

Metallographic Characterization of Rubber-Modified Poly(methyl Methacrylates)*

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Synopsis

The microstructure of rubber-modified samples of poly(methyl methacrylates) was characterized by depositing a thin layer of gold on a polished surface and then applying the conventional techniques of metallography. Samples were prepared with a known volume fraction of rubber comprising particles of known size. It was shown that the methods of quantitative microscopy were successful in estimating these parameters. The method was also shown to provide information about crazing or cracking, which was viewed near the tip of an arrested crack. It is recommended that adoption of the metallographic method be extended to characterize other polymeric systems.

INTRODUCTION

Information about the microstructure of rubber-toughened glassy polymers has been obtained previously mainly by electron and phase-contrast microscopy. These techniques are unsuitable for quantitative analysis of the volume fraction of the rubber microphase and its distribution. The objective of the present work was to coat a polished surface of the polymer with a thin layer of metal in order to investigate whether the microstructure could be characterized quantitatively by metallography. For example, if the rubber microphase could be left with an irregular surface, it would be expected, after coating with metal, to reflect light in many directions and to appear as dark features against a mirror-like background due to the glassy matrix. Poly(methyl methacrylate) (PMMA) was chosen to provide the glassy matrix because of the use of rubber-modified polymers of this type in dentistry. In some cases these materials were also examined by conventional electron microscopical techniques for comparison with the data obtained by metallography. As far as is known, no microstructural characterizations of any kind have been reported previously for rubber-modified PMMA.

* Part of this work was previously reported at the International Association for Dental Research, Las Vegas, 1972.

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EXPERIMENTAL

Materials

PMMA (Grade VM-100 Plexiglas Acrylic Molding Powder) and a rubber-modified PMMA (Inplex F) were donated by the Rohm and Haas Company, Philadelphia.

Lucitone 199 is believed to be a rubber-modified PMMA, marketed for use in dentistry, made by admixture of a monomer with a polymeric powder (L. D. Caulk Company).

Sample I was made starting from a natural rubber latex which had been grafted with 40%, by weight of total polymer, of PMMA (Heveatex P-1340-L; Firestone Tire and Rubber Company). The polymer was completely separated from serum by coagulation with dilute sulfuric acid. A weighed portion of the coagulum was immersed in acetone (5 g/100 ml), and the system was exposed to ultrasonic waves until a uniform colloidal solution was obtained. This took about 5 min, using a Branson Sonifier set at a dial position of 10. The colloidal solution was then thoroughly mixed with an acetone solution of PMMA (5 g/100 ml). The total polymer was recovered from acetone by shock precipitation into methanol. It was dried by heating in a vacuum at 140°C for 24 hr. The crumb obtained in this way was repeatedly passed through the heated rolls (170°C) of a mill and provided a powder with particles of diameter 100–500 μ .

Sample Preparation

Powder was placed in a cylindrical mold cavity (diameter 2.5 cm, length 0.3 cm) at 180°C. After 10 min, a pressure of 100 kg/cm² was applied and maintained for a further 10 min. The mold was allowed to cool to 50°C, while still under pressure, before the sample was removed.

A sample of Lucitone 199 was prepared according to the manufacturer's instructions with the assistance of personnel of the Philadelphia Department of Public Health.

Samples were dry polished with emory paper through grades 1 to 3/0 and then wet polished, in succession, with alumina of particle size 0.3 and 0.5 μ . The technique was similar to that described by Kehl.¹ A gold film, of thickness approximately 200 Å, was deposited in a direction normal to the polished surface. This type of deposition is a routine procedure in laboratories set up to prepare samples for scanning electron microscopy.

Thin films, approximately 800 to 1500 Å thick, were microtomed with glass knives from samples which had been hardened and stained with osmium tetroxide according to Kato.²

Replicas of polished surfaces were obtained by successive deposition of Victawet, silicon monoxide, and germanium (45° incidence). The surface was then cut into small squares which were floated off in water and collected on a copper gride.

Sample Examination

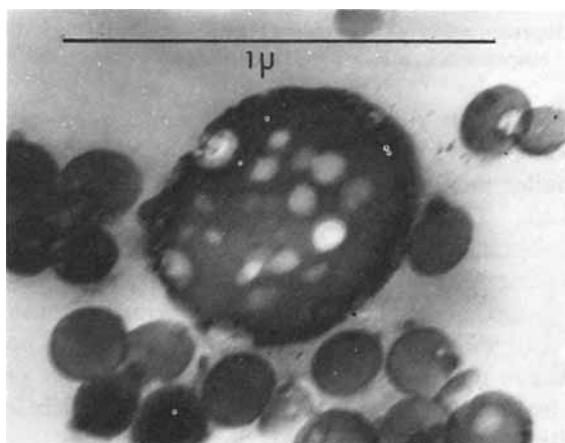
Thin films and surface replicas were examined by transmission in a Jelco Electron Microscope.

Metallized surfaces were viewed by reflected light of wavelength 5300 Å in a Bausch and Lomb Research Metallograph. Maximum magnification was attained with an oil immersion objective of numerical aperture 1.4.

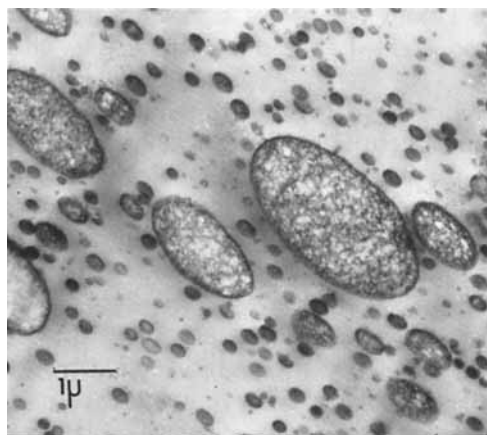
A fine slot was cut into a disc with a jeweller's saw and a crack initiated by forcing in a razor blade. One surface of the disc was covered with gold and the crack propagated by screwing in a wedge.³

RESULTS AND DISCUSSION

Transmission electron micrographs show that materials obtained from commercial sources have a complex microstructure (Fig. 1). The larger



(a)



(b)

Fig. 1. Electron micrographs of sections treated with osmium tetroxide: (a) Implex F; (b) Lucitone 199.

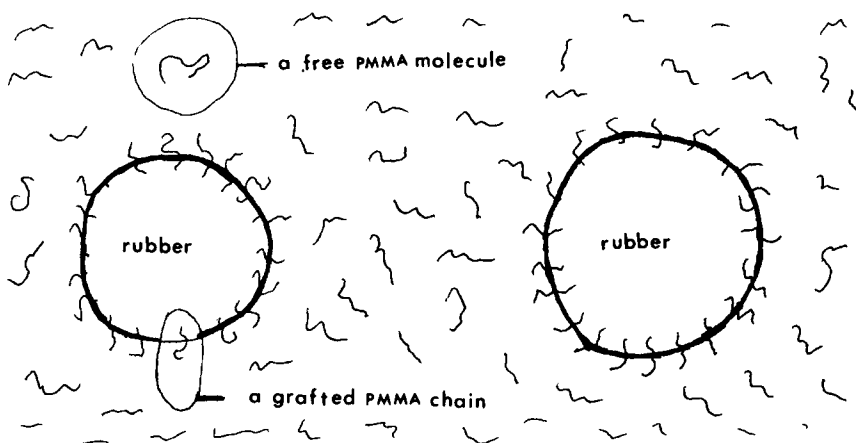


Fig. 2. Idealized representation of rubber latex particles grafted with PMMA, in colloidal suspension in a solution of free PMMA in acetone.

particles comprise both rubber, which is stained more darkly by the osmium tetroxide, and PMMA. These composite particles are present, along with smaller particles of indeterminate structure, in a continuous matrix of PMMA. The microstructures resemble ones reported for rubber-toughened polystyrenes.⁴ The information obtained by metallography is similar, recognizing that the elliptical shapes in Figure 1b are artefacts caused by the distortion of spherical particles during microtomy (cf. Fig. 8, B). A disadvantage of the metallographic method is the poor resolution relative to electron microscopy. An advantage is that it provides information about features defined on a planar surface which is suitable for proceeding with a quantitative analysis of microstructure. However, because of the complexities of the commercially available materials, evidenced by Figure 1, and because of a lack of background information about them, it was decided to prepare the simpler material (I) as described previously.

The idea underlying the preparation of the PMMA-rubber system (I) is that it might be possible to transpose the rubber particles in a latex, with their relatively simple shape and determinable distribution of sizes, into a PMMA matrix. An unmodified rubber latex would appear unsatisfactory for two reasons: first, because it would be difficult to avoid irreversible aggregation, or even coalescence, of the tacky rubber particles during sample preparation; second, because eventually it would be desirable to correlate microstructure with mechanical properties. A simple interface between rubber and PMMA would not be expected to result in a toughened product.⁵ Both these problems might be avoided by use of a rubber latex in which the surface of the particles is chemically grafted with PMMA. It has been shown that the conventional preparation of PMMA-grafted natural rubber latex gives a product which approximates to this condition.⁶ The particles from such a latex can be colloiddally dispersed in acetone.

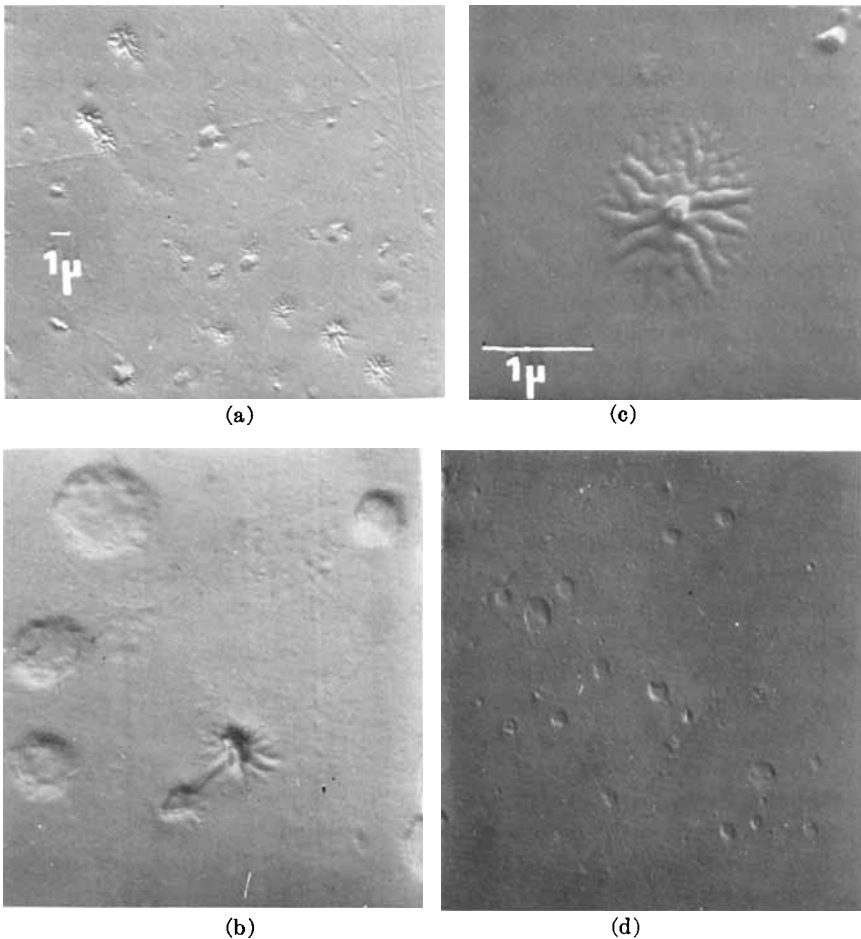


Fig. 3. Electron micrographs of replicas of polished surface of Sample I ($V_r = 0.05$): (a) 2700 \times ; (b) 18000 \times ; (c) 18000 \times ; (d) 2700 \times .

Presumably, the grafted PMMA chains at the surface are solvated and serve to stabilize the rubber, which otherwise is insoluble.

To help bring the preceding description to mind, reference is made to an idealized sketch showing two rubber particles with surface-grafted PMMA. These particles are represented as in colloidal dispersion in a solution of free PMMA in acetone (Fig. 2). The best chance of eliminating the acetone with retention of this dispersion is by shock precipitation of the whole mass of polymer into a nonsolvent.

Evidence of a transposition of individual latex particles into the PMMA matrix may be seen in transmission electron micrographs (see Fig. 5). First, it is to be noted that individual particles are evident with no indication of aggregation. A second point is that the range of sizes is generally consistent with reports that the particles in *hevea brasiliensis* latex range

down from a maximum value of 2 or 3 μ . The final point is that the rigid coating of grafted PMMA has evidently served to preserve the generally spherical shape of the rubber particles. It is known that occasional larger particles have a pear shape.⁷ Such a particle may be seen most clearly from a surface replica (Fig. 3 b).

Quantitative Microscopy

The rubber disperse phase may be characterized by a number of parameters which can be estimated from measurements on a plane of polish. Attention will be concentrated on two of these for which comparisons are available. The volume fraction of rubber, V_r , may be equated to the fraction of the intersections which superpose on the rubber phase when a grid is placed over a photograph.⁸ A number-average particle diameter, d may be estimated from eq. (1):

$$d = \frac{3V_r}{N_{rm}} \quad (1)$$

in which N_{rm} represents the average number of interfaces between the rubber and the matrix phases per unit length.⁹ N_{rm} was estimated from a set of lines inclined at 15° apart and drawn through the center of each photograph.

Preliminary examinations were made by electron microscopy of replicas of polished surfaces. The surface seems to include two types of feature, one of which preponderates in Figure 3 a and the other in Figure 3 d. These features are contrasted at higher magnification in Figures 3 b and c. Inasmuch as the type of feature shown in Fig. 3 b was formed by applying a higher pressure during polishing, it may correspond to the case in which a rubber particle is plucked out of the matrix. If the perimeter of both types of feature is used to define the boundaries of the rubber phase, then the value estimated for V_r approaches twice the value obtained from the made-up value, V_{r*} , calculated according to eq (2):

$$V_{r*} = \frac{0.6 W_c}{\rho_r} \left(\frac{0.4 W_c}{\rho_p} + \frac{W_p}{\rho_p} \right)^{-1} \quad (2)$$

where W_c = weight of coagulum, W_p = weight of PMMA subsequently added to coagulum, ρ_r = density of rubber (0.92 g/cm³), and ρ_p = density of PMMA (1.18 g/cm³). A similar discrepancy was observed for other samples with higher volume fractions of rubber. The method was judged to be inaccurate as well as laborious; it was discontinued.

Typical photographs obtained by metallographic examination of the metallized polished surface are shown in Figure 4. Apparently, the mere process of differential abrasion serves to provide contrast between the two phases without recourse to any more elaborate etching technique. Moreover, the estimate of the volume fraction of the rubber made from such photographs (V_r) is in excellent agreement with the made up values (V_{r*}) (Table I).

The metallographic method is not expected to provide a definitive measure of the distribution of particle sizes of the rubber phase, because the

TABLE I
Parameters Estimated by Quantitative Microscopy^a

V_r^* (volume fraction as made up)	0.04	0.08	0.13	0.20	0.30	0.36
V_r (volume fraction as estimated)	0.04	0.10	0.14	0.21	0.32	0.36
d (average particle diameter), μ	0.9	1.0	1.1	0.9	1.9	0.8

^a The standard deviations of V_r and d were, respectively, $\pm 15\%$ and $\pm 55\%$ of the tabulated values.

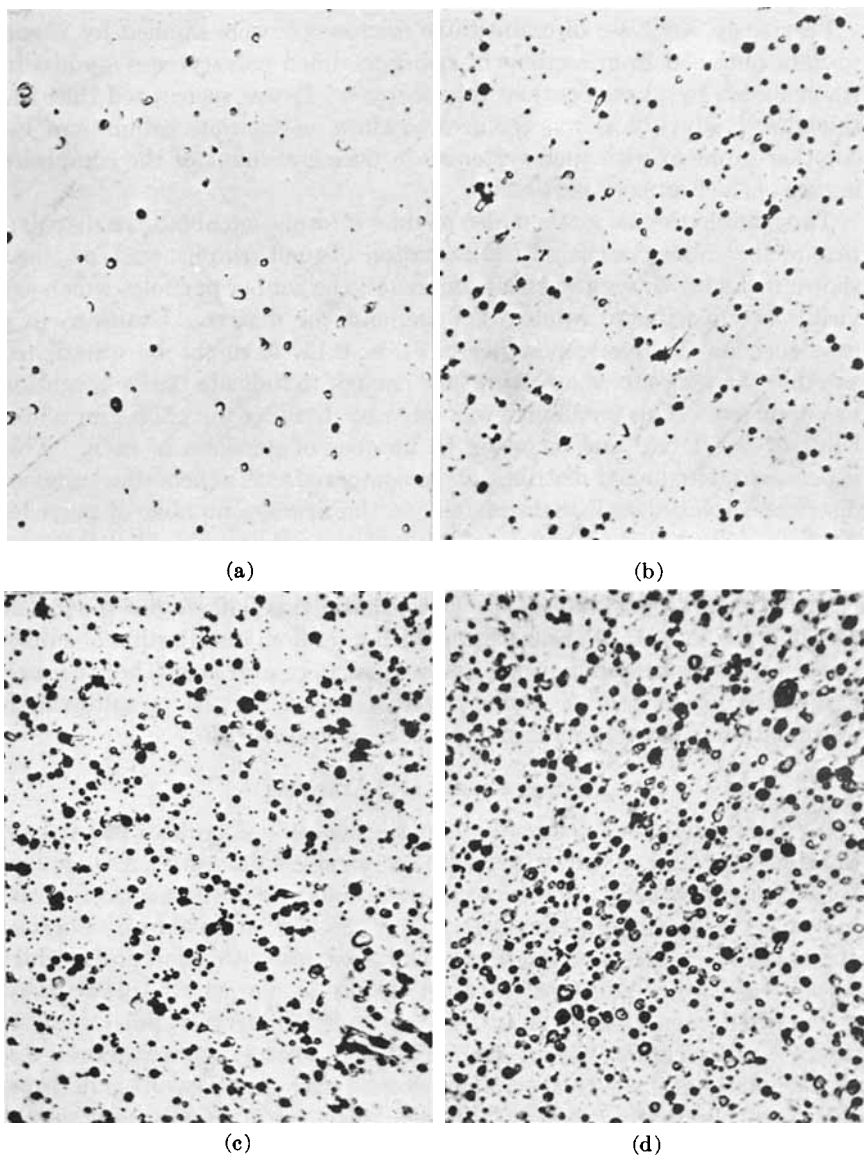


Fig. 4. Micrographs showing rubber particles in PMMA matrix I ($\times 2000$): (a) $V_r = 0.04$; (b) $V_r = 0.14$; (c) $V_r = 0.32$; (d) $V_r = 0.38$.

limit of resolution under the present conditions is about 0.2μ , and much smaller particles which are known to be present would be ill defined both in shape and size, or even undetectable. Nevertheless, two points of comparison may be made. First, the upper size of the rubber particles was observed to approximate the expected value of 2 or 3μ . Second, Lucas¹⁰ has estimated a number-average particle size of 0.26μ for a hevea brasiliensis latex by direct-counting transmission microscopy with ultraviolet light of wavelength 2537 \AA which allowed a resolution of 0.1μ . Given the poorer resolution in the present work, the value obtained of 0.8 to 1.1μ (Table I) does not seem inconsistent with the earlier estimate.

Previously, analyses of quantitative microscopy were applied by Cigna to data obtained from sections of rubber-modified polystyrenes studied in transmission by phase-contrast microscopy.¹¹ It was recognized that the thickness studied (2μ) was too great to allow an accurate estimate of V_r . Another problem with such systems is in taking account of the composite nature of the "rubber" particles.

The metallographic method also provides information about the distribution of the rubber particles. Examination of photographs, such as those shown in Figure 4, suggests that, in general, the rubber particles which are visible are distributed randomly throughout the matrix. However, in a case such as that corresponding to $V_r = 0.14$, it might be questioned whether the unoccupied areas are large enough to indicate that segregation has occurred. This possibility was tested by dividing the photograph into fields of size 1 cm^2 and counting the number of particles in each. This experimental frequency distribution was compared with a theoretical random distribution calculated, with reference to the average number of particles per field, from Poisson's equation. Reference to Pearson's chi-square test showed that sampling of a random distribution would be expected to give a larger value in 43% of the cases. On this basis, it is judged that the results obtained for $V_r = 0.14$ are consistent with a random distribution of rubber particles. This procedure is not documented at greater length here because a detailed account of a similar analysis, based on the metallographic examination of silver spheres in bakelite, is on record.¹²

Stress Crazing and Cracking

An important phenomenon caused by the presence of a rubber microphase in a toughened glassy polymer is that an increased deformation is realized before fracture occurs. The increased deformation is due to a great increase in regions of localized yielding, termed crazes,¹³ which comprise polymer chains aligned in the direction of stretching together with small pores, which in one case were judged to be about 200 \AA in diameter.¹⁴ Previously, crazing had been studied mainly by transmission electron microscopy of samples treated with osmium tetroxide, which provides contrast because of its accumulation in the craze pores. Optical microscopy has been informative mainly in systems which form wide crazes, such as poly(bisphenol A carbonate). In the case of PMMA, this technique has provided little information because of the small craze width. Against this background, it is of interest to report information obtained by metallography.

Preliminary experiments indicated that, generally, the magnification in metallography was too low to recommend its use for the study of crazing in polymers based on PMMA. This is because, after relaxation of a stressed sample, the width of the crazes is only about 0.1μ . This is exemplified by

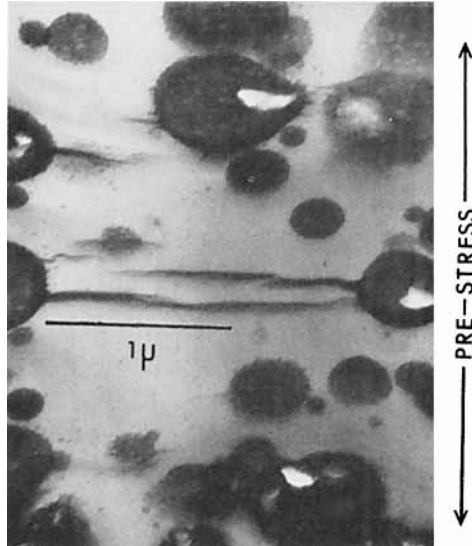


Fig. 5. Crazing in rubber-modified PMMA (I). Electron micrograph of prestressed sample stained with osmium tetroxide.

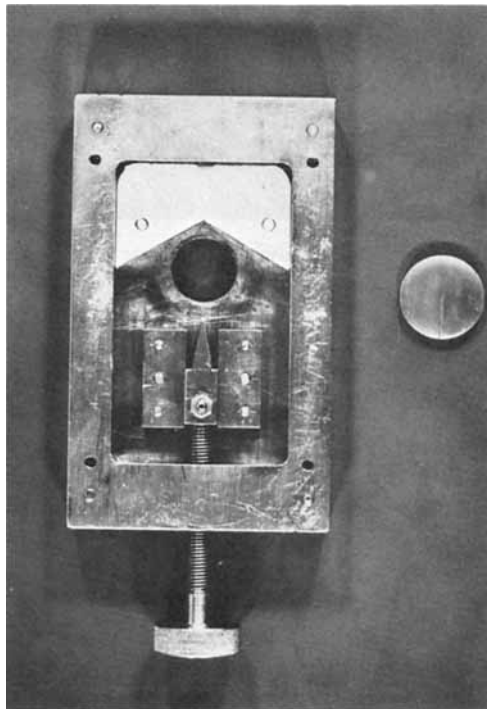


Fig. 6. Jig used to effect limited crack propagation in disc.

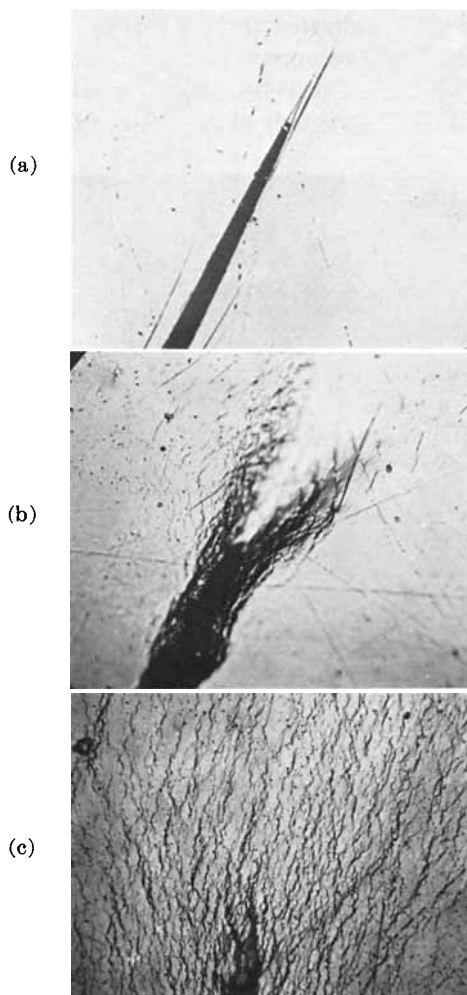
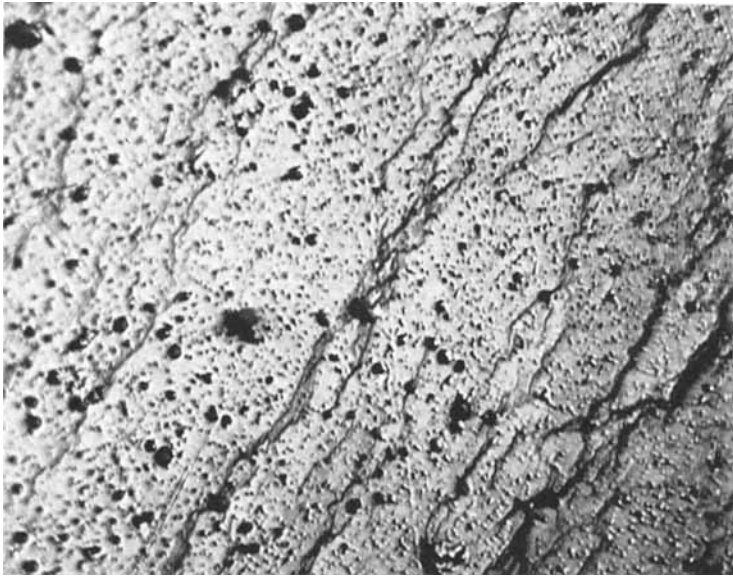


Fig. 7. Influence of rubber microphase on crazing near arrested crack tip: (a) PMMA (not coated with metal), $V_r = 0$ (1000 \times); (b) sample I, $V_r = 0.04$ (500 \times); (c) sample I, $V_r = 0.2$ (500 \times).

an electron micrograph (Fig. 5) which includes two roughly parallel crazes running from left to right, just above the micron marker, perpendicular to the direction of stretching.

A better case for applying the metallographic technique to the study of crazing and subsequent cracking in PMMA is provided when samples are maintained under stress, since this allows examination prior to contraction. This was done by screwing a wedge into a crack in a disc. The design of the jig used results in a limited propagation of the crack (Fig. 6). In PMMA not coated with metal, craze matter (white) is visible at the tip of the crack (black) in a way closely resembling a report by Van den Boogaart¹⁵ who made a similar study (Fig. 7 a). The effect produced by a rubber



(a)



(b)

Fig. 8. View of wedged metallized samples by reflected oblique light ($\times 2000$): (a) Implex F; (b) Lucitone 199.

microphase, however, was clearly revealed, as shown in Fig. 7 b and c, only when the surface of the disc was coated with metal. The magnification is too low to show the relationship between craze and crack formation and the position of rubber particles. However, at the highest magnification available, this relationship can be seen in the commercial sample with the largest (composite) rubber particles (Fig. 8 b).

CONCLUSIONS

It has been shown that the techniques of metallography may be applied to a number of samples of PMMA which include a rubber microphase. The technique is simple and rapid and involves a combination of procedures which, individually, are commonplace in a well-equipped materials laboratory. The technique has been applied with success also to rubber-modified polystyrenes (ABS and HIPS).³ In these latter systems, larger crazes are formed and it has been possible to use metallography to characterize craze densities. It is envisaged that the metallographic technique would be applicable to other rubber-modified glassy polymers and that it would be of special value in cases where the rubber phase is too unreactive chemically to be stained with reagents such as osmium tetroxide, e.g., copolymers of ethylene and propylene, and polyisobutene.

More generally, it seems likely that the metallographic method may be adapted to study other types of microphase in a matrix which will take a plane of polish. For example, preliminary experiments show that it can be used to provide information about glass-filled composites of PMMA.³

In conclusion, it is believed that adoption of the metallographic technique will help to move the characterization of polymeric materials at the micron level toward the sophistication already achieved with metals and ceramics.

This work was begun in the Department of Metallurgical Engineering as part of the Biomedical Engineering Program at Drexel University.

We acknowledge support from the National Institute of Dental Research as a trainee (H.D.M.) and under PHS Grant No. DE-02668 (D.T.T.).

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Received December 27, 1972

Revised July 17, 1973