13. Fracture Phenomena in Polymers

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ABSTRACT

The effects of some variables on the fracture morphology of polymers, particularly polymethyl methacrylate, are discussed. These include rate of loading, molecular weight, temperature, and orientation. Examples of several types of flaws observed in polymers are shown and their significance is discussed. The observance of colors associated with fracture markings on polymethyl methacrylate is reported.

Introduction

High polymers have not been of sufficient importance to warrant a great deal of interest until recent years. Thus they have not received the attention that other materials have with respect to fracture studies. This paper discusses some aspects of the fracture morphology of high polymers with which the authors have been associated.

A typical photograph of a fracture surface of polymethyl methacrylate, a polymer well suited to fracture studies, is shown in Fig. 1. The surface has certain characteristic features. There is a smooth semicircular area of high specular reflectivity, known as the mirror area. This area contains the initiating source of failure. Surrounding the mirror area is a transition region of increasing roughness, and this in turn is surrounded by an area of still greater roughness. This latter area and, to a lesser extent, the transition region contain a number of geometric figures resembling parabolas or hyperbolas. In some cases, semicircular "ribs"

are also observed in the region of greatest roughness. The significance of these markings has been discussed in the literature.[1-4]

Although the photograph just discussed is considered in the literature as the classical representation of the fracture surface of polymethyl methacrylate, it actually typifies only a fairly narrow set of conditions. It describes the fracture surface of a specimen of unoriented polymethyl methacrylate, having a molecular weight in the range of commercial cast material, broken in tension at room temperature using a rather slow testing speed.
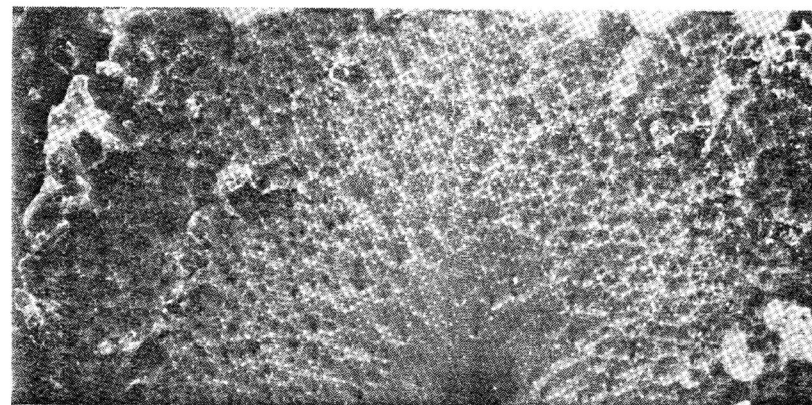

Fig. 1. Fracture surface of tensile specimen of polymethyl methacrylate.

Some of the variables mentioned above have been investigated and reported in the literature. Zandman,[2] for example, has shown how the appearance of the fracture surface of polymethyl methacrylate varies with the type of loading. He also showed that if the rate of loading is varied systematically the series shown in Fig. 2 is developed. The size of the mirror area decreases as the rate of loading increases, and circular ribs become apparent at the higher rates of loading. Polymers are quite strain-rate sensitive, and the stress at fracture increases with rate of loading. At the higher stresses encountered at the high rates of loading, the critical crack size, that is, the minimum size required to produce instability, is smaller than that required for the lower stresses encountered at low rates of loading. Therefore, the mirror area is smaller at the high rates of loading. The semicircular ribs observed at the higher rates of loading may be indicative of a shattering type of failure associated both with the higher stresses and with the more brittle response of the material at these high rates of loading.

The effect of varying the molecular weight of polymethyl methacrylate on the appearance of the fracture surface was described by Newman and Wolock.[5] They found that a series similar to that shown by Zandman is developed when the molecular weight is increased from 90,000 to 3,160,000 (Figs. 3 to 7). At the lower molecular weights, there are no parabolas apparent, and the fracture surface seems to be indicative of the shattering
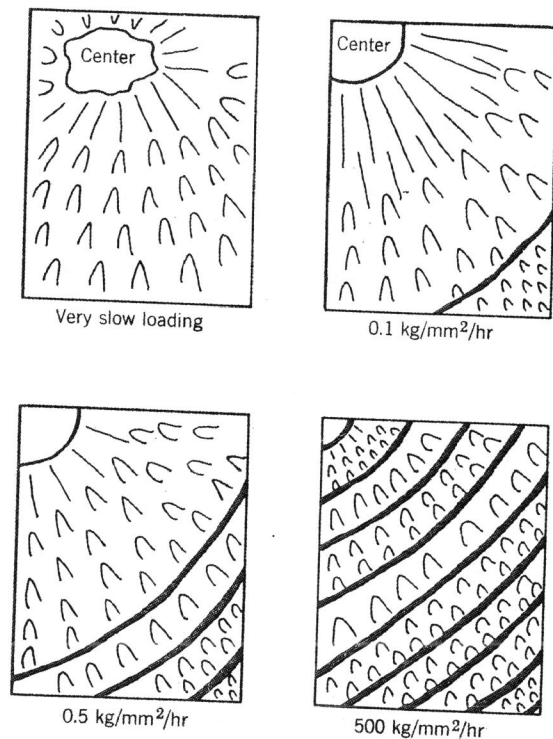

Fig. 2. Effect of rate of loading on fracture appearance of polymethyl methacrylate. (After Zandman.[2])

type of failure mentioned previously, which would be typical of a brittle material. The stress at failure is relatively low in these materials,[6] and there is little or no advance nucleation in front of the main crack front. The energy involved in crack propagation is probably rather low, and the crack advances at rapid velocity. As the molecular weight increases, parabolas become apparent surrounding the mirror area and covering an increasingly large portion of the fracture surface. The parabolas become larger and less numerous per unit area with increasing molecular weight, possibly because of the smaller number of flaws that would be
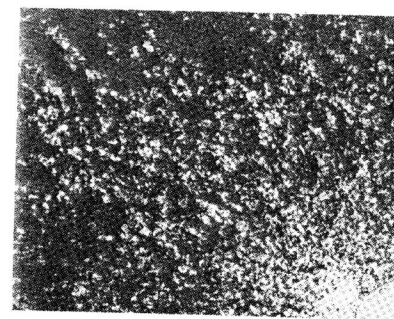
Fig. 3. Fracture surface of tensile specimen of polymethyl methacrylate. Molecular weight = 90,000.
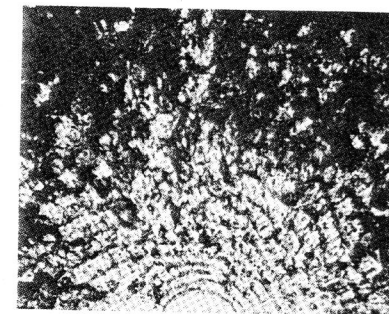

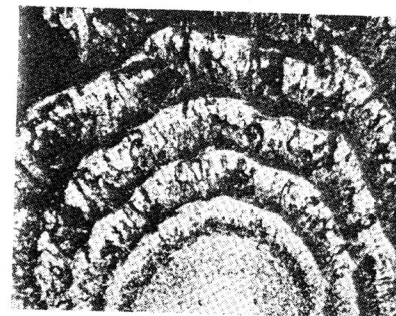Fig. 4. Fracture surface of tensile specimen of polymethyl methacrylate. Molecular weight = 120,000.

Fig. 5. Fracture surface of tensile specimen of polymethyl methacrylate. Molecular weight = 200,000.
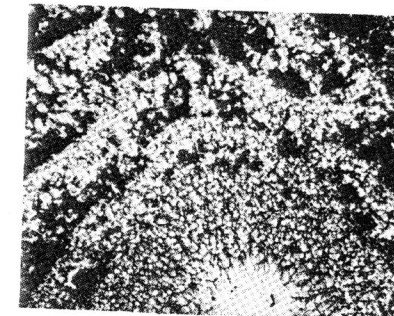

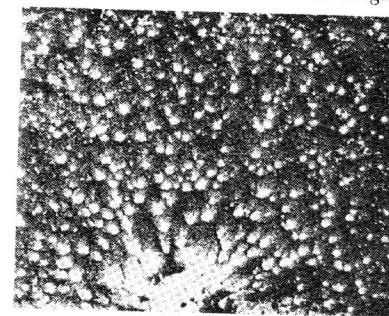Fig. 6. Fracture surface of tensile specimen of polymethyl methacrylate. Molecular weight = 490,000.

Fig. 7. Fracture surface of tensile specimen of polymethyl methacrylate. Molecular weight = 3,160,000.

associated with fewer long chains as compared to more shorter ones. At the higher molecular weights, the stress levels are higher, and parabolas are formed by advance nucleation. The increasing resistance to crack propagation decreases the tendency for the shattering type of failure apparent at the lower molecular weights.

Effect of Temperature

Another variable that obviously affects the failure behavior of polymers is temperature, but little has been written about its effects on fracture morphology. A group of specimens of cast polymethyl methacrylate were broken in short-time tensile tests at temperatures ranging from 23° to 80°C. From Fig. 8, it is obvious that the nature of the fracture surface, as well as the mode of fracture, changes between 40° and 50°C. At 40°C and below, the fracture surface is relatively flat and perpendicular to the faces of the specimen. Above 40°C, the fracture surface becomes oblique, and there is some indication of failure by shear. This transition is also apparent from the top view of these specimens, shown in Fig. 9. At 23° and 40°C, the mirror area is relatively structureless and occupies a small portion of the fracture surface. Above 40°C, the mirror area occupies a larger portion of the surface and is ribbed with radial "tear" lines.

Above 40°C, the material apparently becomes tougher, and the critical crack size greater, so that the mirror area is increased in size. The ductility of the material also increases at 40°C, and, with this increased ductility, stress concentrations at the end of the main crack front are relieved by flow. The material then fails by a tearing process or a flowing apart, rather than by a sharp brittle separation; this type of failure probably results in the tear lines that are observed in the mirror area.

The obvious question arises as to why the appearance of the fracture surface changes in this temperature range. The tensile properties of polymethyl methacrylate at different temperatures are shown in Fig. 10.[7] It is apparent from these curves that the elongation at failure rises sharply in the region of 40° to 50°C (104° to 122°F). The tensile strength and the modulus of elasticity, on the other hand, do not change drastically in this region. Sherby and Dorn [8] conducted studies of the creep behavior of polymethyl methacrylate as a function of temperature. They found that the energy of activation for creep increases sharply above 40°C and that the volume of the flow unit associated with creep also increases in the same region. In addition, Maxwell [9] measured the dynamic mechanical properties of polymethyl methacrylate over a wide range of frequencies and temperatures. His results indicate that the loss factor
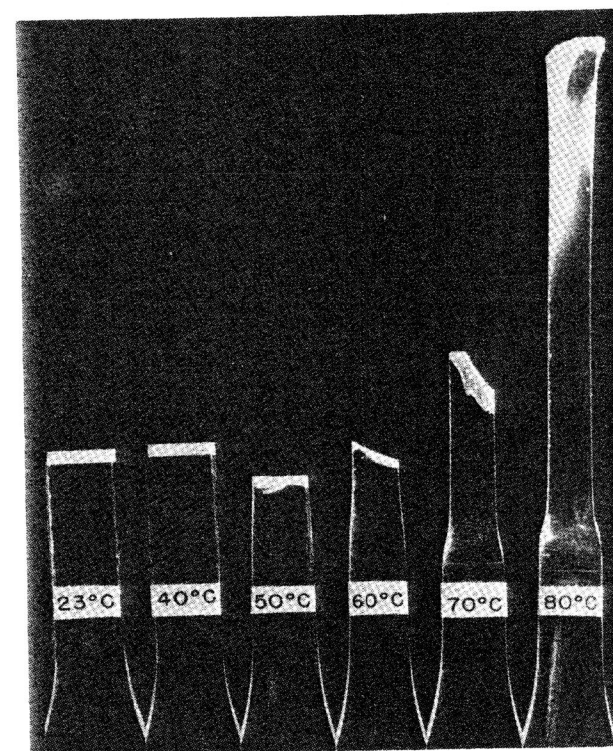

Fig. 8. Tensile specimens of polymethyl methacrylate broken at various temperatures.
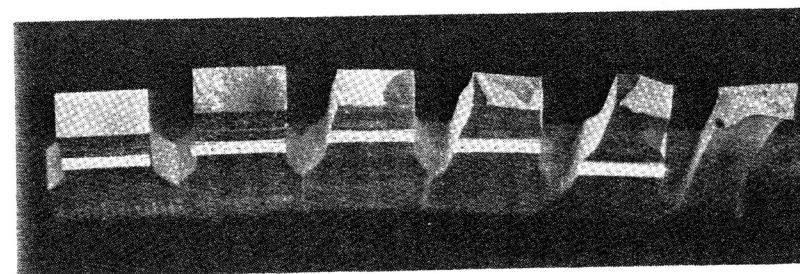

Fig. 9. Tensile specimens of polymethyl methacrylate broken at various temperatures (see Fig. 8).

increases sharply in the neighborhood of 40°C for frequencies so low that they might be associated with a static test. This would seem to indicate a change in the mechanism of deformation in this temperature range. This peak in the loss factor-temperature curve has been associated with the carbomethoxy group [10,11] of the polymethyl methacrylate chain, as well as with the methyl group.[12] Thus the present evidence indicates that the change in fracture behavior observed in polymethyl methacrylate at 40°C is due to a change in the mechanism of deformation, but the exact reason for this transition is not yet known.
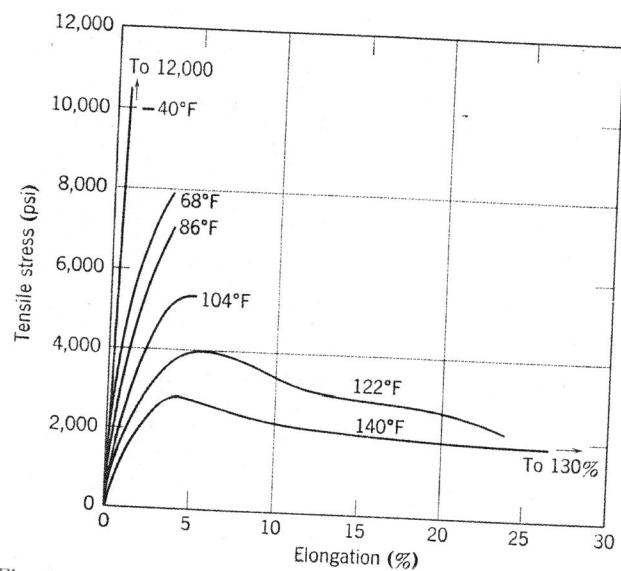

Fig. 10. Effect of temperature on tensile stress-strain curve of polymethyl methacrylate. (After Alfrey.[7])

Through variation in the test temperature, similar fracture surfaces can be produced in polymers differing widely in chemical structure and composition. Figure 11 is a photograph of the fracture surface of a polyvinyl chloride plastisol broken at room temperature. A plastisol is made by heating a resin in a liquid plasticizer at a sufficiently high temperature so that a gel-like solid is formed, essentially by the solution of the resin in the plasticizer. It is rubbery at room temperature. One can observe a series of radial "tear" lines emanating from the fracture origin, which in this case was a bubble. This area is similar in appearance to the mirror area of the specimen of polymethyl methacrylate broken at 50°C, shown in Fig. 9, and it is probably formed in a similar manner. On the other hand, if a plastisol specimen is broken at low temperatures,

its fracture surface resembles that of polymethyl methacrylate broken at room temperature.

If a tensile specimen of a cast polyester resin, which is a thermosetting polymer, is broken at elevated temperatures, the fracture surface (Fig. 12) shows characteristics similar to those observed in polymethyl methacrylate broken at elevated temperatures and those in the plastisol broken at room temperature. Yet these three polymers differ greatly in chemical structure and composition. Fracture morphology gives no indication of chemical structure of high polymers.
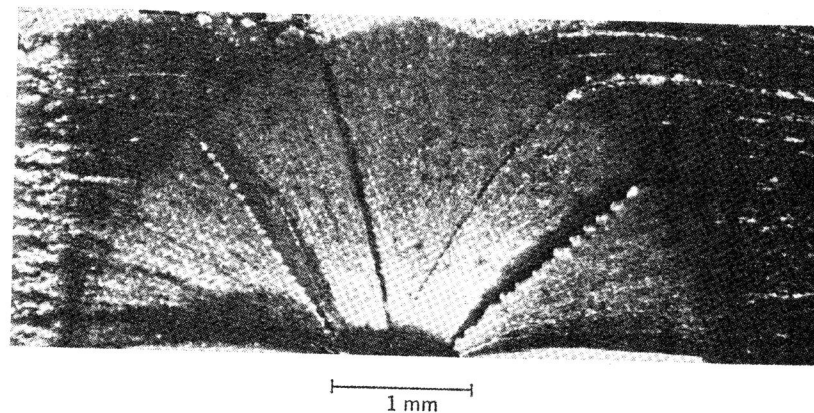

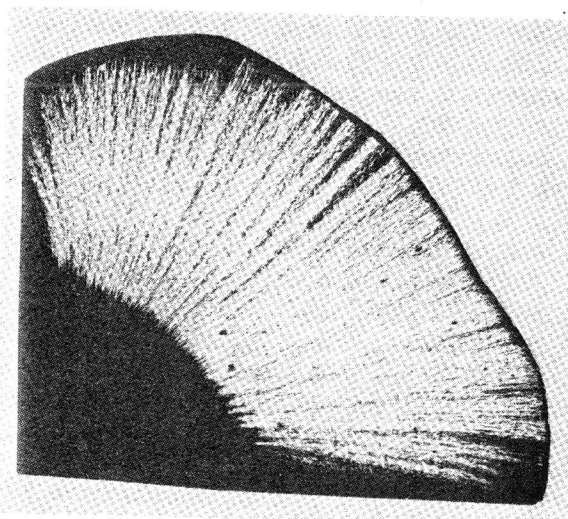Fig. 11. Fracture surface of tensile specimen of polyvinyl chloride plastisol.

Fig. 12. Fracture surface of tensile specimen of cast polyester resin broken at elevated temperatures.

Effect of Orientation

Polymers, consisting of long chains, can be relatively easily oriented, and, as one might expect, orientation affects the failure behavior and the appearance of fracture surfaces. For example, as the degree of biaxial orientation of polymethyl methacrylate is increased, the resistance to crack propagation increases and the fracture surface becomes rougher, as shown in Fig. 13. In the specimens shown, cracks are initiated prior to testing so that the fracture surfaces differ somewhat in appearance from those of the standard tensile specimens. One can postulate the development of a laminar structure in the polymer as a result of biaxial stretching.

If one varies the temperature from −40° to 120°F, the resistance to crack propagation of unoriented polymethyl methacrylate does not change appreciably, nor does the appearance of the fracture surfaces, as shown in Fig. 14. If, however, one varies the temperature over the same range for polymethyl methacrylate that has been biaxially stretched to, for example, 90%, the resistance to crack propagation changes sharply in the region of 40°F. One can observe a change in the appearance of the fracture surface in this region also, as shown in Fig. 15. The usual rough surface of the oriented material becomes smooth, resembling unoriented material. It would appear that one of the "degrees of freedom" of the oriented material becomes fixed in this temperature range. Thus a change in the fracture behavior of this polymer as a result of orientation, as well as a change in the behavior of the oriented material as a result of temperature variation, is reflected in the appearance of the fracture surfaces. Additional investigation is required to determine the reasons for the changes in mechanical behavior of the oriented material.

Nature of Flaws

The importance of flaws or inhomogeneities in failure behavior is well recognized and has been dealt with extensively. Each parabola or hyperbola on a fracture surface is attributed to a flaw that was sufficiently disturbed by the stress wave as to be a source of failure. Several types of flaws have been observed in high polymers.

Figure 16 shows a craze crack associated with a particle of dirt or dust in the interior of a specimen of cast polystyrene. Not all of the craze cracks observed in the specimen were associated with visible particles of dirt, but one might conjecture that submicroscopic particles were present and responsible for the initiation of these cracks.

It is interesting to note that internal crazing, or the formation of these

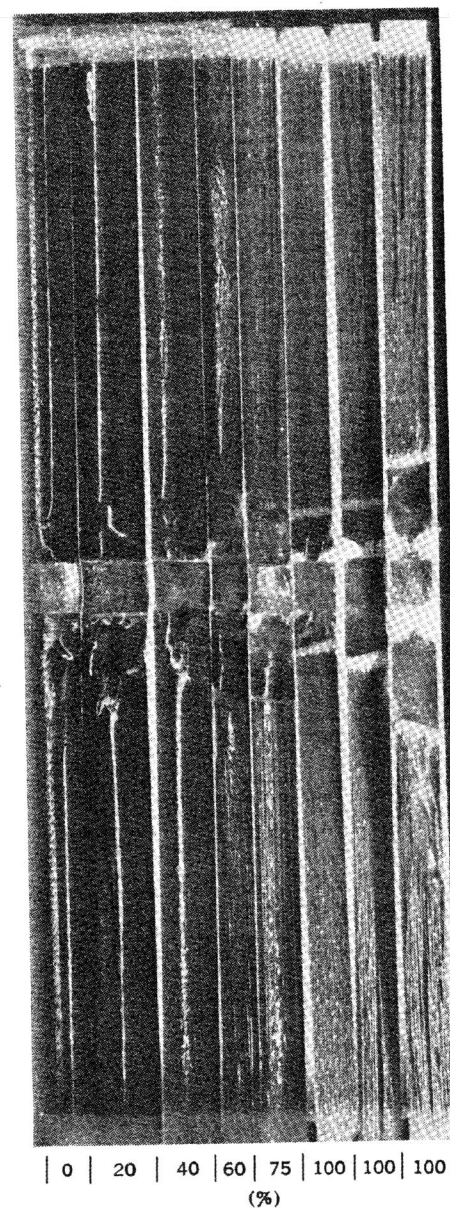| 0 | 20 | 40 | 60 | 75 | 100 | 100 | 100 |
(%)

Fig. 13. Effect of orientation on fracture appearance of polymethyl methacrylate crack propagation specimens. Numbers indicate degree of biaxial stretching in percent.

| −40 | 5 | 30 | 50 | 70 | 100 | 125 |
Temperature (°F)
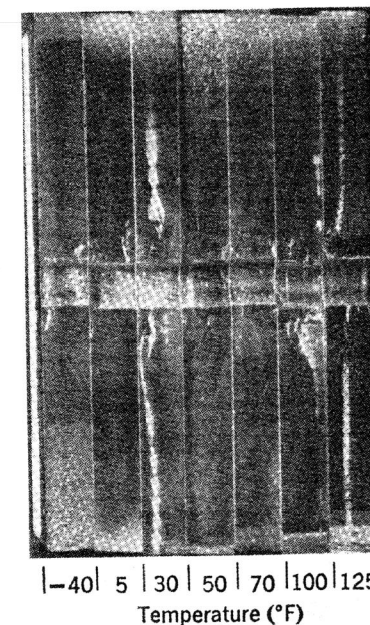
Fig. 14. Effect of temperature on fracture of polymethyl methacrylate.

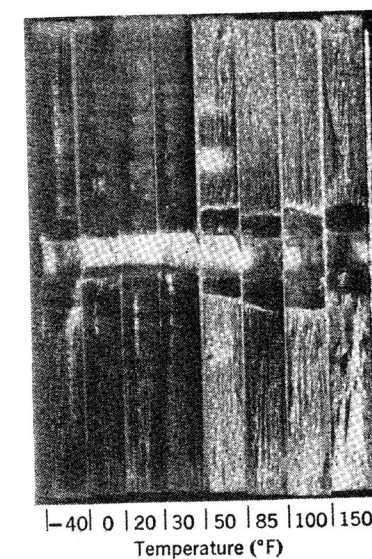| −40 | 0 | 20 | 30 | 50 | 85 | 100 | 150 |
Temperature (°F)

Fig. 15. Effect of temperature on fracture appearance of polymethyl methacrylate biaxially stretched 90%.
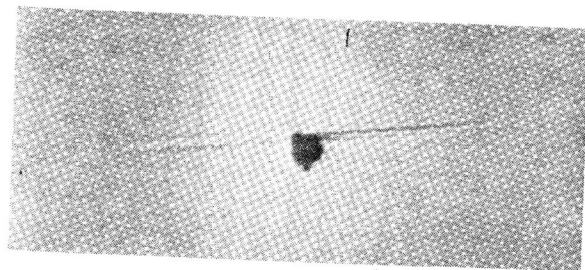
Fig. 16. Craze crack associated with dirt particle in interior of specimen of cast polystyrene.
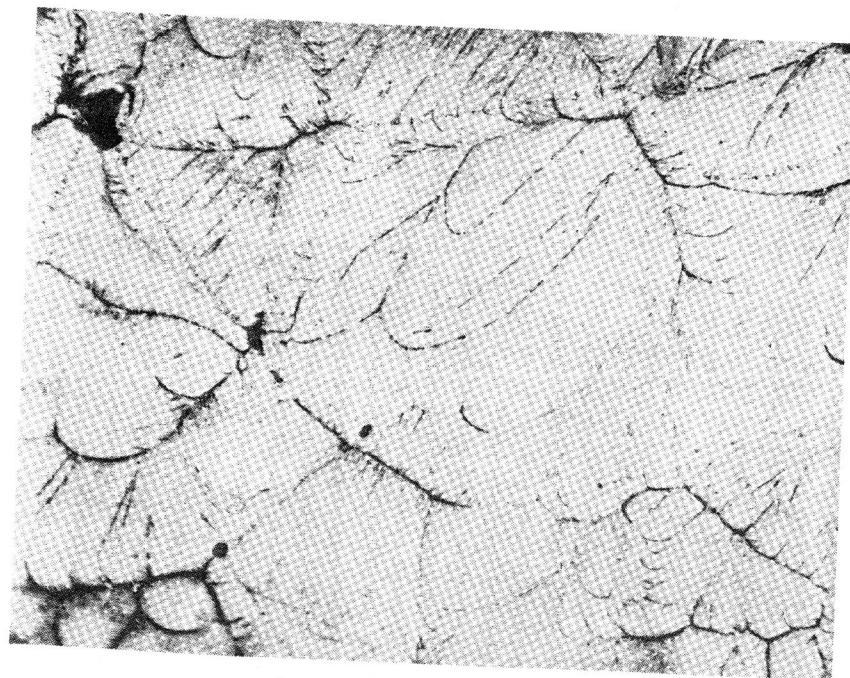

Fig. 17. Flaws along granule boundaries of improperly molded polymethyl methacrylate. (After Kies, Sullivan, and Irwin.[1])

cracks throughout the matrix of the specimen, was observed for this material. In the examination of another transparent polymer in the developmental stages, polymethyl alpha-chloroacrylate, dust particles were often observed in the interior. In the case of polymethyl methacrylate, however, dust or dirt particles are not observed in the interior, and crazing is confined to the surface regions. It would thus appear that the formation of these craze cracks, which can be considered the initiation of failure, is associated with dirt particles. Particles of this type, which
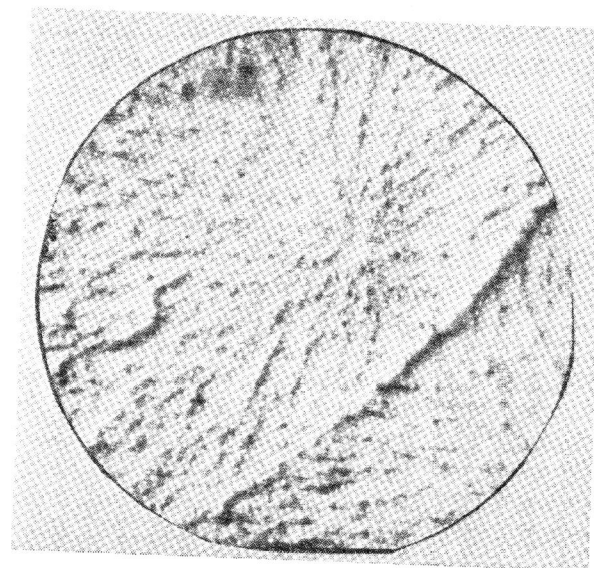

Fig. 18. Electron micrograph of focus of parabola from broken tensile specimen of cast polymethyl methacrylate.

if sufficiently large might be visible in transparent materials, would not be obvious in opaque materials. They represent one potential type of flaw in polymers that can be eliminated, however, by closely controlled manufacturing conditions.

A second source of flaws can be observed from Fig. 17, which is the fracture surface of a specimen of improperly molded polymethyl methacrylate.[1] One can observe that the boundaries between the improperly molded granules provide the foci for a series of fracture initiation points that develop as parabolas. This second type of flaw can be overcome or reduced by proper processing.

A third type of flaw is shown in Fig. 18, which represents the focus

of a parabola from the fracture surface of a specimen of cast polymethyl methacrylate. There is no obvious defect to which the initiation of failure can be attributed. Possibly the use of higher magnification would reveal a physical flaw of some sort. Barring this, one can attribute the failure to the basic molecular structure of the material. This is not unreasonable, since commercial cast polymethyl methacrylate is a relatively refined polymer, as indicated by its previously mentioned crazing behavior.

Recently, colors associated with specific fracture markings were observed on fracture surfaces of polymethyl methacrylate. They were observed on specimens broken with a rapid overstress, as when broken using a nail punch and hammer, but were not observed in specimens broken in a standard tensile test. The colors were apparent when the surfaces were examined in an optical microscope using vertical illumination. The observation of colors on the fracture surface of polymethyl methacrylate has been reported previously,[13] but in that case the colors were broad bands. The color markings discussed here are associated with specific fracture markings, such as parabolas, and the color changes sharply at the edge of the parabola. An area of the fracture surface that is apparently rather flat and devoid of fracture markings has a single color. All of the colors fade gradually with time. Much work will be required to determine the cause of these colors, and the answer should shed more light on the nature of flaws and the mechanism of fracture in polymers.

ACKNOWLEDGMENT

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DISCUSSION

J. P. BERRY, *General Electric Company*. It is clear from the experiments carried out by Wolock and others that factors such as molecular weight, rate of loading, and temperature all play a part in determining the characteristics of the fracture surface in polymers. It is possible that the variation in the types of surface features observed in any one polymer is due primarily to variations in the velocity of crack propagation and that the influence of the experimental variables studied is due to their effect on the crack velocity. Support for this point of view is given by some experiments carried out recently in our laboratories. With use of a cleavage technique, a crack in polymethyl methacrylate could be made to grow at a controlled rate. When the crack velocity was low (1 mm/min), the surface features were quite different from those observed when the crack grew rapidly (at a rate approaching the maximum). In the latter case, the characteristic parabolic patterns were found. In the former case, two different types of surface features have been observed, both of which are of interest.

The first of these bears a very strong resemblance to the river systems in metal and ionic crystals, described by Low, and those in glass, described by Orowan. In the crystal, such patterns have been considered to arise when the advancing crack meets a screw dislocation; in glasses, they can arise by the bifurcations of a rapidly moving crack. However, neither of these explanations is valid for a slowly growing crack in an amorphous polymer. There is thus a danger in trying to determine from the appearance of the fracture surface itself the mechanism of the process that produced a fracture surface. In all cases, the molecular constitution of the material and the conditions under which the fracture occurs should be taken into account.

The brilliant colors on the surface of freshly fractured polymethyl methacrylate, described by Wolock, have also been observed in our

samples when the crack velocity is low. The explanation offered by Wolock for this effect is that the color is due to interference from a sub-surface crack, presumably arising by a bifurcation mechanism; this would not apply, however, to our case. Since the color is constant in tint over quite large areas (of the order of square millimeters), the postulated subsurface crack would have to remain parallel to the surface over this area, even though the surface itself is frequently nonplanar. If the color is due to interference in a surface film, the refractive index must be different from that of the bulk polymer, and some chemical or physical modification of the surface must have occurred. Some rather crude experiments indicate that the mechanical properties are also different; the surface layer appears to be softer than the substrate. In view of the fact that our experiments were carried out at low velocity rates, we considered the possibility that a ductile flow process resulted in orientation of the molecules normal to the surface, and that this oriented layer was responsible for the color. If it is assumed that the color is due to first-order interference, the thickness of the film can be calculated to be between 2500 and 3000 Å. This distance corresponds to the fully extended length of a polymethyl methacrylate chain of molecular weight between 50,000 and 60,000. Such a high degree of orientation in this polymer is highly unlikely. It is clear that a good deal of further work under carefully controlled conditions is necessary before a satisfactory explanation for the effect can be given.

I. WOLOCK, J. A. KIES, AND S. B. NEWMAN (AUTHORS' REPLY). The variations in the fracture appearance of polymers referred to by Berry may well be due in part to the rate of crack propagation, but this is not always a unique function. The effects of changes in crack velocity on the appearance of the fracture surfaces of polymethyl methacrylate have been discussed by Schardin. He showed that the appearance of the surface was a function not only of crack velocity but also of rate of loading.

The similarity in the appearance of fracture surfaces of materials of widely differing chemical and physical structure has also been reported in the literature, and it has been pointed out that the same mechanism of failure on a microscopic or molecular basis cannot be valid for these widely differing materials, even though their fracture surfaces showed similarities. However, the interpretation of fracture markings on a macroscopic basis should be valid regardless of chemical or physical structure.

The authors doubt that the deformation occurring during crack propagation is sufficient to account for surface coloring in terms of the formation of an oriented layer.