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INITIATION AND GROWTH OF CRAZES IN GLASSY POLYMERS

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ABSTRACT

In glassy polymers crazes initiate at surface or interface stress concentrations which localized plastic flow produces microvoids by intense inhomogeneous plastic shear at a molecular scale. The rate of such cavity formation depends primarily on the local concentrated deviatoric stress while their subsequent plastic expansion into craze nuclei is driven by their mutual interaction in response to the global negative pressure. Once a craze nucleus forms into a spongy heterogeneity of significant aspect ratio it grows by the meniscus instability in which new craze matter, having continuously interconnected air passages, forms by the repeated convolutions of the concave interface of air and yielded polymer at the craze tip. The proposed theory not only gives quantitative agreement with the experimental measurements on the rates of initiation and growth of crazes at room temperature and below, but also predicts the scale factor of the structure of craze matter.

INTRODUCTION

Crazing in glassy polymers has long been known to play a dual role. When their initiation and growth is carefully controlled, as in the case of multi-phase high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) polymers, crazes can be a source of toughness. On the other hand, in most single-phase glassy polymers crazes are precursors to fracture. The phenomenology of crazing is rich in detail for which the reader is referred to recent comprehensive reviews [1,2]. Here we will concentrate only on the mechanisms and kinetics of the nucleation and growth of crazes in single phase, unoriented glassy polymers under normal dry conditions.

Maxwell and Rahn [3] were the first to study the kinetics of nucleation of crazes from surfaces of stressed polystyrene (PS) and polymethyl methacrylate (PMMA). They were also the first to emphasize the key role of surface stress concentrations and effect of solvents in accentuating crazing. Following the clarification of the important role of crazing in the toughness of rubber modified polymers by Buckhiller and Smith [4] interest in crazing was concentrated on: the development of phenomenological stress or strain criteria for so-called craze-yielding [5-10]; and on consideration of crazes as the source of plastic dissipation in the crack propagation process in dry polymers [11,12], and in solvent crazing both in the presence of fluids [13-17], and in the presence of gases [18,19]. In addition, however, the structure [20,21] and mechanical behavior of craze matter [22,23] received attention, the effect of molecular weight on the structure of craze

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matter was studied [24-26], and some recognition was given to the source of
tive detail became known as a result of these studies, the mechanisms of
atures for each of these studies, the mechanisms of
tivity, for example, theorized that crazing requires a devitrification
of the glass into a rubbery state by the enhanced negative pressure
stress, the very large stress concentrations which this mechanism requires
motions of inhomogeneous plastic deformation, and crazing of the order of 50-
material under the action of the negative pressure existing in the stress
on the negative pressure by well-known continuum plasticity solutions of
on microscopy earlier [33] have furnished confirmation for the theory. Here we will
 summarize the nucleation of crazes that demonstrate the correctness of the pre-
posed mechanism.

The kinetics of growth of crazes has also received attention. Apart from
and previous studies of Besenov and Kuvushinskii [35] and some iso-
cuences have concentrated on the growth of crazes, however, most of
sion [15,17,18]. A Fourier transform solution for stress distri-
which the extension criterion for crazes is elastic stress at the tip. This solution, however, has many charac-
ters that are important in the stress
. On the other hand, planar yield can occur.
Such solutions usually assume: either a critical strain or a critical energy release rate (or cavitation work) [15];
dependent stress relaxation of the crazed matter.

On the other hand, Argon [29] has suggested a specific mechanism, which in their case involves plastic expansion of cavities whose mode of formation was left unspecified.

Repeated nucleation of pores ahead of the main craze due to the same in-}

flow processes that are responsible for the formation
of the main craze nucleus, when the local condensation conditions at the tip of the
craze, however, have some shortcomings: first the stress intensification at the
nucleation of isolated pores leads to a topologically different craze

structure from that of crazed matter in which the "vacant phase" is isolated

too much, and this can prevent the effective crazing mechanism from

happening. For this reason it was proposed [33] that
the yielded matter at the air-polymer interface is unstable to perturbations of a well-defined wavelength, breaks
up, and by repeated convolutions produces the topologically correct form

\[ \Delta \sigma^* = 0.15 \frac{V}{t} \left( \mu \sigma_0 \right) \]

where \( V \) is the shear modulus of the polymer at the given tempera-
ture and \( \phi \) is the relative density of the shearability region (usually a
molecular dimension characteristic of the polymer, such as the molecular
diameter). It was shown further that although the critical radius of the
slip planes is only of the order of \( 10^{-4} \), once formed, the plane may expand
der under falling local stress to a size large enough to provide for the sur-
face free energy of an additional, on the order of \( 10^{-4} \), appreciable
length of molecular heterogeneities. When arrested it has then enough concentration of
local strain energy to provide for the surface

It must be emphasized that this relatively crude mode of plastic flow
described above, as well as its free energy for formation (1), are funda-
mentally different from the more local mechanism of plastic flow in glassy
polymers by the thermally activated rotation of segments of molecules described in detail by Argon [42].

Under a multi-axial state of stress, and in consideration of the molecular heterogeneity, the shear stress \( \tau \) is interpreted as the local deviatoric stress \( s \) for a definition of \( s \), see \[42] \) existing at a stress concentra-
tion, that is near the deflection of a surface groove, but can also be a protrusion on a dust particle or a latex inclusion in a rubber modified polymer.

Neuber [43] has considered in detail the stress concentrating effect of
surface grooves beneath any general state of stress shown in Figure 2. The
cracked local stress \( \sigma_{11}, \sigma_{22}, \text{ and } \sigma_{12} \) are according to Neuber (for a
Poisson's ratio of 0.3 where yielding begins)
where $Q(s/Y, \beta)$ is a normalized locus for pore expansion which is shown in Figure 4 for a porosity of $\beta = 0.01$. Clearly, when the material is nearly at a state of yield, $Q_0$, and therefore, the required $\sigma$ are very small, but so is the rate of expansion of the pores. In practice, the actual level of $Q$ will be governed by the rate sensitivity of the material.

In previous descriptions of the theory of craze nucleation [29, 33] it was stated that the plastic expansion of pores by elastic unloading of the surroundings requires a negative pressure exceeding a critical amount. This condition that was derived for a porous material that has not been previously brought to a state of flow by the presence of a large deviatoric stress is completely relaxed when the material is already at a state of flow.

Equations (6) and (7) together give the time $t_{\text{in}}$ after which the craze nucleus formation by plastic interaction of the already formed pores begins under a local deviatoric stress $\sigma$ and a background negative pressure $\sigma_0$:

$$t_{\text{in}} = (1/\tilde{B}_0) \exp \left[ (\Delta G_{\text{pore}}^s/kT) - (\xi/Q_0) \right]$$

where $\xi$ was defined by equation (5b).

Additional time will, however, be required to expand pores by elastically unloading the surroundings before a craze nucleus becomes of visible size. An estimate of this growth time can be obtained by considering a phenomenological, power-law form of the relationship between effective strain rate $\dot{\varepsilon}^e$ and effective stress $\sigma^e$ (eqs. 5) i.e., $\dot{\varepsilon}^e = \tilde{C}_0 \sigma^e^m$ where $\tilde{C}_0$, $Q_0$, and $m$ are phenomenological, temperature dependent constants of the material. It can then be shown [44] that the additional time for growth of pores under the background negative pressure $\sigma$ is

$$\Delta t_{\text{growth}} = (2/3\tilde{C}_0)(\xi/Q_0)^m \int_{\tilde{B}_1}^{eta_1} \frac{1}{\beta - 1} \exp \left( \frac{\xi}{Q_0} \right) d\beta$$

where $\beta_1 = 0.005$ the initial porosity given by equation (6) where growth commences and $\beta_2 = 0.1$ is the final porosity where the nucleus is large enough to scatter light. Thus, the total time for formation of a visible craze nucleus will be the sum of the times given by equations (8) and (9), as

$$t_{\text{craze nucleation}} = t_{\text{(initiation)}} + \Delta t_{\text{growth}}$$

As is apparent from equation (9) the growth time makes up a significant fraction of the total only when the background negative pressure is very small. In pure shear where $\beta = 0$ craze nuclei cannot form even though much micropore formation will take place.

It can be assumed that surfaces of commercial polymers have a family of randomly positioned microgrooves (scratches). Experience (and experiments to be discussed below) suggest that the surface density $N$ and severity $k$ of such grooves are distributed approximately according to a normal distribution function as

$$N = N_0 \left[ 1 - (1/\sqrt{2\pi}) \int_{-\infty}^{(k-\bar{k})/\sigma_0} \exp \left( \frac{x^2}{2} \right) dx \right]$$

where $N_0$ is the mean number of grooves per unit area, $\bar{k}$ is the mean severity, and $\sigma_0$ is the standard deviation.
where \( N_0 \) is the total number of grooves (normal to the maximum principal tensile stress) per unit area on the surface, \( k \) the mean aspect ratio of the distribution of grooves, and \( \sigma \) the standard deviation of this aspect ratio. The local deviatoric stress \( \sigma \) depends on \( k \); hence, the initiation time \( t_{\text{in}} \) of grooves becomes progressively longer as \( k \) decreases, and the observed increase in the surface density of craze sites with time under constant stress reflects directly the operation of this stress on the spectrum of surface grooves [33,17].

Under a constant state of stress crazing eventually ceases at an apparent saturation density of crazes that increases with increasing levels of applied stress [6,33]. This occurs when the previously nucleated crazes have grown enough to interfere with each other and also absorb other potential crazeable sites at which the craze nucleation condition has not yet been met. This condition of craze saturation can be expected to be satisfied when a certain fraction \( f \) of the entire surface is covered by crazes. This fraction \( f \) is given by

\[
f = 2\pi \left( \frac{d}{d t} \right) \left( \frac{N_{k}^{(\text{sat})}}{N_{k}} \right) \left( t_{k}^{(\text{sat})} - t_{k} \right)^2 dN \tag{12a}
\]

\[
f = \frac{2\pi}{3} \frac{N_0}{\sigma_0} \left( \frac{d}{d t} \right)^2 \exp\left( -2\left( 1/\lambda \right) \right) \left( \frac{\exp \left( \frac{\Delta \rho \delta_{\text{par}}(k_{k}^{(\text{sat})})}{kT} \right) \exp \left( \frac{\Delta \rho \delta_{\text{par}}(k_{k})}{kT} \right) \right)^2 \tag{12b}
\]

where \( a \) is the half-craze growth rate which, as will be discussed below, depends only on the maximum principal tensile stress. In equations (12a,12b) the growth time for pores, given in equation (9) was neglected.

Growth of Crazes

After a craze nucleus has formed at a surface groove, the stress at the site of the nucleus is reduced while it is increased around the perimeter of the nucleus. In an isotropic polymer this will make the craze grow across the stress that can produce the largest opening displacement, i.e., across the maximum principal tensile stress. It is natural to expect that the mechanism of hole nucleation that gave rise to the craze nucleus will continue to add new craze matter to the already established nucleus at its most highly stressed periphery. As has been mentioned in the introduction, however, when quantitatively evaluated [40], such a mode of craze growth does not only fall short by orders of magnitude from accounting for the observed rate of growth of crazes and its stress dependence, but also gives a closed-cellular craze structure that is topologically different from the known meandering structure in which the vacant phase (air gaps) are continuously connected. The mechanism that fits all requirements is one in which craze tufts are produced by the repeated break-up of the concave air-polymer interface at the craze tip as shown schematically in Figure 5. Such convolutions of the yielded polymer at the craze tip results from a basic instability of all fluid (whether linear or non-linear) monomer advancing under the action of a suction gradient created in the fluid [46]. This is because such interfaces are unstable to perturbations above a certain wavenumber that decreases with an increasing suction gradient (negative pressure gradient).

To determine the rate of growth of an already established craze we consider it as a narrow discontinuity transmitting a normal traction \( \sigma_0 \) that can as a first approximation be taken as \( \gamma \lambda \) where \( \lambda \) is the natural draw ratio of the polymer in the craze matter and \( \gamma \) the tensile yield stress of the polymer. Under an applied tensile stress \( \sigma_{\text{in}} \), there will be a plastic zone of extent \( R \) (see Figure 6) at the tip of a craze of length \( 2a \) that is given by an elementary small scale yielding theory.

\[
R = a \left( \frac{\sigma_{\text{in}} - \sigma_0}{Y - \sigma_0} \right) \tag{13}
\]

Upon such local yielding, the craze tip, which is considered to be free of surface traction, will blunt to a radius of curvature of \( R \) and then establish a steady state transverse corrugation with a wavelength \( \lambda \), by the monicuss instability mechanism that will, by repeated convolutions, produce new craze tufts and advance the craze tip steadily forward as shown in the sketch of Figure 5. When the craze grows, a material point enters a new plastic zone at the far end, advances in a field of intensifying plastic strain, and finally appears at the polymer-air interface ready for the interface convolution process that forms craze matter. Argon and Salama [46] have shown that the condition corresponds to a craze tip velocity of

\[
\frac{d a}{d t} = \frac{\Delta \rho \delta_{\text{par}}(k_{k}^{(\text{sat})})}{kT} \tag{14}
\]

where \( \delta \) is the critical craze tip opening displacement at which a new increment of craze matter is added to the craze and \( \frac{1}{2} \) is the plastic strain rate of a solid polymer corresponding to an applied stress \( \gamma \) and temperature \( T \) according to an expression given by the theory for the yield stress developed by Argon [42]. This gives for the craze growth rate upon substitution

\[
\frac{d a}{d t} = \frac{\Delta \rho}{\gamma} \delta \exp \left( \frac{A \delta}{kT} \right) \left( \frac{1}{1 - \frac{T}{T_{c}}} \right)^{\frac{3}{2}} \tag{15a}
\]

\[
A = \frac{3\pi n_0 b^3}{16(1 - v)^2} \tag{15b}
\]

\[
\gamma = \frac{0.133}{(1 - v)} \tag{15c}
\]

In equations (15a), (15b) and (15c) \( n_0 \) and \( b \) are the angle or rotation of a segment of a molecule, or cluster of molecules, having a radius \( b \), \( \delta \) is a frequency factor \( (0(10^{13})) \) and \( k \) is Boltzmann's constant. Experimentally determined values for \( \delta b^3 \) have been given by Argon and Bosenov [47] for a large group of glassy polymers. Argon and Salama [46] who have examined the described mode of craze growth by the monicuss instability find that the steady state craze opening displacement \( \delta \) is given by

\[
\delta = 24n_0^2 b^3 \theta (1/m) \frac{X}{Y} \tag{16}
\]
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where Y is the surface tension of the polymer and B(1/m) is a function of the reciprocal of the phenomenological strain rate sensitivity exponent introduced above in connection with the stress-partitioning equation (9). For most polymers in which a ranges between 5-25 B(1/m) ranges from 10 down to 3 [46].

If a steady state growth exists for crazes in polymers with a relatively sharp elastic to plastic transition, it can be assumed that both the craze matter traction $\sigma_0 = Y/\eta$ as well as Y have the same strain rate and temperature sensitivity entering equation (15a), and that after a short transition period, the extent of the plastic zone at the craze tip makes an ever decreasing fraction of the craze length. Equations (15a) and (16) then show, this enables the craze to speed up to a final steady state velocity until it reaches to almost the level of $\sigma_0$ and Y to $\lambda_{1,0}$. Equations (15a) and (16) then give the asymptotic (steady) velocity of mature crazes as

$$
\begin{align*}
\frac{da}{dt} & = \frac{D}{\lambda_{1,0}^3} \exp \left\{ \frac{-A}{\gamma} \left[ 1 - \frac{\lambda_{1,0}^3}{Y} \right] \right\} \\
D & = \frac{24\pi^2\gamma B(1/m) \lambda_{0}^3}{Y}
\end{align*}
$$

where $D = \frac{24\pi^2\gamma B(1/m) \lambda_{0}^3}{Y}$

Our development assumes that the traction across the faces of the established craze remains constant at $\sigma_0$. Since the relative displacement between faces must increase with increasing craze length and since the craze matter is known to undergo orientation hardening, it is necessary that some new polymer be drawn out from the faces at this constant level of traction. Most observations are in support of this. The crazes in the polymer matter produced by the meniscus instability permits solvent to flow readily to the craze tip. Second, the presence of the solvent at the craze tip will accelerate growth by: a) reducing the surface energy [15], and b) dissolving into the polymer locally to reduce its modulus and thereby reducing both A and Y in equations (17) and (18) [15].

It is also worth noting that the presence of a second principal stress, algebraically smaller than the first, will produce only minimal changes on the growth rate given by equations (17) and (18). This is because the meniscus instability process that governs the rate of addition of craze matter is influenced primarily by the positive gradient of negative pressure at the tip of the crack which blunts by plastic flow. This blunting, however, is a result of the maximum principal tensile stress alone, and is largely uninfluenced by the specific shape of the plastic zone that is known to depend on both principal stresses. Experiments discussed below confirm that under multi-axial stress the craze growth rate depends only on the level of the maximum principal tensile stress.

EXPERIMENTS

Material and Experimental Procedure

Since the rate of craze initiation depends on the level of local deviatoric stress and the global negative pressure on the surface, it is essential not only to control these components of the stress, but also control the degree of surface roughness. For these reasons the crazing experiments were conducted on specially manufactured tubular specimens having a central, thin walled hour-glass section that could be subjected to combined tension and torsion, making possible a controlled variation of the global stress from pure deviatoric (i.e., $\sigma_0 = 0$) to pure tension (i.e., $\sigma_0 = 1\sigma$). As discussed in more detail elsewhere [34, 44], the specimens were precision machined from annealed blocks made by pressure molding of Dow 686 grade tactic poly-1-styrene pellets [*] at 165°C and 7.58 MPa. Gel permeation chromatography gave a number average molecular weight of $M_w = 8.95 \times 10^5$ and a weight average $M_w = 3.36 \times 10^6$ for this material. For this material, the small yield stress of this material was found to be 101 MPa and 165 MPa at 293K and 253K, respectively, which is 0.0717 and 0.0966 times the shear modulus at these respective temperatures. The machined tubular specimens were not annealed further but were given a featureless finish on both inside and outside surfaces by polishing with 0.1um gamma alumina and were subsequently provided with a controlled roughness on their outside surfaces by touching the centers of spinning specimens for 10 seconds with wet polishing cloth bearing 4um sized SiC particles. This produced grooves typically of a depth of 0.1 - 0.25um [33]. The topography of such roughened surfaces was measured for reference by interference microscopy from high resolution metal replicas of the surface [33, 34]. The aspect ratios k of the primary micro-grooves obeyed roughly a normal distribution. Secondary roughness along grooves, the presence of which could only be inferred by comparing experimental results with theory, could not be reliably measured.

Experiments were conducted on a specially constructed tension-torsion machine, the details of which are described elsewhere [34], in which it was eventually possible to limit the spurious interaction between the two modes of loading to about 1%. In spite of all the care in controlling specimen dimensions, concentricity, surface roughness, and machine cross interaction, the variability of experimental results was at best only within a factor of 2 in craze density or craze time (see the data for $n = 25.51$ MPa, $\sigma_0 = 12.41$ MPa at 253K in Figure 8c). Increases in surface density of crazes with time were measured photographically by using a technique of total reflection of light from the craze initiating interface to the camera [34]. Such films were also used to determine craze growth rates under multi-axial stress. Multi-axial craze initiation and growth experiments were carried out on the tubular specimens with experiments with plain cylindrical specimens with $\sigma_0$ performed in tension in thin sheets of commercial polystyrene ($M_w = 3 \times 10^5$, $M_w = 9 \times 10^5$) and polymethyl-methacrylate ($M_w = 2.46 \times 10^5$, $M_w = 2.52 \times 10^5$) which were machined into narrow gauge length specimens, annealed, and polished with 0.1um gamma alumina to suppress stray craze nucleation. These specimens, however, were not specially treated. They always contained sufficient numbers of imperfection from which a light density of crazes could nucleate. These commercial materials must have contained unknown additives. Craze growth measurements under tension in such commercial grade materials were again made by photographic recording of craze length at both 293K and 253K.

*Craze Initiation

Figures 7a, b, c and 8a, b, c give the measured increase in surface craze density (number of crazes per cm$^2$) as a function of time at 293K and 253K, respectively, for different combinations of nominal (global) deviatoric stress and nominal (global) deviatoric strain.

*We are grateful to Dr. C. Arends of Dow Chemical Company of Midland, Michigan for kindly supplying us with this material.

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stress and negative pressure in the specimens manufactured from the DOW 686 type polystyrene. The curves are theoretical results which will be discussed below. The data shows that at a given negative pressure an increase in deviatoric stress gives an increase in the nucleation density for a given value of r and produces eventually a higher density of crazes at a saturation occurs. The same is true for an increase in negative pressure at constant deviatoric stress (see data for s = 17.92 MPa in Figures 7a, 7b and 7c). The behavior at 253K and 293K are rather similar, except that the levels of stress for a given craze nucleus density at a given time are much higher at 253K. In each instance the observed crazes were always perpendicular to the maximum principal tensile stress. In addition, the appearance of surfaces where crazing followed suggested that crazing interference had taken place stopping not only the nucleation of new crazes but also slowing down and even stopping the growth of established crazes.

Craze Growth

Figures 9a, b, and 10 show examples of craze length as a function of time in commercial PS and PMMA at 253K and 253K. In a large number of other similar measurements only constant rates of craze growth were observed under a constant stress as long as the craze remained intact and as long as crazes did not interfere. All cases of observed craze deceleration were attributable to craze interference on surfaces that had reached craze densities near saturation levels. In Figure 11 the results of all of these measurements of terminal craze velocity for both 253K and 253K are plotted against the 5/6th power of the ratio of the applied tensile stress to the athermal tensile flow stress y at the respective temperatures. The straight lines represent the least square fits to the experimental data. Note that Figure 11 contains also the data from DOW PS data in a large selection of different multi-axial stress states showing that in this case the maximum model principal tensile stress governs the craze growth rate.

DISCUSSION

Craze Initiation

The theory on craze initiation presented earlier requires knowledge of the considerable amount of molecular and microstructural information on the structural parameters of plastic hole growth when a deviatoric stress is present, that appears in equation (7) and sec, the actual magnitude of the pre-exponential factor A0 in equation (6) and sec, and the total integrated surface density of craze nuclei in equation (11). The best-fit parameters have not been fixed ab initio. Instead, their best-fit values have been determined by systematically fitting the theory to the experimental results. The magnitude and orientation parameters have been compared with expected ranges of values and were all found to be quite satisfactory. Thus, however, makes the theory somewhat less than fully predictive, but gives an invaluable mechanistic insight into crazing and suggests methods by which the crazing process can be affected. Below we discuss how the values of the remaining parameters can be determined by a systematic procedure. A more detailed discussion of this procedure can be found elsewhere [44,46].

The knee in the N vs t curves given in Figures 7 and 8 are convenient references. The pairs of N, t values at the knee were plotted on log-lag coordinates for the deviatoric stress s = 17.92 MPa at the three negative pressures of 2.07, 4.14, 6.21 MPa, respectively. Since the local deviatoric stress is constant for a given craze density (given by k), given global negative pressure of grooves, given global deviatoric stress, and given negative pressure, any change in the logarithm of the crazing time at constant N and changes g directly the coefficient Q which was found to be 0.0113 in global s gives directly the coefficient Q which was found to be 0.0113 and 0.945/s(1/2) indicating that in the yielded material at the tips of surface grooves the "effective" plastic resistance to hole growth had dropped down to 1.3% of its value in the absence of a local deviatoric stress.

The craze density N depends only on the aspect ratios k of the grooves from which crazes nucleate. Considering that the pore initiation time t is given in equation (8) usually makes up most of the craze initiation time, as long as the negative pressure is not too small, an initial evaluation of pressure, any change in the logarithm of the crazing time at constant N and changes $g$ directly the coefficient $Q$ which was found to be 0.0113 and 0.945/s(1/2) indicating that in the yielded material at the tips of surface grooves the "effective" plastic resistance to hole growth had dropped down to 1.3% of its value in the absence of a local deviatoric stress.

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Thus, the correct choice of $\frac{N}{(1/2)} \frac{dN}{dk}$ should give a linear plot between k and the function under the square root sign of equation (20). Such a choice is 1.255, with the use of which $k$ and $g$ can be obtained from the intercept and slope of this line. This and $g$ of 0.958, $10^5$ cm$^{-2}$, $k = 1.35$, and $g = 0.259$. The theoretical fit is completed by
obtaining the actual saturation levels of craze density where craze interference takes place. This is readily achieved by using in equations (12a, b) the measured craze growth rate for 293°C for the DOW 686 PS given in Figure 11, for which the best fit of the form of equation (17) is

$$\frac{da}{dt} = \frac{4.192 \times 10^{-11}}{(E + n)n} \exp \left[ \frac{30(E + n)n}{58} \right] \text{cm/sec.}$$  \hspace{1cm} (21)

The final levels of craze saturation shown in Figures 7a, b, c are obtained for a value $f = 10^{-4}$ in equation (12b), which is far shorter than full coverage of the surface with cracks. This is partly the reason for such a low level for $f$ may lie in a missed scale factor in the measurement of velocity of equation (21). On the other hand, actual observations confirmed that in all cases nucleation of new craze sites ceases far sooner than craze growth does, indicating that after the most severe grooves have been used up in craze production the times of nucleation of new crazes from lesser grooves are significantly increased by small reductions of local stress from crazes growing in the vicinity.

Using the values for the factors of $k_n (\varphi_0 \exp(-aV/YK_T))$, $N_0$, $f$, $q$, $Q$ and $f$ that we established by fitting the theory to the data at 293°C, and the experimental craze growth rate information in Figure 11 for DOW 686 PS, the $N$ vs. $t$ curves for 293°C can now be calculated. To obtain the fit shown in Figures 8a, b, c it was found necessary to shift these curves along the time axis by a constant amount which finally fixes $aV$ at $3.983 \times 10^{-29}$ cm$^2$ and $\varphi_0 = 4.645 \times 10^{-11}$ sec$^{-1}$. If $f$ is the product of the average hole relaxation strain after a microcrack is formed, and the ratio of the hole to the heterogeneity spacing, is taken as 0.1, then the size of the hole and hence the heterogeneity spacing is found to be of order $1.6 \times 10^{-7}$ cm. Then the magnitude of the frequency factor, $\varphi_0$, is expected to be related to the molecular segment frequency of $\sim 10^{12}$ sec$^{-1}$ by the ratio of $\varphi/\lambda$. It is also found to have the appropriate magnitude.

Comparison of the theoretical curves with the experimental data in Figures 7 and 8 shows that although there is no systematic deviation there are considerable departures from what could be considered a good fit. These departures result from: unavoidable eccentricities in the specimens, unavoidable low level spurious coupling between the tension and torsion devices, a below-than-normal distribution in the grooves with large stress concentration and random variation of the actual distance of the specimen from the overall average. In spite of these random departures in the fit between the experimental results and the theory, the latter reproduces all the features of the experiments to a very satisfactory level.

**Bi-axial Crazing Initiation Locus**

It is of interest to present the craze initiation theory and the experimental results of the craze initiation locus in the bi-axial principal stress plane of $\sigma_1/\gamma$ and $\sigma_2/\gamma$ (or in the $E, n$ plane), as has been pioneered by Steinberg and co-workers [6-8]. Although such loci have been given many times [6-8, 9] the exact criteria of what is considered a craze-yield stress level has not been well defined. In our theory several different criteria are possible. A criterion which corresponds to a visually detectable level at a given time, such as e.g. the locus of stresses $S_1$, and the normality of $N = 10^{-12}$ cm$^{-2}$ at a time of $t = 10^6$ sec would come close to what has been initially used by Steinberg [6]. Such a bi-axial craze initiation locus can be obtained by equating the total craze nucleation time in equation (10) to $10^6$ sec, substituting $k = 1.76$
stress can only give craze growth rates that are many orders of magnitude lower than experimentally measured rates \[44\]. On the other hand, at high stress levels, near general yield, the hole nucleation mechanism would dominate the propagation of crazes, even though none of the reports appear to dominate the measured level of craze growth. The measurement of craze growth rates must be ruled out. The possibilities that remain are: a bi-axial residual compressive stress in the surface layers of the tension torsion specimens resulting from a thin surfacing layer of higher coefficient of expansion, or an unusual strain hardening behavior in the craze tip plastic zone of the DOW 686 PS at 255\(^\circ\)C. Aside of this unusual behavior of the DOW 686 PS, a comparison of the experimental values of A/T with the theoretical prediction shows that these are in a ratio of 0.72 for 253\(^\circ\)C and 0.52 for 253\(^\circ\)C for PMMA, while the ratio is 0.8 at 273\(^\circ\)C for PMMA.

The major part of this reduction of the experimental values of A/T must be related to the significant lowering of the shear modulus in a glassy polymer by a negative pressure. In PS, e.g., the ratios of the plastic shear in tension to the plastic shear resistance in compression is 0.71 \[48\], which is almost exactly the same magnitude as the ratio of the A/T values listed in the last row of Table I. Although no information order of the only relatively mild variations in plastic resistance is necessary. Although the exact nature of these variations is not clear in the flexible chain polymers, such as PS and PMMA, in distinction to the semi-flexible chain polymers, such as polyisomides \[47\], they must be a result of variations in molecular packing. Whatever their source, such inhomogeneities in plastic flow at a near molecular level have been observed to develop and form cavities in thin films \[25,26\] that lends support to our mechanism.

The development of a craze nucleus in the yielded material by the interaction of a critical volume fraction of holes at surface grooves where localized plastic flow has occurred has been modelled purely on the basis of continuum plasticity which should be applicable at this scale. This process in bulk material would be difficult to follow. Yet, the many detailed low angle x-ray diffraction measurements of Zhurkov and co-workers \[51,52\] on cavitation in stressed glassy polymers comes very close to a direct verification of this process.

At some stage after the craze nucleus has formed and has acquired a significant aspect ratio normal to the maximum principle tensile stress, it can grow by the faster mechanism of craze matter production involving hole nucleation with that of the meniscus instability. The comparison of the kinetics of craze growth by hole nucleation with that of the meniscus instability shows that the former has a much steeper stress dependence and at the usual levels of crazing...
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Table I Experimental and Theoretical Parameters for Craze Growth in PMMA and Two Types of PS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PMMA</th>
<th>PS</th>
<th>NOV 686 PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A’T) / [(1 / n)(a)</td>
<td>96.34</td>
<td>65.35</td>
<td>74.76</td>
</tr>
<tr>
<td>(A’T) / n[sec]</td>
<td>4.58x10^-16</td>
<td>7.73x10^-16</td>
<td>3.86x10^-15</td>
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<tr>
<td>(A’T) / n[sec]</td>
<td>47.90</td>
<td>46.92</td>
<td>44.72</td>
</tr>
<tr>
<td>[c] / [a]</td>
<td>2.313</td>
<td>1.983</td>
<td>1.853</td>
</tr>
<tr>
<td>R(a) / (a)</td>
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<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>X / [a]</td>
<td>1.75x10^-10</td>
<td>1.82x10^-10</td>
<td>3.02x10^-10</td>
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<tr>
<td>[c] / [a]</td>
<td>1.84x10^-13</td>
<td>0.93x10^-13</td>
<td>0.93x10^-13</td>
</tr>
<tr>
<td>D / A</td>
<td>6.76x10^-5</td>
<td>2.77x10^-5</td>
<td>2.77x10^-5</td>
</tr>
<tr>
<td>(A’T) / n[sec]</td>
<td>60.22</td>
<td>81.67</td>
<td>62.16</td>
</tr>
<tr>
<td>(A’T) / n[sec]</td>
<td>0.80</td>
<td>0.52</td>
<td>0.72</td>
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</table>
Figure 1  Formation of micro-cracks by arrest of micro-shear bands (from [33], courtesy of Butterworths).

Figure 2  Surface groove under the application of a bi-axial state of stress (from [33], courtesy of Butterworths).

Figure 3  Porous rigid plastic region about to undergo cavitation under the action of a negative pressure applied by stressed elastic surroundings (from [33], courtesy of Butterworths).

Figure 4  Locus of pore expansion under a combined negative pressure and deviatoric stress (after McClintock and Stowes [45]).
Figure 5 Schematic rendering of craze matter production by the mechanism of meniscus instability: a) outline of a craze tip, b) cross section in the craze plane across craze matter tufts, c), d) advance of the craze front by a completed period of interface convolution.

Figure 6 Craze as a planar yield zone; showing craze tip plastic zone, craze tip opening displacement and radius of curvature, and craze matter producing craze face traction.

Figure 7 Increase of craze nuclei with time in samples subjected to different combinations of global deviatoric stress and negative pressure at room temperature. Curves computed using equations (8), (11) and (12b).
Figure 8  Same as preceding figure except at 235°K.

Figure 9  Examples of non-interfering craze growth in commercial PS under two different levels of stress and at two different temperatures. Lines are best fits to the data.

Figure 10  Examples of non-interfering craze growth in commercial PMMA under one stress level at room temperature.
Figure 11 Dependence of normalized craze velocity on normalized maximum principle tensile stress at two temperatures for both commercial PS and DOW 686 PS (free of additives), and for commercial PMMA.

Figure 12 Density of potential craze producing surface sites on the DOW 686 PS specimens as a function of groove aspect ratio. Data points represent the saturation craze densities at room temperature given in Figure 7. The scale of the horizontal axis, as well as the best fitting normal distribution shown by the solid curve, have been obtained by a systematic fit discussed in the text.
Figure 13  Bi-axial craze locus representing normalized stresses $\eta$, and $\xi$ for a craze density of $10^5$ sites/cm$^2$ in 100 seconds, for the DOW 686 PS, at 293°K and 253°K. The other solid curve is computed for a hypothetical PS with higher surface perfection.