mm diameter for PC, PMMA, and PTFE and 25.4 mm for PS. The rods were machined into cylindrical tensile specimens 12.7 and 6.4 mm diameter with the same uniform gauge length of 25.4 mm. The radius of curvature between the uniform gauge section and the threaded ends was 12.7 mm for specimens of both sizes. The stress concentration at the shoulder of the 12.7 mm specimen was 1.15 compared to 1.05 for the 6.4 mm size. This difference in stress concentration is small, but it would work to slightly reduce the expected size effect.

The specimens were carefully machined by the same procedure in order to produce the same surface. The polishing procedure started with number 400 wet emery paper whose grit size is 25 μm and was finished with 0.3 μm alumina. The bulk structure was equilibrated relative to the as-received structure by annealing for 18 h at a temperature of 0.92 T_g or T_m, the melting point.

The crazes were observed by sectioning longitudinally and metallographically polishing the specimens which were imbedded in epoxy. The craze density was obtained by counting the number of intersections of the crazes with the outer surface of the specimen after scanning the specimen in order to obtain representative regions. The variation in craze density for a given specimen was about ± 20%. The craze density of the specimens craze are shown in Table I. The reason for the large variation in the craze density of PMMA is not known. Crazes are not easily seen in PTFE of this craze are shown in Table I. The reason for the PTFE. The evidence for crazing in PTFE in liquid nitrogen has been presented by Fischer and Brown [5]. All specimens used for the stress–strain test were in the as-received state with the 0.3 μm surface finish.

TABLE I Craze Density (mm^{-1})*

Material	PS	PMMA	PC	PTFE
Small Specimen	9	44	10	Not
Large Specimen	10	15	8	Visible

*The number of intersection of crazes with a longitudinal line on the surface.

2.2. Testing procedure

The stress relaxation experiments were done on an Instron machine. The relaxation of the machine itself was negligible compared to the relaxation with a specimen. The specimens were fully loaded in 45 sec, the cross-head was stopped, then the load was recorded as a function of time. All specimens of a given polymer were loaded as closely as possible to the same stress. The spring constant for the system was obtained from the initial slope of the load versus extension curve as recorded on the Instron chart.

Identical specimens were tested in pure He and liquid nitrogen in order to measure the amount of relaxation that occurs without crazing. These polymers all craze in liquid nitrogen but not in He [1, 4, 5, 6, 7]. As shown in Fig. 1, the amount of relaxation in He for PS and PMMA is negligible compared to that in liquid nitrogen. For PC, the amount of relaxation in He is appreciable compared to that in liquid nitrogen. The difference between the curves in N_2 and He gives the contribution from crazing for each polymer. Duplicate tests were done to test the reproducibility of the stress relaxation curves. The reproducibility was always much less than the observed size effect.

The stress at which crazing was initiated was based on a visual observation of the specimen with the naked eye through a window in the container with liquid nitrogen.

The stress–strain tests for PS, PMMA, and PC were all conducted at a strain-rate of 2×10^{-3} min^{-1} and for PTFE 5×10^{-3} min^{-1}.

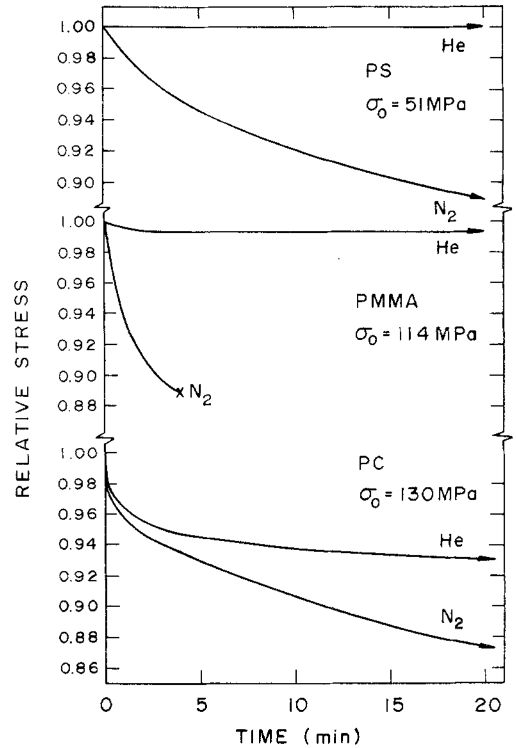

Figure 1 Stress-relaxation curves in He and N_2 at 77 K for PS, PMMA, and PC.

3. Theory

The purposes of the theoretical section are twofold: to present a parameter for stress relaxation which normalizes the differences in gauge length and stiffness that exist between specimens of different sizes and to show how the intrinsic size effect is related to the stress relaxation curve.

The stress relaxation experiment is shown in Fig. 2; the system consists of a spring in series with an element which produces a time-dependent strain. The spring and the element are stressed and then held between rigid walls. As the non-elastic deformation, $\Delta l(t)$ develops in the element, the spring relaxes elastically by an amount Δl_e so that

$$\Delta l_e + \Delta l(t) = 0 \tag{2}$$

$$\Delta l_e = (F - F_0)/k \tag{3}$$

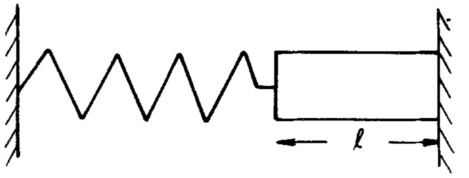

Figure 2 Model for stress relaxation. Spring with spring constant k is in series with a non-elastic element of length l between rigid walls. An increment of non-elastic strain equals $\Delta F/kl$ where ΔF is a change in force.

where F is the force on the system at time t, F_0 the force at $t = 0$, and k is the spring constant of the system. k includes the stiffnesses of the specimen, the grips and the rest of the testing machine; it was measured from the initial slope of the load versus overall deformation curve. Experiments show that k does not depend on the amount of crazing, and this is expected because the volume of crazed material is a small fraction of the total volume.

$$\Delta l(t) = \epsilon(t) l \tag{4}$$

where $\epsilon(t)$ is the time dependent strain and l is the length of the gauge section in which the strain $\epsilon(t)$ occurs; l is obtained by directly observing where the crazes occur on the specimen. Combining Equations 2, 3, and 4

$$\epsilon(t) = (F_0 - F)/kl \tag{5}$$

Thus, in the following figures the non-elastic strain as measured by the parameter $(F_0 - F)/kl$, will be used to describe the stress relaxation process.

The non-elastic or time dependent strain, $\epsilon(t)$ may consist of the following components: craze strain, shear flow, and visco-elastic strain. In these experiments the major component of $\epsilon(t)$ will be the craze strain ϵ_c; the other components occur during relaxation in the He environment (Fig. 1) and can be subtracted from the total time dependent strain in order to observe the size effect. The size effect originates only from the craze strain. The craze strain is given by:

$$\epsilon_c = \int_0^t \dot{\epsilon}_c \mathrm{d}t \tag{6}$$

where the craze strain rate $\dot{\epsilon}_c$ is given by Equation 1. Thus

$$\epsilon_c = \int_0^t \rho b \gamma (\mathrm{d}A/\mathrm{d}t) \mathrm{d}t \tag{7}$$

The stress relaxation experiment is conducted by rapidly loading all specimens of the same polymer to the same stress. Since the density of crazes, ρ, for environmental crazing at low temperatures depends on the peak stress and not on the time [2], ρ is constant and independent of size. The crazes are uniform in thickness except near their ends so that b is also a constant and independent of size. The change in area of the craze with respect to time, $\mathrm{d}A/\mathrm{d}t$, is related to the craze velocity and is a strong function of the instantaneous value of the stress which of course is relaxing with time.

Therefore

$$\epsilon_c = \rho b \gamma \int_0^t (\mathrm{d}A/\mathrm{d}t)\mathrm{d}t \qquad (8)$$

The size effect is reflected in γ, the ratio of surface to volume of the specimen. Thus, for a given time, the amount of craze strain should be greater for the specimens with the smaller diameter. In order to calculate the size effect from Equation 8 it is necessary to know how $\mathrm{d}A/\mathrm{d}t$ depends on stress, and how the stress changes with time. For the purposes of this paper, the magnitude of the size effect can be represented by the ration of the values of ϵ_c for the two sizes measured at the same time.

The quantitative connection between craze deformation and the resulting stress–strain curve has been detailed in a previous paper [3]. The size effect will manifest itself in the stress–strain test in two ways: the yield point should be greater for the larger specimen and the stress for a given strain beyond the proportional limit should be greater for the larger specimen. The latter criterion must be used if the specimen fractures before it yields. The size effect in this paper is not associated with fracture, but only with the plastic part of the

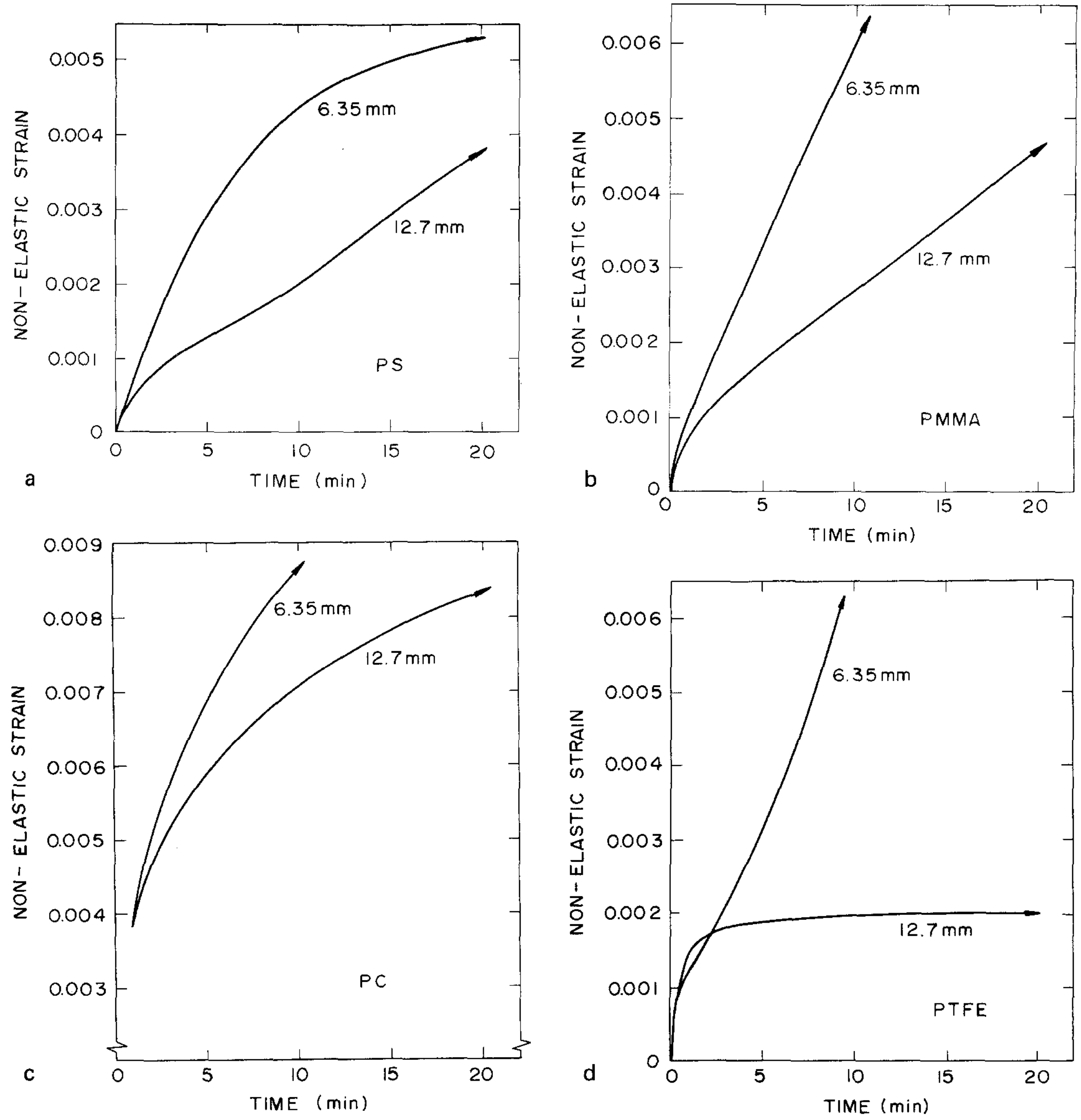

Figure 3 Non-elastic strain versus time during stress relaxation in liquid nitrogen for 12.7 mm and 6.4 mm diameter specimens (a) PS at $\sigma_0 = 45$ MPa, (b) PMMA, $\sigma_0 = 110$ MPa, (c) PC, $\sigma_0 = 135$ MPa, (d) PTFE, $\sigma_0 = 83$ MPa.

stress–strain curve. It turns out that a decade change in size is equivalent to a decade change in strain rate. Therefore, it is most important to keep the strain rate constant or compensate for a difference in strain rate when the size effect is being measured.

4. Results

4.1. Stress relaxation

None of the polymers craze when they are deformed in He at 77 K. Fig. 1 shows that the brittle polymers, PS and PMMA exhibit negligible relaxation in He, and therefore all their relaxation in N_2 is caused by crazing. PC is ductile in He at 77 K as indicated by its relaxation and by its stress–strain behaviour. The relaxation of PC in N_2 therefore has two components: (1) bulk shear flow which is independent of size and (2) crazing which should depend on the size of the specimen. Previous work with PTFE [5] indicated that it should behave like PC in He.

The size effect for each polymer is shown in Fig. 3a, b,c,d. In all cases the expected size effect was observed in that the small specimens relaxed faster than large ones. In the case of PMMA there is a question as to how much of the size effect is intrinsic, because the craze density in the small specimen is about three times that of the large one and the rate of relaxation was also about three times greater.

The shape of the relaxation curve for the small specimen of PTFE (Fig. 3d) is different from all the other curves in that the relaxation curve shows an acceleration. Crazing experiments with other polymers show that the creep rate varies exponentially with stress so that a deceleration in the stress relaxation curves would be expected. Possibly the interior of the starting rod of PTFE had different bulk properties than the exterior and this produced the differently shaped relaxation curve. Thus, the size effect observed in PTFE may not be entirely intrinsic.

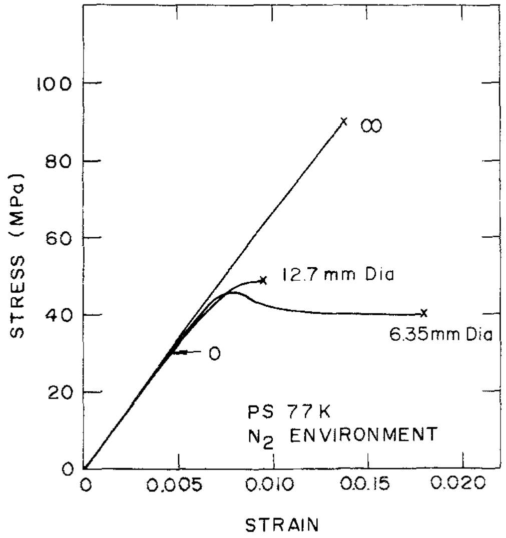

Figure 4 Stress–strain curves of PS, in N_2 at 77 K for

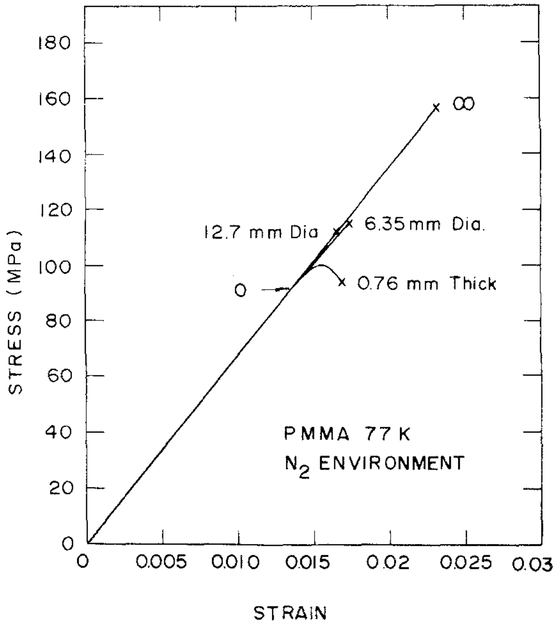

Figure 5 Stress–strain curves of PMMA, in N_2 at 77 K for various size specimens. The zero size (0) corresponds to the stress for craze nucleation and the cuve for infinite size (∞) was obtained in an inert environment without crazing. 0.76 mm curve from Imai and Brown [6].

4.2. Stress–strain curves

In the tensile test the large specimen should have a larger yield point. If fracture occurs before yielding, the stress for a given amount of non-linear strain should be larger for the large specimens. The results are generally in accord with the expected size effect. In PS (Fig. 4) the larger specimen has a slightly larger yield point. The 0 point corresponds to the stress where the first craze is initiated and this should correspond to the behaviour of an extremely thin specimen which would fail when the first craze forms. The ∞ point corresponds to a specimen of very large size; any crazing that occurs makes a negligible contribution to the strain since the surface to volume ratio is essentially zero. The ∞ curve corresponds to the stress–strain curve in He where no crazing occurs. Thus, the 0 point

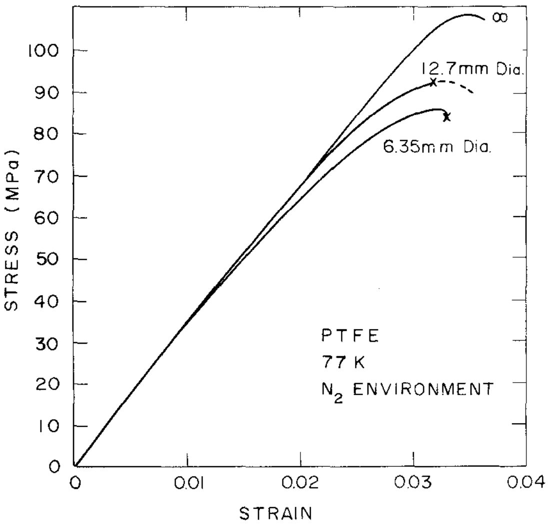

Figure 6 Stress–strain curves for PTFE, in N_2 at 77 K for various size specimens. The zero size corresponds to the stress for craze nucleation and the ∞ curve is estimated from data by Fischer and Brown [5].

and the ∞ curve represents the lower and upper limits for the size effect respectively and are considered to be direct measures of the extent of the size effect.

For PMMA (Fig. 5) the size effect was not very evident becasue the large and small diameter specimens fractured in a brittle fashion. The data were supplemented by using the stress–strain curve for a thin sheet specimen from another investigation [6]. The expected size effect is exhibited but the effect may not be completely intrinsic since the bulk and surface properties of the thin sheet may be different than for the cylindrical rod. PTFE (Fig. 6) shows the expected size effect clearly. No zero point was given because crazes are not easily observed in PTFE; the ∞ curve was estimated from data by Fischer and Brown [5]. For PC (Fig. 7) the expected size effect is indicated even though the large specimen fractured before the yield point.

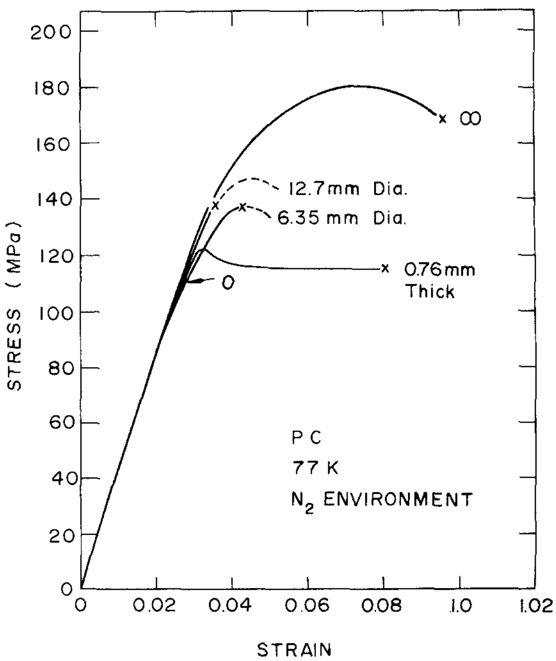

Figure 7 Stress–stress curves for PC. The zero size corresponds to the stress for craze nucleation and the curve was obtained in an inert environment without crazing. 0.76 mm curve from Imai and Brown [7].

5. Discussion

It is of interest to determine the functional relationship between size measured by the surface per unit volume γ and the tensile strength σ_c. The form of the function is suggested by theory [3] wherein

$$\sigma_c = F(\dot{\epsilon}/\gamma)$$

where $\dot{\epsilon}$ is the strain rate. The dependence of σ_c on $\dot{\epsilon}$ has been measured [8] for several polymers which deformed by crazing in liquid nitrogen as shown in Fig. 8; these curves all have the same shape. It is expected that σ_c versus γ should have a similar shape. The σ_c versus γ curve, for a specific polymer is obtained from the stress–strain curves as follows: the lower and upper bounds of the curve is determined by the 0 and ∞ points respectively, the horizontal position of the curve is given by the data for the intermediate sizes. Fig. 9 shows the curve of σ_c versus γ for PC as obtained from the data in Fig. 7. It would seem to be desirable to have more experimental points to more rigorously establish the shape of the curve between 0 and 10^{-1} mm and between 10 mm and ∞. However, data points in the large size range would be very difficult to obtain. For example, a 10 inch diameter specimen would require a testing machine with about a 2×10^6 lb. capacity and would have to be machined from about a 20 inch diameter rod in order to avoid fracture in the grips. Sizes below 10^{-1} mm would be extremely difficult to machine if they were made from the same rod as the larger sizes. Actually the contraints on the shape of the curve as given by Fig. 8, along with the upper and lower bounds, fairly well establish the shape of the curve. It only requires one or two data points for the intermediate sizes in order to establish the

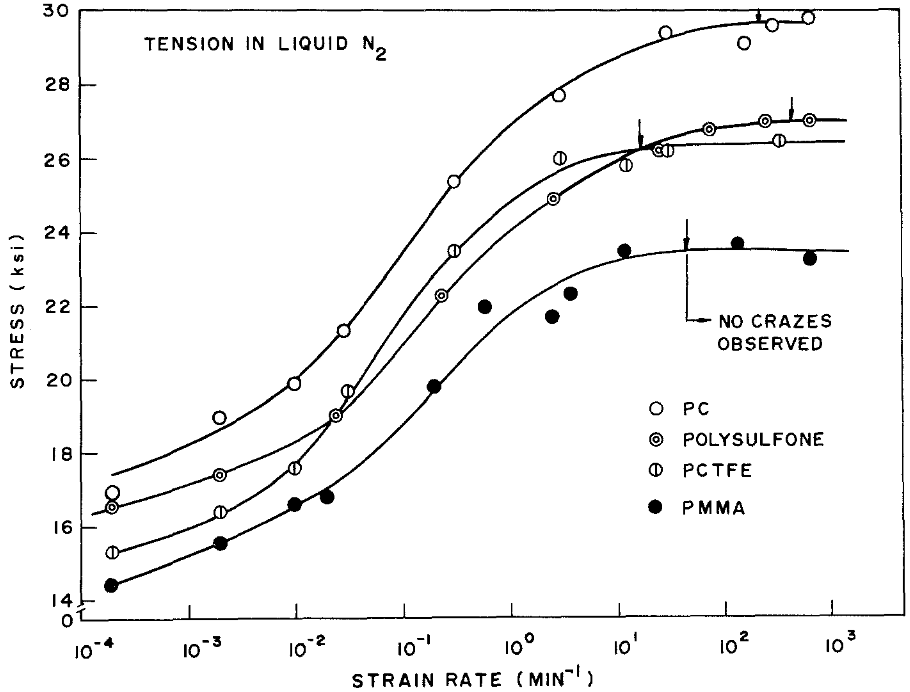

Figure 8 Craze yield point versus strain rate for several polymers whose ratio of volume to surface area are the same. From Imai and Brown [8].

horizontal position of the curve. The great usefulness of Fig. 9 is that it is now possible to estimate the tensile strength of a very large or very small specimen without requiring a very expensive and difficult test.

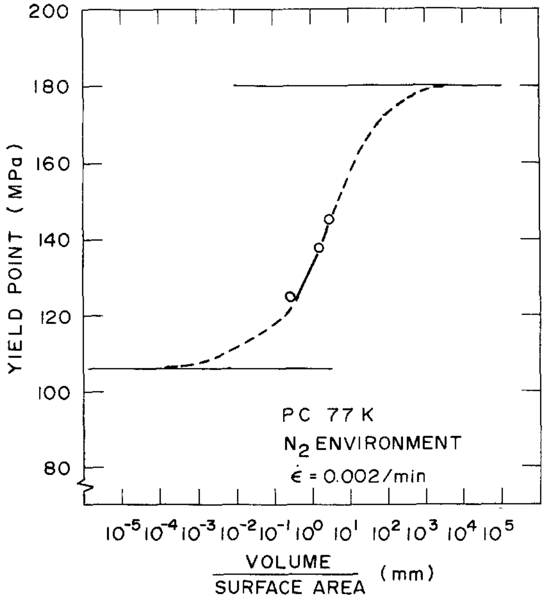

Figure 9 Craze yield point versus ratio of volume to surface area of test specimen of PC.

For purposes of engineering design, it is suggested that a useful curve of σ_c versus γ for a new polymer can be obtained with a minimum of effort by making only two tests. One test is made in the environment that produces crazes and the other in the non-crazing environment. The latter test gives the ∞ point; the former gives the intermediate point. The 0 point corresponds to the stress to nucleate the first craze. If it is experimentally difficult to determine the 0 point by direct observation, then it can be estimated from the stress where one curve initially deviates from the other. Knowing the general shape of the curve as shown in Figs. 8 and 9, the curve for the new polymer is fairly well determined.

The range of the tensile strength for each polymer as the size ranges from 0 to ∞ is shown in Table II.

TABLE II Maximum variation in tensile strength with size

Polymer	$\sigma_c(0)$(MPa)	$\sigma_c(\infty)$(MPa)	$\sigma_c(\infty) - \sigma_c(0)$(MPa)
PS	30	90	60
PMMA	82	156	74
PTFE	60	110	50
PC	105	180	75

The $\sigma_c(0)$ result for PTFE was estimated from the initial deviation of the N_2 and He curves in Fig. 6.

The $\sigma_c(\infty)$ result for PTFE was obtained from the observation by Fischer and Brown [5] that the difference between the tensile strength in He and liquid nitrogen at an $\dot{\epsilon}$ of 2×10^{-3} min^{-1} was independent of crystallinity and was 27 MPa for a 0.76 mm thick sheet specimen. Table II indicates that the maximum range of σ_c from the size effect is a large fraction of the values obtained with the usual laboratory specimens.

The effect of size on the mechanical properties of crystalline solids has been discussed by Kelly [9], who emphasized the experimental difficulties in measuring an intrinsic size effect. Nielsen [10] and Deanin [11] have mentioned the possible existence of a size effect in polymers. This is the first paper to give experimental support to the idea that there is an intrinsic size effect on the mechanical properties of polymers that deform by crazing. The effect occurs because the unit of deformation, the craze, generally grows from the surface inward. In general the intrinsic size effect may be compounded or obscured by pseudo-size effects which stem from a variation in surface properties and from bulk properties which are not homogeneous throughout the original material.

6. Conclusions

(1) Polymers that undergo craze deformation at low temperatures exhibit an intrinsic size effect on the mechanical properties. The size effect is such that the greater the surface-to-volume ratio of the specimen the greater the rate of stress relaxation and the lower the craze yield point.

(2) The lower bound of the curve for size versus tensile strength is the stress to nucleate a craze and corresponds to extremely small specimens, and the upper-bound, for extremely large specimens, is the strength under conditions where no crazing occurs as in an inert environment.

Acknowledgments

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