

Stress Crazing of Some Amorphous Thermoplastics

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INTRODUCTION

Crazing is a phenomenon of considerable interest among the thermomechanical properties of amorphous thermoplastics. As part of a study of this phenomenon, a detailed microscopic examination of the nature of crazing was undertaken. During this examination it became apparent that virtually all stress crazes formed by uniaxial tensile loading contain craze matter.¹ This fact, when considered with other results of this study, leads to the conclusion that the craze matter is most likely oriented polymer aligned in the direction of the applied tensile stress. We define the word craze to denote the individual seams or veins in a crazed specimen which are composed of craze matter.

This new evidence has prompted a thorough reconsideration of the experimental observations and tentative explanations reported in the past. The result is the formulation of a new hypothesis for the mechanism of craze formation. The hypothesis places its emphasis on totally different parameters than those usually considered.

The existence of connected matter within crazes which characterizes stress crazing of amorphous thermoplastics was somewhat speculatively predicted by Bessonov and Kuvshinskiĭ^{2,3} unknown to us until the present work was completed. Some features of the supposition of these authors are similar to those which will be discussed below. However, we intend to present evidence which will not only substantiate the existence of craze matter in stress crazes, but also will lend considerable credence to the new hypothesis which follows. It will be evident how the new hypothesis differs from the essence of previously held ideas and how it partakes, nevertheless, of some of their features.

The new mechanism is not supportable as yet with precise quantitative studies. This is due partly to the very small physical size of the crazes and to the statistical nature of the crazing phenomenon with its attendant wide distribution of data.

Other difficulties are those of regulating the large number of variables contributing to the phenomenon, i.e., resin characteristics, resin and specimen preparation, specimen treatments, and testing conditions. However, the proposed mechanism does find substantial corroboration in its ability to explain and unify many old and new observed facts. These include the actions of the major variables of stress, time, and temperature. The physical appearance of crazing and its growth kinetics, together with experiments on the strength and coherence of crazes, are presented and related to the new mechanism. The amorphous thermoplastics studied by us were polystyrene, poly(methyl methacrylate) and poly(bisphenol-A carbonate), hereafter referred to as polycarbonate. The word stress is to be used in the sense of a tension which creates a positive strain in the direction of application.

EXPERIMENTAL

The data presented in reference to Figures 1 to 8 were obtained from compression- and injection-molded tensile bars measuring $5 \times \frac{1}{2} \times \frac{1}{8}$ in. Samples other than the standard test bars were also studied and will be individually described in the text. Little if any difference in the structure of craze matter could be directly attributed to molding conditions or specimen type.

The test bars were subjected to uniaxial tensile loads at 25°C. for polystyrene and poly(methyl methacrylate), and at 100°C. for polycarbonate. It was found that stresses of 2000-3000 psi, applied over very long periods of time, favored the formation of large crazes in polycarbonate and polystyrene, whereas, higher stresses were required for poly(methyl methacrylate). These large crazes, which penetrated deep into the body of the test bars, facilitated the examination of the crazes by optical and electron microscopy. The crazes always develop in a plane normal to the applied

stress. The convention of indicating the tensile stress as being applied in a horizontal direction will be adopted in this paper, except when otherwise stated.

Surfaces of Crazed Specimens

Figure 1 is an optical micrograph of the surface of a compression-molded test bar of polycarbonate which was loaded for several months at 2850 psi. This unusually large craze developed two voids, as seen in the upper region of the craze, which was confirmed by focusing into the crevice. Some of the debris reported by Bessonov and Kuvshinski³ was found and can be seen as an out-of-focus reflection in the larger of the two voids. However, the lower half of the surface of the craze contained solid matter which at first was thought to be a skin formed during the molding operation. The dashed lines indicate the boundaries of the craze when viewed by transmitted light. To our surprise, only an extremely small number of the hundreds of crazes in the bar contained voids, and then only in the largest crazes.

Figure 2 is an electron micrograph of a negative replica of the surface of the same specimen, but different area, shown in Figure 1. Since this is a negative replica, the surface of the crazes are actually depressed regions, a fact which was



Fig. 1. Optical micrograph of a partially broken craze on the surface of a polycarbonate tensile test bar.



Fig. 2. Electron micrograph of a negative replica showing a small narrow craze and a portion of a wide craze. Same sample as Figure 1.

expected by the previous optical examination. The end of a very large craze appears in the lower left corner of the micrograph, and immediately to the right is shown a very small craze which is only 0.001 in. long; on the far right is the central region of a well developed craze.

Before continuing, it would be desirable to define several terms in order to identify some of the surfaces to which reference will be made. Figure 3, then, indicates what is meant by the crazed surface of the bar, the surface of crazes, the walls of ruptured crazes, and the cross section of crazes. The latter is of greatest interest, since a cross-sectional view of crazes will reveal not only the depth to which crazes extend, but also whether or not the craze matter extends throughout the entire depth of the craze.

Cross Section of Crazes

Figure 4 is an electron micrograph of the surface of a cross section of a craze in polycarbonate. The section was obtained by impact fracturing of a small strip of the tensile bar, such as sketched in Figure 3, which had been precooled to the temperature of liquid nitrogen. These conditions help minimize orientation effects which might otherwise occur under a more favorable thermal environ-

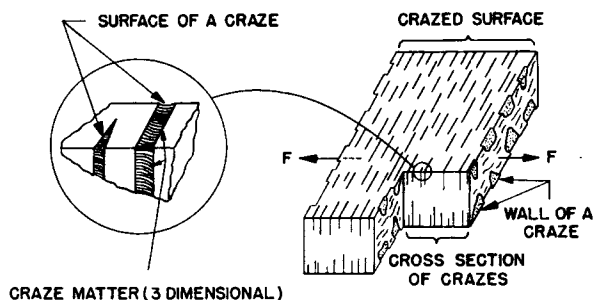


Fig. 3. Pictorial definition of terms.

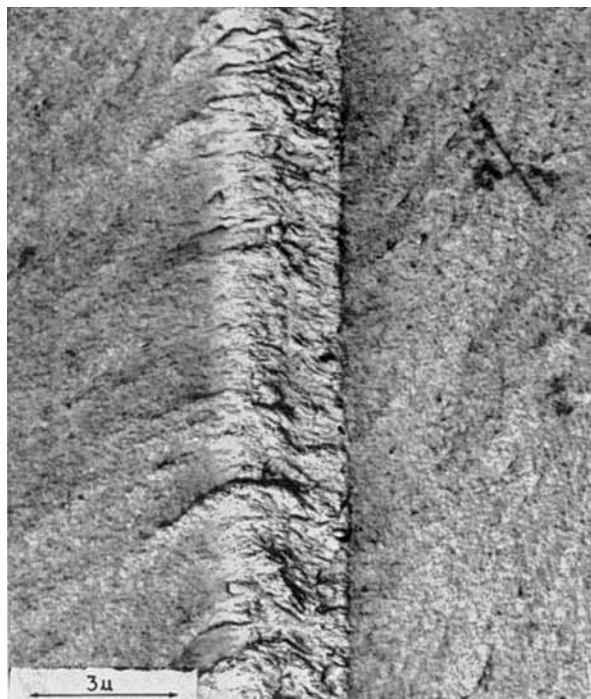


Fig. 4. Impact-fractured polycarbonate. Electron micrograph of the cross section of a craze.

ment. We noticed no essential difference in the appearance of the section whether the fracture originated from the surface of the strip or from the side. It happens that the fracture depicted in Figure 4 originated from the side, resulting in the formation of a small shoulder on the side of the craze. The orientation inside the craze is aligned in the direction of the stress which induced the craze and occurs in most cross sections of crazes regardless of the direction in which fracture occurs.

Similar results were obtained for poly(methyl methacrylate) and polystyrene, as demonstrated by Figures 5 and 6, respectively. However, it was difficult to study the crazes in the latter two resins because of the narrow widths of the crazes which rarely were greater than 1μ . For this

reason and because the crazes often were constricted or vanishingly thin at the specimen surface, it was virtually impossible to define crazes on a specimen surface with assurance by electron microscopy. Nevertheless, electron micrographs were obtained of the cross section of crazes from fractured surfaces of these resins. Several criteria were established in order to assure that artifacts and scratches were not erroneously identified as crazes. First, the replica was shadowed in a specific direction with respect to the crazes, so that crazes could be correctly oriented with respect to the shadow direction in the electron microscope. Then, the suspected craze was followed for a minimum of 500μ ; any deviation from the unique linearity and regularity in the width of a craze was sufficient to reject this craze from consideration. In addition, after examining hundreds of different crazes, it became apparent that a craze could be identified on sight. However, no compromise of the aforementioned criteria was made.

Examination of similar cross sections with an optical microscope at high magnification with oblique illumination likewise reveals the presence of solid matter in the crazes. Unfortunately, this effect is difficult to display in photographs and is not illustrated, particularly since electron micrographs such as Figures 4, 5, and 6 reveal the structure in more detail.

Both the electron micrographs and examination by optical microscopy reveal the extraordinary regularity of the crazes in width and path as they penetrate up to distances exceeding half the thickness of the specimen for polycarbonate and perhaps somewhat less for the other two resins. The depth-to-width ratio is very large, since the width of polycarbonate crazes ranges from 1 to 10μ and those in poly(methyl methacrylate) and polystyrene are considerably narrower. The cross sections also reveal that craze matter exists throughout the entire depth and breadth of most craze crevices formed under the conditions described earlier. Moreover, the electron micrographs indicate that some craze matter orientation exists along the direction of the applied stress in all these resins.

Fractured Walls of Crazes

Very little is known about the orientation in crazes from the evidence presented so far. It is possible to argue that the orientation suggested in electron micrographs of cross sections could be an artifact introduced during the fracture of the sample, even though the orientation is always in

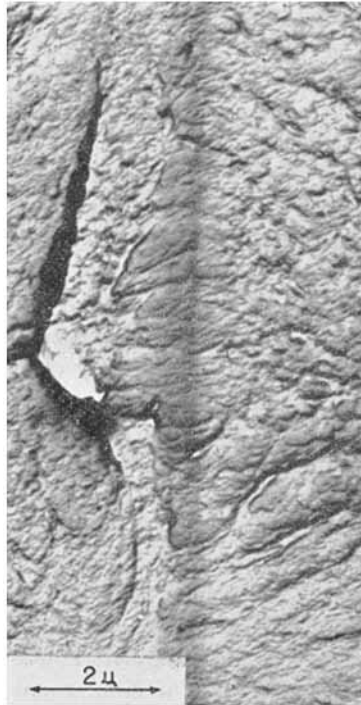


Fig. 5. Impact-fractured poly(methyl methacrylate). Electron micrograph of the cross section of a craze.



Fig. 6. Impact-fractured polystyrene. Electron micrograph of the cross section of a craze.

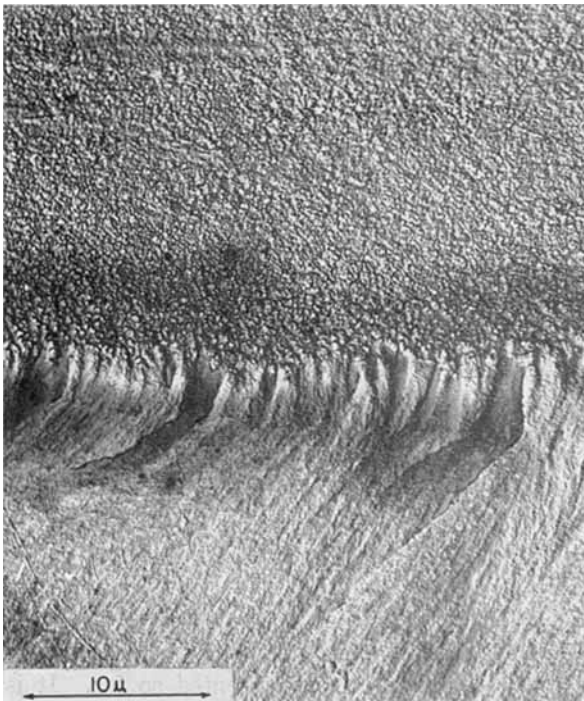


Fig. 7. Tensile test bar of polycarbonate impact-fractured so as to reveal the wall of a craze: (upper region) fractured surface of craze matter; (lower region) fractured uncrazed matter.

the same direction regardless of the direction of impact. For this reason we examined the walls of crazes. This surface was obtained by impact fracturing the bar from above which obviously favors this sort of break (see Fig. 3). Figure 7 is an example of a typical transition region between the walls of a craze in the upper part of the micrograph, and uncrazed material in the lower portion. The difference in appearance of the two regions is significant and is interpreted as follows. The walls of the craze are more irregular as compared to those of uncrazed regions. We feel that the bumps may have been regions or bundles of oriented molecules. When the bundles are impact-fractured, the energy imparted to the bundles at the instant of failure is transformed partly into heat, thereby melting the ends of the ruptured bundles so as to form the bumps shown in Figure 7. The lower portion, on the other hand, which had essentially no oriented regions, broke far more smoothly. The clifflike transition which joins these two areas also suggests orientation of craze matter, since in this micrograph the applied stress is perpendicular to the surface.

Microtomed Cross Sections of Crazes

Microtomed sections of polycarbonate crazes were prepared. These sections correspond to the surface replica of Figure 4, except that microtomed sections are capable of revealing details within the resin which can never be determined from surface replicas alone. A L.K.B. Ultratome microtome, fitted with a Rawlyer diamond knife was used.

craze matter (Fig. 8c). It is difficult to conceive of this fine structure as being an artifact, since it almost invariably exists within craze matter and is found in varying degrees wherever there is craze matter.

Microdiffraction of Craze Matter

An attempt was made to obtain selected area electron diffraction patterns of craze matter in micro-

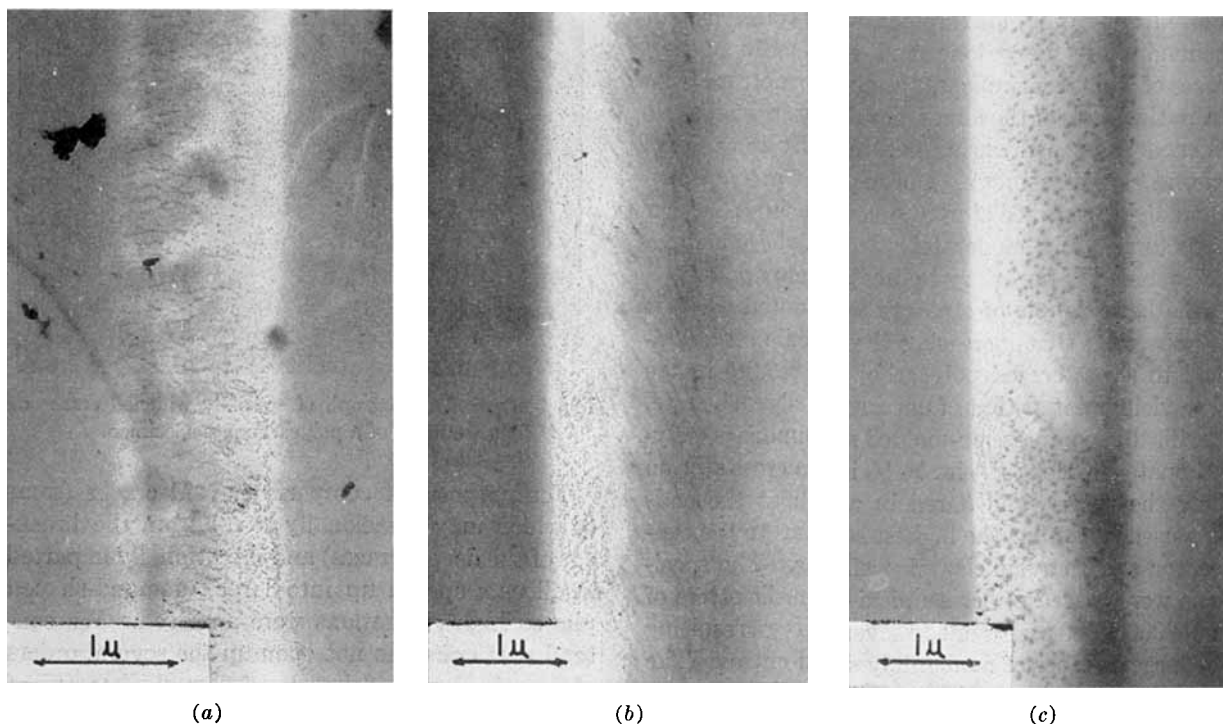


Fig. 8. Electron micrographs of microtomed cross sections of polycarbonate crazes: (a) section cut along length of craze; (b) and (c) sections cut oblique to cross section of craze. (Courtesy of Mrs. P. Holbert, Rutgers University Microbiology Laboratory).

Figure 8a is a section about 200 Å. thick, which essentially proves the continuity of craze matter in crazes. The section was cut perpendicular to the craze and reveals some fine structure in the form of tiny particles about 500 Å. in diameter which are connected to each other and appear to be oriented in the direction of the imposed stress. It was found, however, that the direction of alignment of fine structure is dependent upon the direction in which the section is cut. For instance, a section was cut obliquely at an angle of about 60° to the long direction of craze shown in Figure 8b, and close examination reveals that the fine structure is more or less aligned along the direction of cut. In still other sections, the fine particles are disconnected and are more or less randomly scattered throughout the

microtomed sections, but results were inconclusive, partly due to the small size of the crazes and to the unknown amount of orientation imparted to the samples by microtoming. However, x-ray micro-diffraction of highly crazed regions adjacent to unusually large inhomogeneities in compression molded polycarbonate films produced oriented diffraction patterns which established the occurrence of orientation in the direction of the imposed stress. It can not be established that the orientation in our patterns was due solely to craze matter, since a number of small crazes together with adjoining, uncrazed matter contributed to the overall diffraction patterns produced by a 50-μ beam. However, non-crazed regions immediately adjacent to highly crazed areas showed no evidence of orientation.

Strength of Stress-Crazed Thermoplastics

It is well known that most plastic specimens when stress crazed suffer loss of strength, particularly under flexural or multiaxial loading conditions. However, it is noted occasionally that crazed specimens can continue to exhibit unexpected strengths in long term dead-loading tests. For instance, compression-molded films of polystyrene about 10 mils thick and 2 in. wide were uniaxially loaded to a tension of 1000–2000 psi at 25°C. for three months. Soon after loading, crazing became extensive with predominantly very long and extremely narrow crazes of which a significant number penetrated the entire thickness of the film. Yet the crazes were not widened or opened during additionally long times nor did the films break. Subsequent attempts to manually widen or distort the crazes showed them individually to be moderately strong, there being a noticeable force necessary to break them apart.

Another example of strength was noted when it was observed that increasing the tensile stress applied to stress crazed polycarbonate results in the same yield point as that of uncrazed polycarbonate. Specifically, compression-molded specimens of polycarbonate 8 in. long, $\frac{1}{2}$ in. \times $\frac{1}{8}$ in. in cross section along the center, and flared in width at the ends were used to confine the highest stresses to the center area and to avoid clamping effects. The specimens were crazed under a uniaxial tensile stress of from 2000–4000 psi for one to several days, resulting in a large number of moderately sized crazes. The stress then was increased on individual specimens to about 6000 psi without the occurrence of an anticipated catastrophic fracture. Instead, the tensile stress reached the conventional yield stress of uncrazed specimens.

Effect of High Elongations on Crazed Polycarbonate

The polycarbonate specimens described in the preceding section yielded to the increased stress by the formation of a neck, the shoulders of which traveled with moderate speed toward the ends of the specimen. In this way, permanent elongations of about 100% could be imparted to the crazed specimens.

The striking feature revealed by this technique is that the original crazes are carried through and survive this necking process virtually unchanged in size or shape. The only apparent change is that the microscopic separation between specific neighboring crazes in the direction of the elongation is in direct proportion to the macroscopic elongation of the specimen.

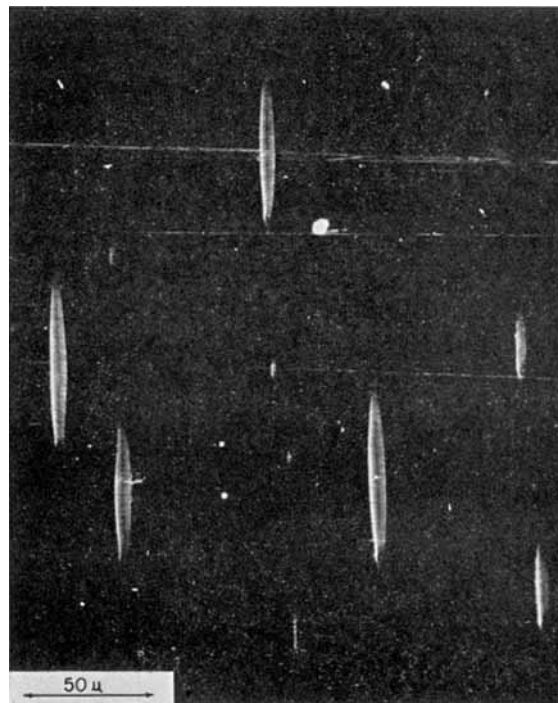


Fig. 9. Optical micrograph of specially widened crazes on the surface of a polycarbonate specimen.

For purposes of comparison, void cracks (some of which may occasionally result from the breakage of the deeper crazes) and intentionally imparted small cuts opened up into large, diamond-shaped pits as high elongations were achieved. We contend that crazes do not open up the several orders of magnitude in width noted for cracks because of their nonvoid and load-bearing character.

Later in our investigation, a somewhat different high elongation of similar polycarbonate specimens was obtained. The specimens were placed under a tensile stress of about 2500 psi at 135–140°C. They crazed quickly and after about 10 min. very gradually elongated approximately 100% in a uniform manner, i.e., without formation of a neck. It was discovered that the crazes again survived the elongation without breaking, but in this case, a number of original crazes had been considerably widened. This is illustrated in Figure 9, from which it should be noted that the wide crazes are not void. Electron micrographs of replicas of the surface of a similar specimen show that the crazes are widened about 165% more than the elongation of the surrounding uncrazed resin. This was deduced from the craze widths and the offset of original oblique surface scratches and markings. Hence, under the special conditions noted, the craze matter on the specimen surface is extended by a factor of

about 3.6. Crazes were widened in polystyrene and poly(methyl methacrylate) by this same technique at 75–90°C.

Additional experiments on the unique necking elongation behavior of polycarbonate have been carried out in order to further study the mechanical continuity of craze matter. Larger surfaces of polycarbonate resin have been stress-crazed so that subsequently strips were cut with the crazes aligned parallel with the long axis of the individual strips. A strip then was elongated past the yield point at 100°C. These crazes were found to be stretched in the axial direction and the separation between the centers of the crazes increased in the axial direction in roughly the same ratio as the macroscopic elongation. In addition, very numerous short crazes were generated perpendicular to and along both sides of the original crazes. These subsidiary crazes perhaps are initiated from the parallel orientation in the craze matter of the original crazes.

The observations and remarks offered in this paper are predominantly confined to the phenomenon of crazing as induced by mechanically applied external stresses. However, this does not necessarily exclude environmental stress crazing from the applicability of the concepts developed here. Indeed, it is felt that environmental stress crazing is basically the same phenomenon. Specifically, crazing induced by specimens contracting a small amount of solvent while under a small bending or tensile stress is identical in appearance to purely stress induced crazing. The only difference may reside in the mechanical extensibility and strength of the matter within the crazes. If a specimen of polycarbonate at room temperature is slightly bent while benzene is lightly and quickly brushed across the surface, crazing occurs instantly. When this specimen is elongated 100% at 100°C. in a direction perpendicular to the crazes, these crazes open up into void pits. However, examination of the shoulder regions of the specimen, where transition from low to high deformation is occurring, shows the crazes first becoming wider by the microscopic extension of coherent craze matter and then by the irregular tearing of this matter. Thus, the structural occupancy of the crazes is directly observed.

Effect of Heat and Solvents on Crazed Thermoplastics

Stress-crazed specimens of polystyrene, poly(methyl methacrylate), and polycarbonate may be

returned to their uncrazed, optically homogeneous condition by heating above their respective softening temperatures. Newman and Wolock⁴ have reported this effect with poly(methyl methacrylate) heated up to 15 hr. at 150°C. We find that similarly dramatic results can be obtained by much briefer heating at temperatures just above the softening temperatures. Crazes in polycarbonate resin, for instance, disappear in one to a few minutes after being placed in an oven at 160°C. No excessive softening or distortion of the resin is noted in this duration of time. The crazes are no longer evident to the eye, and only faint outlines of them at the specimen surface are seen with a microscope. Similar healing of crazes in polystyrene or poly(methyl methacrylate) may be accomplished by placing the crazed specimens in an oven at 100°C. for about 5 min. In these resins the crazes may still be very faintly visible to the eye.

This heat-healing effect is attributable to the presence of an oriented craze matter in the crazes. Heating to the softening point triggers a well known contraction phenomenon in oriented amorphous thermoplastics. The healing mechanism, therefore, may involve the reversion of the craze matter back to a nearly random state. The continued faint visibility of the craze outlines probably is due to some molecular scission and distortion in the craze matter, such that it cannot attain completely its original uncrazed state. Incidentally, the brief heating treatments quickly reveal void cracks, since these remain quite visible.

Again, applying a uniaxial tensile stress to heat healed specimens does not cause an immediate reappearance of the crazes. Figure 10 illustrates this observation in a compression molded, carefully annealed specimen of polystyrene. The specimen was crazed with a stress of 1500 psi at 25°C. The crazes in a selected area are shown in Figure 10*a* (inclined 10° to the microscope stage) as they appeared after 100 hr. under tension. The crazes then were healed, as indicated in Figure 10*b*, by the specimen being placed in an oven at 100°C. for 5 min. The specimen was loaded again to 1500 psi, and the crazes in the selected area were photographed after 3 hr. and 90 hr. as displayed in Figures 10*c* and 10*d*, respectively. It is seen that the original crazes do not immediately reappear, but again are formed by a slow decelerating growth rate. Indeed, the heat-healed specimen may be somewhat less susceptible to crazing than was originally the case since a few of

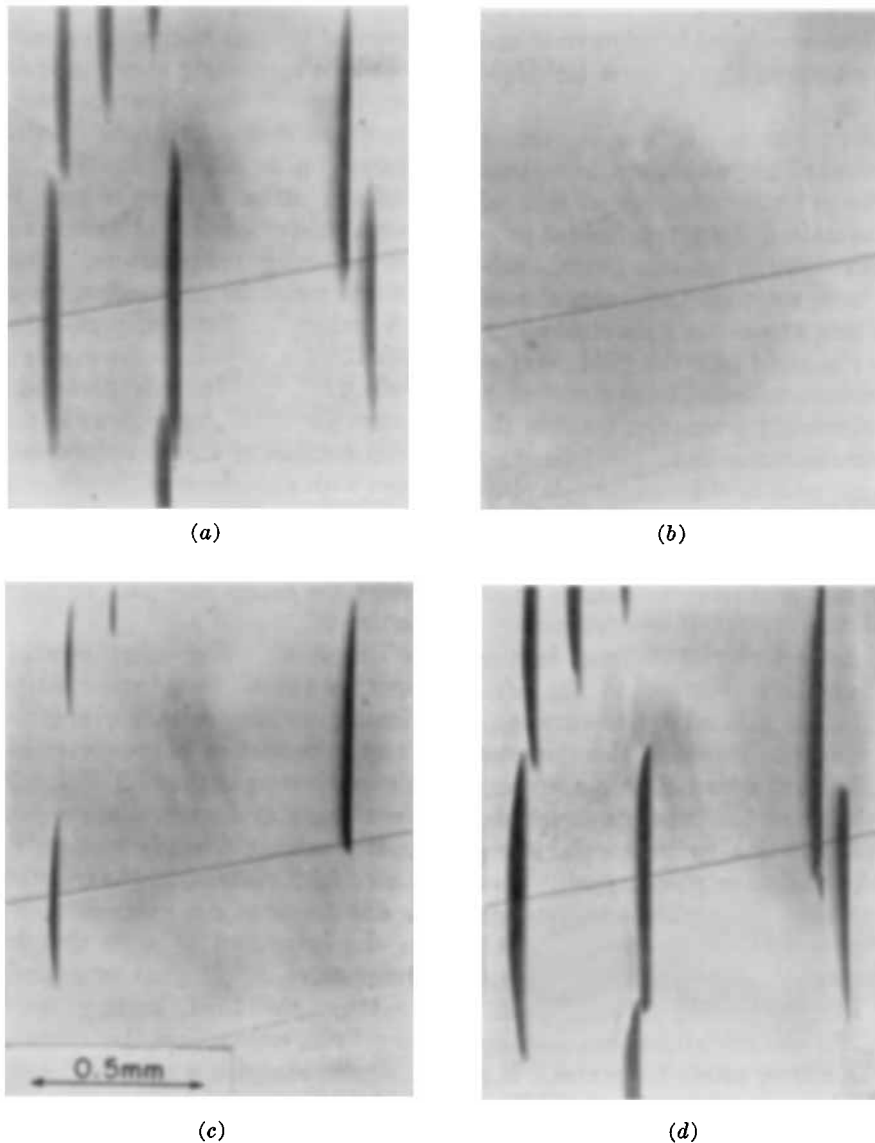


Fig. 10. Optical micrographs taken 10° off normal to the surface of a polystyrene specimen: (a) crazes formed after 100 hr. at 1500 psi and 25°C .; (b) crazes healed by heating at 100°C . for 5 min.; (c) crazes reformed after 3 hr. at 1500 psi and 25°C .; (d) crazes reformed after 90 hr. at 1500 psi and 25°C .

the original crazes do not reappear at all during the second stress application (not shown).

It is interesting to note the effect of heat healing previously stress-crazed and 100% neck-elongated specimens of polycarbonate. As before, the crazes disappear and do so slightly preceding or concurrent with the macroscopic recovery of the elongation. Thus, the reversion of the craze matter is akin to the contraction of the orientation in the bulk specimen. Specially widened crazes, as shown in Figure 9, do not completely heal on heating, suggesting that the craze matter in

these cases is elongated past the maximum recoverable extension.

Solvents, in addition to inducing crazing if the specimen is under a slight tension, can heal crazes. Exposing specimens of normally stress-crazed poly(methyl methacrylate), polystyrene, or polycarbonate to an atmosphere of chloroform vapor at room temperature will produce the same apparent results as heating. That is, the crazes disappear, leaving only macroscopic outlines behind, on or near the specimen surfaces. The action is not always as rapid or as complete as

heat healing. In the case of solvent healing, closure of the top portions of the crazes (through craze matter contraction and surface swelling) may impede the penetration of solvent to the lower portions of the crazes. The mechanism is, as before, suggested to be the retraction of the oriented craze matter through the ability of the dissolved solvent to lower the softening point below room temperature. Furthermore, if the solvent-healed specimen is aged for several days which allows for loss of dissolved solvent, the specimen will slowly craze again when the tension is reapplied.

The action of solvent vapor on a highly elongated stress crazed specimen of polycarbonate is somewhat different. In this case the crazes widen gradually and then split apart into open pits. It seems that a combination of the softening of the craze matter by preferential absorption of the solvent and the contraction of the surrounding elongated normal resin stretches the craze matter, widens it, and eventually breaks it.

Special Networks of Crazes

Networks of mutually perpendicular crazes may be created by alternately stressing a square plaque in one direction and then a perpendicular direction. Such networks have been produced in compression-molded specimens of polystyrene, poly(methyl methacrylate), and polycarbonate by uniaxial and flexural loading. Figure 11 is a drawing which represents the formation of such a network as viewed on the specimen surface. (The width of individual crazes as represented by the

width of the lines is exaggerated for purposes of illustration.) The vertical lines indicate crazes which were formed during the first tensing and remain virtually unchanged upon subsequent perpendicular tensing. The horizontal lines indicate crazes which were formed during this subsequent perpendicular tensing and are shown in earlier and later stages of growth in Figures 11a and 11b, respectively. The terms vertical and horizontal will be used in this context hereafter in this section.

If, as in Figure 11a, the horizontal set of crazes is not allowed to develop beyond moderate lengths, examination of the surface craze pattern reveals the initiation and growth sites of the horizontal set of crazes. Some of them originate from sites completely unrelated to the vertical set of crazes. This indicates that some potential craze sites are directionally sensitive, i.e., not generating crazes when tensed in the first direction, but doing so when tensed in the second direction. Many of the horizontal crazes do, however, originate from vertical crazes, growing outward from both sides of vertical crazes and thereby forming crosses on the specimen surface. Some cross origins contain visible specks of dirt, etc., while most of them do not contain obvious microscopic inhomogeneities.

The fact that the horizontal crazes lie in undeviating paths from one side of the vertical crazes to the other is evidence for the existence of non-void crazes. The craze matter, which may act as initiators for perpendicular crazes, mechanically connects the two opposite walls such that horizontal

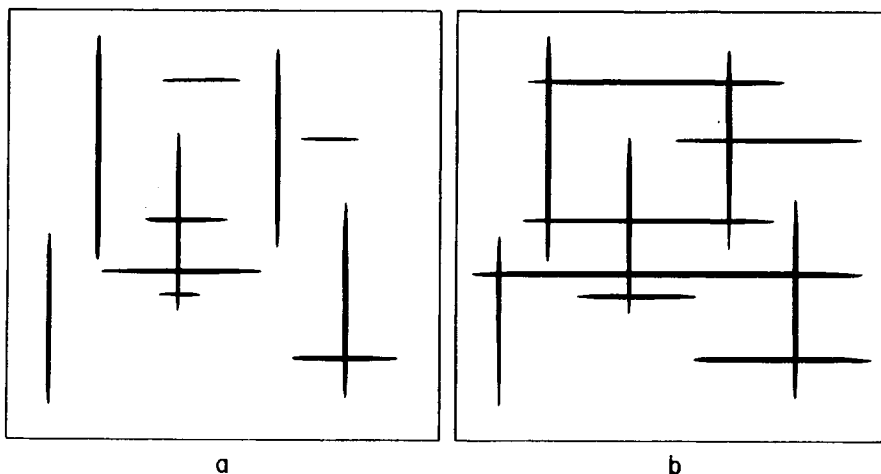


Fig. 11. Graphic representation of the development of a network on the surface of a specimen by perpendicular crazes

crazes generate outward from both walls. It should be noted also that some vertical crazes initiate several horizontal crazes along their lengths.

Of greater interest is the effect of producing a right angle network of crazes by tensing to produce longer crazes as illustrated in Figure 11b. These longer crazes not only cross at sites of initiation, but also intersect as they grow horizontally towards neighboring vertical crazes. In inorganic glasses and other brittle substances intersection of two surface cracks almost invariably results in the termination of one of them. Significantly, in the above noted amorphous thermoplastics, the horizontal crazes can continue to propagate through the intersections. This fact is evidence of the material structure of crazes, in that the craze matter mechanically links the craze walls so that the intersecting crazes may propagate through.

It is possible that actual void cracks will intersect and cross each other if the growing crack is significantly deeper than the crack it is meeting. It was necessary to eliminate this as an explanation for the crossing of crazes, since they do often propagate faster in the interior of the specimen than on the specimen surface. However, microscopic examination revealed several instances where individual horizontal crazes crossed several vertical crazes at depths distinctly shallower than the penetration of the vertical crazes. This is not universally the case because most often the horizontal crazes, even if generally shallower than vertical crazes, are susceptible to an equal or greater penetration at the intersection. This latter observation may be a consequence of the oriented nature of the craze matter.

Kinetics of Craze Growth

A number of specimens of polystyrene, poly(methyl methacrylate), and polycarbonate were uniaxially tensile stressed at appropriate temperatures to induce stress crazing. The specimen surfaces were concurrently photographed through a telemicroscope with a resultant magnification of 4X. From the photographs taken at 1 min. intervals initially and at progressively less frequent intervals, the lengthwise growth rate of individual crazes could be reconstructed.

Typical data are plotted in Figure 12. Each symbol represents an individual craze on the specimen surface and the curve represents an average length of the crazes chosen. The different craze lengths at each time suggest the distribution of lengths present. An exhaustive appraisal of

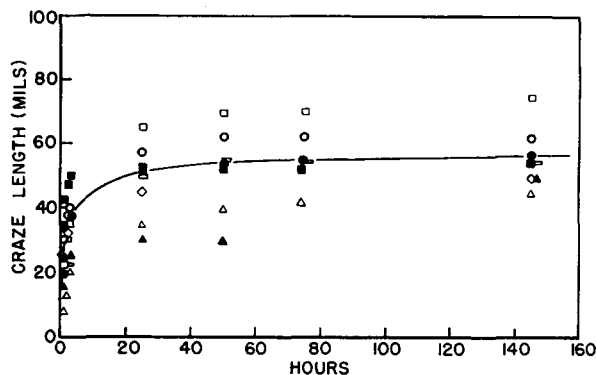


Fig. 12. Lengthwise growth of crazes on the surface of a polystyrene specimen at 1600 psi and 50°C.

every craze in the selected area gives essentially similar results. In every case, rapid initial growth rates are observed which, after comparatively short times, diminish towards very low rates such that it might be said the lengthwise propagation has virtually terminated. The number or density of crazes created usually remains very nearly constant once propagation starts. However, the duration of time over which new crazes appear may be longer at lower stresses and temperatures. Hence, the magnitude of the quantities involved may vary considerably depending on the nature of the resin, the prior history of the specimen, the tensile stress, and the temperature. For instance, with increasing temperatures up to the softening point, other conditions being the same, the number of crazes and their growth rates are increased. Similarly, higher tensile stresses produce greater numbers of crazes with faster initial growth rates. However, the higher stresses tend to terminate the lengthwise growth sooner and therefore at shorter lengths. Conversely, at lower stresses above some minimum critical value, the crazes ultimately grow to significantly longer dimensions.

Although these results specifically apply to the lengthwise craze growth, they likely are applicable also to the depthwise craze growth. The dimensions in the two directions often are dissimilar but yet may increase in approximate proportion to one another. This is difficult to establish rigorously since the progression of individual crazes inward may fluctuate along their edges producing irregular shaped profiles. Other resins may form long shallow crazes, while still another may form almost perfect semicircles.

The kinetic results stated above are general for the behavior of the resins reported here. They tend to confirm the results of Regel,⁵ who has made

similar measurements with poly(methyl methacrylate).

An additional well known feature of stress crazing is that there is often an observable time lapse between the application of the tensile load and the first appearance of crazes. The unaided eye is deemed to be sufficiently critical for determining the presence of crazing. Electron micrographs failed to reveal crazes on the surface of a polycarbonate specimen which was stressed for 45 hrs. with a load slightly less than that needed for visible craze appearance within a comparatively short time. A similar conclusion is stated by Newman and Wolock⁴ for the crazing of poly(methyl methacrylate). Thus, the time lapse is probably not the time necessary for submicroscopic crazes to grow large enough to become visible. Craze growth starts, therefore, after an induction period similar to induction periods observed in other activated kinetic processes. In stress crazing the induction period may vary drastically, such that at higher stresses and temperatures crazing may seem to occur instantaneously, and at lower stresses and lower temperatures crazing may not commence for hours or days.

DISCUSSION

The experimental evidence reported here leads to the conclusion that uniaxial tensile stress induced crazes are not cracks in the usual sense of open void cleavages. Rather, the crazes contain craze matter which exists as a structural and mechanical continuity between them and the surrounding polymer. The craze matter is undoubtedly created by a mechanism in which localized portions of the bulk polymer are converted into the distinguishable craze structure as the result of a local tension.

We hypothesize the following mechanism for the formation of stress induced crazes which is conveniently divided into three parts: initiation, propagation, and termination. The initiation step includes the conditions which determine the location of individual crazes and the events which occur during the induction period preceding the first appearance of the crazes. The propagation step comprises the details of the initially rapid and subsequent decelerating craze growth. The termination step represents the long-time behavior of the crazes wherein their growth has virtually ceased.

Briefly stated, the hypothesis for the mechanism is as follows. The individual crazes are

initiated at sites of inhomogeneities, both macroscopic and submicroscopic, which act as points of weakness or stress concentrators when an external tension is applied. The induction period, however short or long, represents the time necessary for an energetic buildup and for molecular movements at sites under the influence of the tensile stress field. The craze starts to develop as molecular segments attain some critical predisposition to the direction of the tension. Propagation is maintained by the continued yield and flow of resin at the craze periphery. Stress relief in the craze and over-stressing in neighboring regions propagate the crazes in generally long dimensions perpendicular to the applied tension. However, the craze matter is proposed to be significantly oriented in the direction parallel with the applied tension. Termination, but yet continued strength, is achieved by strain-hardening of the craze matter, the dilution of the overstressing along enlarging craze peripheries, and the creep and distortion of the surrounding resin.

The Initiation Step

The probable factors dictating the craze site have been thoroughly noted by previous investigators.^{6,7} Experimental observations make it difficult and probably unnecessary to select one factor as dominant over others. Many of them may be operating simultaneously in the same specimen. Inhomogeneities and flaws most often are noted as craze site determiners. These include all sorts of impurities ranging from dust particles, gel, salts, and catalysts, to scratches, bubbles, voids, or other internal defects. Also, since many crazes show no association with a visible defect, even under microscopic examination, it must be concluded that submicroscopic defects have a critical effect as well. These may be the alignment of small groups of molecular chains perpendicular to an applied stress such that they are easily separated internally. This, in general, is the point of a domain theory presented by Hsiao and Sauer.⁸ In addition, on a molecular scale, because of statistical compositional fluctuations,⁷ there may be weak regions with a preponderance of chain ends or with a less than average density due to excess void space. Indeed, microvoids and weak regions could be created by the action of the applied stress itself. These defects, then, act as sites of mechanical weakness or, in another view, as stress concentrators.⁹

One of the earlier suggestions for the cause of crazing was the action of residual stresses or strains^{10,11} left during resin and specimen preparation. It is easily shown that when these residual tensile stresses are not annealed out, crazing is much enhanced. However, carefully annealed specimens will readily craze. Thus, residual stresses, although not initiators themselves, serve to increase the severity of defects in the resin specimens.

Another observation often made in the investigation of crazing is that there is an apparent critical strain^{6,12} associated with the phenomenon. However, the attainment of a critical strain (or stress) is perhaps necessary but not sufficient for crazing, since these critical values can be exceeded without crazing in conventional rapid tensile strength measurements. In other words, an induction period often is observed between application of load and first appearance of crazing. Thus, even with the existence of a craze site determining defect and with a significant macroscopic strain, time is often required for the craze to start propagating. The induction period has every aspect of an activation process in which time is required for the accumulation of a critical amount of energy in order to overcome an energy barrier. The molecular strains or rearrangements at the defect sites, associated with the energy changes are unclear; but one may suppose they involve the movement of polymer chains in the direction of the applied tensile stress, with an attendant segmental directional predisposition for that direction.

This is consistent with the fact that these localized deformations are occurring during the time of the most rapid macroscopic creep or stress relaxation. The fact that the number of crazes formed is greater as the stress and/or temperature is increased can be explained on the basis that less severe defects come into play under these conditions. The less severe defects, as well as more severe defects, are then able to concentrate the necessary energy to trigger the precursory movements of craze propagation. The duration of the induction period, likewise, depends on the applied tensile stress and temperature; the length of time being less as the stress and temperature is increased. This is consistent with the increased frequency of molecular movements in the direction of the applied tensile stress under these conditions. It should be noted that stress crazing does not occur above the softening temperature, so that the effect of increasing temperature referred to in this

paper must be confined to temperatures below the softening point. The elimination of crazing above the softening point is quite likely explained on the basis of the enhanced mobility of the resin and its inability to maintain any localized stress concentrations.

The localized resin movements of the initiation step and those to be proposed in the propagation step are analogous to the plastic deformation and molecular orientation believed to precede and to accompany the seemingly brittle fracture of some plastics.^{13,14} Of course these fractures, unlike crazing, are the actual cleavage of matter.

The Propagation Step

When proposing the second step of the mechanism, the propagation step, one must shift attention away from intramolecular strengths and chain breakage and think instead of intermolecular forces and chain slippage. No longer should one explain a physical break in the resin; instead one must explain the creation of craze matter. It is highly attractive and completely consistent with the evidence presented in the experimental section to propose that the craze matter is significantly oriented. This is proposed on the basis of: the indications in Figures 4 and 7, the x-ray micro diffraction patterns, the strong directional disposition of crazes perpendicular to the applied tensile stress, the uniaxial strength of crazed specimens, the ability of the crazes to withstand the gross elongation of the surrounding resin, the measurements on the specially widened crazes, and the ability of the crazes to be coherently healed rapidly by heat and solvent vapor.

Bessonov and Kuvshinskiĭ^{2,3} suppose the existence of a filamentary matter holding the craze walls together and arising from alteration of packets of aligned molecules naturally existing in the linear polymer prior to stressing. Earlier, it was suggested by Sauer, Marin, and Hsiao¹⁵ that stress crazing is associated with orientations generated in polystyrene specimens and initially might not be mechanical cracking. Similarly, it is proposed here that the formation of a craze is a special ductile flow, rapid creep, or localized yield of the polymer in the vicinity of a defect site. During the induction period the resin surrounding the defect has adjusted itself into a state favorable for its subsequent sudden and rapid oriented distortion. The ability of the resin to pass over into this second deformation mechanism likely depends critically on its general lubricity and

molecular weight profile. The newly created craze matter is detectable, undoubtedly through a change in refractive index from the surrounding resin and perhaps because of the presence of some light-scattering porosity.⁹

This proposed propagation mechanism has an analogy in the macroscopic behavior of some thermoplastics. It is observed in creep tests, particularly at higher stresses, that a specimen will support a load for a period of time with only a small elongation rate, and then suddenly will elongate rapidly to form an oriented section. The oriented section is found to be stable and strong over additionally long times of load application.

Another indication of the flow nature of craze matter propagation is revealed by the widening of crazes during the slow extension of specimens at temperatures just below the softening temperature. In these experiments, the conditions which favor enhanced resin deformation are directly seen to generate additional craze matter in the stressing direction. Indeed, the length-wise growth rate of crazes somewhat follows the logarithmic creep law, as Regel⁵ notes, further suggesting an association between crazing and resin deformation.

The fact that crazes are usually generated from or very near the surface of a specimen is consistent with this type of propagation. As is well known, the surface most likely contains the severest defects from contamination and mechanical damage as a result of molding, processing or handling operations. Perhaps of greater importance is the probability that the stressed surface has more freedom for resin deformation. However, internally initiated crazing is observed in injection molded specimens (which are believed to have a relatively craze resistant oriented surface layer) and in specimens containing particularly severe internal flaws.

Analysis of the craze shapes and growth kinetics would indicate that initial growth represents relief of the stress concentration or elimination of the mechanical weakness at the initiation site. This probably is accomplished by the rapid slippage and orientation of the surrounding polymer chains. Relief of the stress at the initiation site passes excess stress to the neighboring resin in a plane perpendicular to the applied tensile stress. This neighboring resin, in turn, is converted to the oriented craze matter. The craze outline then grows outward from the defect along the specimen surface and inward into the specimen. The

narrow craze width compared to its length and the nearly constant width along the length indicates the existence of craze matter with a property of strain hardening. This property is demonstrated in the ability of the crazes to tolerate the rapid necking elongation of polycarbonate resin described in the experimental section. The fact that the craze matter remains sharply visible after the surrounding resin has achieved a deformation of about 100% suggests that the craze matter has significantly higher orientation. Moreover, the craze matter must have a reasonably firm attachment to the surrounding resin along the craze walls. Although the crazes appear sharply defined when examined optically, the electron micrographs shown in Figures 4 and 7 depict a rootlike structure extending into the surrounding resin. This indicates that a continuity exists physically and mechanically through the craze walls.

After the initial rapid propagation rate, the subsequent slower growth of the craze lengthwise and depthwise is probably a result of the dilution of the original excess local stress over the increasing craze periphery. Its continued growth at an ever slower rate, no doubt, is attributable to the simultaneous bulk creep of the loaded specimen such that localized stress relaxation is discouraged. Also, if the craze tip is composed of mechanically unstable resin in the act of passing from normal to craze matter, a very small incremental stress would be sufficient to change it to craze matter. The penetration of the craze into surrounding resin by this rather low level effect then depends on the randomness or alignment of the surrounding resin. As this fluctuates, so does the path and shape of the craze periphery.

The Termination Step

After long stressing times, the craze growth virtually ceases and the specimen will continue to support the applied tensile load for additional long times. It is reasonable that the apparent termination step results from a multiple effect. That is, after long times any excess stress has been diluted to a negligible level over a large craze periphery and the incremental bulk creep of the specimen can no longer sustain significant craze propagation. Also, the resin surrounding the craze tips can gradually build up some oblique flow distortion. This is reported for poly(methyl methacrylate) by Newman and Wolock.⁴ We find that the resin surrounding the craze tips in polycarbonate is strongly birefringent after long

durations of load. It is perhaps this special exterior deformation plus the coherence and strength of the craze matter which leads to the termination.

In a sense, the factors responsible for termination are in competition with factors responsible for propagation. This is indicated by the fact that the ultimate craze size is frequently larger at the lower stress levels even though fewer crazes are formed. At these lower stress levels it seems as if the termination mechanism, perhaps because of reduced distortion in the surrounding resin, is less able to impede the formation of craze matter.

Of course, termination in another sense of the word may occur; that is, catastrophic failure or fracture. There are two situations which lead to this. First, the formation of a few truly void cleavages in a brittle manner may occasionally occur concurrently with the stress crazing. These cleavages are usually larger and distinctly associated with large specks of dirt, etc. They can continue to exist side by side with normal crazing probably because their tips are blunted by plastic deformation. It only takes one, however, to propagate via a modified notch effect to completely sever the specimen.

A second catastrophic failure situation may originate from the actual breakage of one or more of the crazes in a specimen. Such an instance is illustrated in Figure 1. The breakage seems to be most easily commenced at the specimen surface under the stresses induced by bending actions. Of course, craze matter also may break with time under uniaxial loads due to strength fluctuations inside of, and in the border of, the crazes. Indeed, Regel⁶ and Berry¹⁴ consider the crazes as nuclei for ultimate fractures and thus control the specimen's long term strength.

It should be emphasized, however, that the individual stress induced crazes are initiated and extensively propagated by means of a hypothesized ductile yielding of the resin on a minute localized scale. It is only after formation of this craze matter, with its special properties, that cleavage might occur forming the type of void cracks previously envisioned.

CONCLUSION

The direct microscopic evidence and concepts presented refer specifically to uniaxial tensile stress crazing of polystyrene, poly(methyl methacrylate), and polycarbonate. We feel that these findings and ideas are sufficiently fundamental to

apply generally to amorphous thermoplastics as a class. In addition, some of the mechanical experiments noted above indicate that the mechanism occurring in flexural stress crazing and solvent stress crazing is not dissimilar. However, we would like to propose that a rigorous distinction be made in the use of the terms stress crazing and stress cracking. We feel that the former should be restricted to the phenomenon covered in this paper and the latter should be applied to phenomena in which it is demonstrated that void cracks are formed, such as in some polyethylenes.

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Synopsis

Tensile stress-induced crazing in polystyrene, poly(methyl methacrylate), and polycarbonate has been carefully examined by optical and electron microscopy. Examination of the surface of crazed specimens and the cross sections of individual crazes leads to the conclusion that the crazes are not void cracks, but are filled with a craze matter. The craze matter is readily distinguishable from the surrounding resin and is seen to exist in continuity with it. Further experiments confirm the existence of the craze matter and tend to indicate its structural and mechanical properties. These experiments include: microscopic examination of the walls of fractured crazes, micro x-ray diffraction of craze matter, studies of the strength of crazed specimens under

static loads and under increasing tensions, studies of the effect of heat and solvent on crazed specimens, and observations on the ability of crazes to form special networks. The results indicate that the craze matter may be formed by localized resin deformation leading to a load bearing oriented structure. A hypothesis of the mechanism of craze formation is proposed in light of the new and varied information reported in the paper. Study of the kinetics of craze growth suggests the division of the mechanism into three parts: initiation, propagation, and termination. The initiation step describes the concentration of strain energy and the precursory molecular arrangements in the immediate vicinity of inhomogeneities. These are the changes which occur during the time lapse between stress application and first appearance of crazes. The propagation step comprises the sudden and relatively rapid localized resin deformation which creates the craze matter. The shapes of the growing crazes and their diminishing growth rates are attributable to known resin properties. The termination step represents the apparent cessation of craze growth with continued long times of stress application. At this stage in the existence of crazes the proposed hypothesis must blend into the theories of time delayed rupture. It is concluded that stress crazing is basically a molecular slippage rather than a molecular cleavage phenomenon. Considerations, therefore, are to be directed more towards intermolecular forces than intramolecular forces.

Résumé

Les forces de tension provoquant des craquelures dans le polystyrène, le polyméthacrylate de méthyle et le polycarbonate ont été soigneusement étudiées au microscope optique et électronique. L'examen de la surface des échantillons contenant des craquelures et les sections transversales des craquelures individuelles nous amène à conclure que les craquelures ne sont pas des espaces vides, mais sont remplies d'une matière craquelée. La matière craquelée se distingue facilement de la résine environnante et semble être en continuité avec elle. Des expériences ultérieures confirment l'existence d'une matière craquelée et tendent à montrer les propriétés structurales et mécaniques de celle-ci. Ces expériences comprennent: l'examen microscopique des parois des craquelures, la micro-diffraction aux rayons-X de la substance craquelée, des études de la résistance des spécimens craquelés sous l'action des charges statiques et sous des tensions croissantes, des études de résistance à la chaleur et aux solvants, et des observations sur l'aptitude de formation de réseaux spéciaux. Les résultats montrent que la matière craquelée peut être formée par une déformation locale de la résine produisant une tension qui provoque une structure orientée. D'après les informations nouvelles et variées décrites dans cet article une hypothèse sur le mécanisme de formation des craquelures a été proposée. Une étude de la cinétique de la croissance des craquelures suggère un mécanisme en trois étapes: initiation, propagation et terminaison. L'étape d'initiation décrit la concentration d'énergie de tension et les premiers arrangements moléculaires au voisinage immédiat des hétérogénéités. Ces changements ont lieu pendant un laps de temps se situant entre l'application d'une tension et la première apparition d'une craquelure. L'étape de propagation comprend la localisation soudaine et relativement rapide de la déformation de la

résine qui provoque les craquelures. L'étendue de l'accroissement des craquelures et les vitesses de formation décroissantes sont attribuables aux propriétés connues de la résine. L'étape de terminaison est représentée par la cessation apparente de la croissance des craquelures tout en appliquant une tension continue pendant une longue période. Les hypothèses proposées à ce stade de l'existence des craquelures doivent s'accorder avec les théories d'une rupture retardée dans le temps. On en déduit que la tension de craquelage est fondamentalement un phénomène de glissement moléculaire plus qu'un phénomène de clivage moléculaire. On doit donc considérer qu'il s'agit plutôt de forces intermoléculaires que de forces intramoléculaires.

Zusammenfassung

Eine sorgfältige Untersuchung der durch Zugspannung hervorgerufenen Rissbildung in Polystyrol Polymethylmethacrylat und Polycarbonat mittels optischer und Elektronenmikroskopie wurde durchgeführt. Überprüfung der Oberfläche von Proben mit Rissbildung und des Querschnitts einzelner Risse führt zu dem Schluss, dass die Risse nicht leer, sondern mit einer Risssubstanz gefüllt sind. Die Risssubstanz kann leicht vom umgebenden Harz unterschieden werden, dessen kontinuierliche Fortsetzung sie bildet. Weitere Versuche bestätigen das Vorhandensein der Risssubstanz und liefern Hinweise auf ihre strukturellen und mechanischen Eigenschaften. Die einschlägigen Versuche sind: mikroskopische Untersuchung der Wände gebrochener Risse, Mikroröntgenbeugung der Risssubstanz, Untersuchung der Festigkeit von Proben mit Rissbildung unter statischer Belastung und unter wachsender Spannung, Untersuchung des Einflusses von Hitze und Lösungsmitteln auf Proben mit Rissbildung und Beobachtungen über die Fähigkeit von Rissen zur Bildung eines speziellen Netzwerkes. Die Ergebnisse zeigen, dass die Risssubstanz durch eine lokale Deformierung des Harzes entstehen kann, die zu einer belastbaren, orientierten Struktur führt. Ein Rissbildungsmechanismus wird unter Berücksichtigung der neuen, vielfältigen, hier berichteten Ergebnisse vorgeschlagen. Eine Untersuchung der Kinetik des Risswachstums führt zu einer Zerlegung des Mechanismus in drei Teile: Start, Wachstum und Abbruch. Der Startschritt besteht in der Konzentrierung der Deformationsenergie und in der vorläufigen Molekülanordnung in unmittelbarer Nachbarschaft von Inhomogenitätsstellen. Diese Veränderungen treten zwischen dem Zeitpunkt der Spannungsbeanspruchung und des ersten Erscheinens von Rissen auf. Den Wachstumsschritt bildet die plötzliche und relativ rasche, lokale Harzdeformation, welche die Risssubstanz erzeugt. Die Gestalt der wachsenden Risse sowie ihre abnehmende Wachstumsgeschwindigkeit kann auf bekannte Harzeigenschaften zurückgeführt werden. Der Abbruchschritt besteht im augenscheinlichen Aufhören des Risswachstums bei fortgesetzter, langzeitiger Spannungseinwirkung. In dieser Phase des Bestehens der Risse muss die vorgeschlagene Hypothese in die Theorie der verzögerten Bruchbildung übergehen. Man kommt zu dem Schluss, dass die Spannungsrissbildung im Grunde mehr ein molekularer Gleitungsprozess als ein molekularer Spaltungsprozess ist. Die diesbezüglichen Überlegungen müssen sich daher mehr mit den intermolekularen als den intramolekularen Kräften befassen.

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