

On the influence of particle morphology on microdeformation in rubber modified poly(methyl methacrylate)

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Microdeformation in thin films of rubber modified poly(methyl methacrylate) has been investigated using TEM. The effects of two-layer core-shell particles with rubbery cores, and three-layer particles with glassy cores are compared. While the former undergo relatively coarse cavitation and may act to block fibril drawing in matrix crazes, the rubber shell of the three-layer particles tends to fibrillate, and they are readily incorporated in the crazes.

(Keywords: poly(methyl methacrylate); rubber toughening; crazing)

INTRODUCTION

Poly(methyl methacrylate) (PMMA) containing sub-micron sized rubber particles shows improved fracture toughness, without substantial loss of transparency, and has accordingly received considerable recent attention in the literature^{1–6}. It is therefore of current interest to develop techniques for the direct observation by transmission electron microscopy (TEM) of the micro-mechanisms of deformation in these materials. This should permit one not only to identify the nature of matrix deformation but also to clarify the role of the rubber particles. In the present report we present preliminary results obtained by adapting the method of Lauterwasser and Kramer⁷ for the TEM study of microdeformation in thin films of various grades of rubber modified PMMA.

EXPERIMENTAL

The polymers investigated here, supplied by Atochem, were based on a PMMA matrix with a molecular weight average (M_w) of 130 000 gmol^{-1} and a T_g of $\sim 115^\circ\text{C}$. The filler particles were of two types: (i) two-layer core-shell, with a crosslinked butyl acrylate-co-styrene interior and a PMMA shell, with an overall diameter of approximately 160 nm⁸; (ii) three-layer particles with a PMMA core, surrounded by an inner shell of crosslinked butyl acrylate-co-styrene and finally an outer shell of PMMA, with an overall diameter of 250 nm. Samples were provided in the form of 10 mm thick plaques with global particle volume fractions of 15 and 45% for the two-layer particles, and 30% for the three-layer particles.

Cast films of thicknesses ranging from 0.15 to 0.5 μm were obtained by drawing glass slides from solutions of

PMMA and the two-layer core-shell particle modified PMMA in dichloromethane, and evaporation of the solvent (the particles remained in suspension without the need for stirring). Further addition of PMMA to the solution allowed adjustment of the particle content of the cast films where desired, but the tendency of the particles to agglomerate led to highly non-uniform spatial distributions. Thus any given film contained a wide range of local particle volume fractions. To relax the films and to remove residual solvent, they were annealed for 1 h under vacuum at 140°C . They were then floated off the glass slides onto a water bath, picked up on annealed copper grids, dried and bonded to the grids by heating just above the glass transition temperature (T_g).

Since the spatial distributions of the particles in the solution cast films are unlikely to reflect those of melt-processed bulk samples, we adopted the approach taken by Maestrini *et al.*⁹ in their TEM investigation of the effect of sub-micron rubber particles on deformation in polystyrene (PS). Microtomed slices of the order of 0.3 μm in thickness were obtained at room temperature, using a glass knife (Reichert-Jung Ultracut E ultramicrotome). The microtomed slices were picked up on copper grids, dried and bonded to the grids by heating to above T_g as previously.

The films were strained using the MinimatTM miniature tensile test apparatus at a rate of 1 mm min^{-1} (equivalent to a strain rate of about $2 \times 10^{-3}\text{ s}^{-1}$). Individual grid squares were removed for examination in a Phillips EM 300 TEM at 100 kV. PMMA is well known to depolymerize rapidly in the electron beam. Apart from causing mass loss and sample movement, this also has the effect of causing craze fibrils and other small-scale features to coalesce. To obtain artefact free micrographs, the spot size was chosen so that only the field of view was irradiated at the desired magnification

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and screen intensity. After focusing, the samples was displaced and an adjacent unirradiated part of the sample photographed.

RESULTS AND DISCUSSION

Solution cast films containing two-layer particles

PMMA films containing no modifier particles showed crazing on straining, with structures as shown in *Figure 1*, which serves for comparison with those seen in the modified PMMAs.

Figure 2 shows deformation in a $0.15\ \mu\text{m}$ thick solution cast film containing two-layer particles. Even for extremely low overall particle contents (down to 0.2 vol%) the density of localized deformation was considerably increased compared with unmodified PMMA, so that the whole of a given grid square was covered with very dense, fine craze-like features, which were hard to resolve optically. As can be seen from *Figure 2*, the deformation mode in the matrix was indeed crazing. In this case there was little cavitation of the rubber particles, presumably since the particle diameter was about twice

the film thickness, allowing rapid relaxation of through thickness stresses, leaving the particles free to elongate in the direction of the principal stress (even so, in the micrographs, the particle cores appeared light in comparison to the matrix). It is also clear from the figure that isolated rubber particles do not act as nucleating sites for crazes. As suggested by Donald and Kramer¹⁰, the range of the stress concentration in the immediate vicinity of small particles is too limited to promote craze nucleation and growth. Many authors however, have noted that clusters of small particles may provide effective nucleation sites, depending on their geometry, hence the important role of the particle volume fraction for toughening by small particles^{1,11-13}.

For the very thin film of *Figure 2*, rows of three or more closely spaced particles oriented perpendicular to the principal stress axis provide particularly efficient nucleation sites for crazing, although it is interesting to note that where similar rows are oriented parallel to the principal stress axis, they are far less effective. Within large clusters the dominant deformation mode appears to be homogeneous shear banding rather than crazing, with matrix fibrillation tending to occur beyond regions of high particle density.

In thicker solution cast films ($\sim 0.5\ \mu\text{m}$), as shown in *Figure 3*, the craze density is also high, and craze

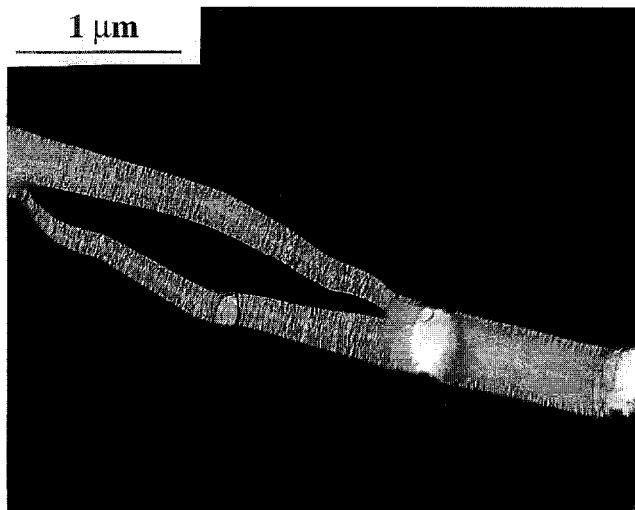


Figure 1 Crazing in a $0.3\ \mu\text{m}$ thick solution cast unmodified PMMA film



Figure 2 Deformation in a $0.15\ \mu\text{m}$ thick solution cast film containing two-layer particles (note the tendency for the particles to agglomerate)

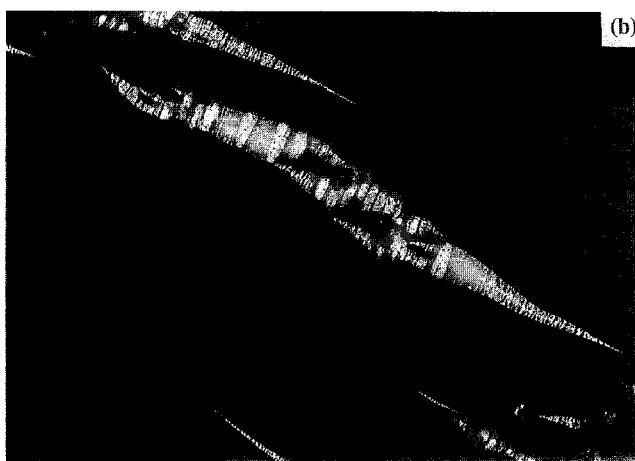


Figure 3 Deformation in a $0.5\ \mu\text{m}$ thick solution cast film containing two-layer particles [(a) and (b) are two exposures of the same region showing the particle distribution and the internal craze structure respectively]

nucleation is again associated with particle agglomerates rather than isolated particles. In this case, however, there is extensive cavitation associated with agglomerates. Thus at large deformations, they appear as highly voided regions with a high degree of apparently homogeneous matrix drawing (although fibril coalescence may be a contributing factor here⁹). Single isolated particles remain ineffective as nucleation sites, whether they cavitate or not (in fact the majority of isolated particles do not cavitate). They also present little barrier to craze propagation, with particles lying along a craze trajectory cavitating, leaving large oval voids within the craze body. Examples of this are visible in *Figure 3*; the residues of the cavitated particles are visible on either side of large voids within the craze body. This may also arise as a consequence of the 'sifter' mechanism proposed in ref. 1, where the craze passes between two particles and then impinges on them as it widens (by 'width' we mean the distance across the craze measured parallel to the tensile axis). Local craze widening is effectively blocked by the rubber particles, leading to a stress concentration as adjacent regions of craze continue to widen, which will result in breakdown either of the fibrils or the rubber particles, leaving a void.

Microtomed films containing two-layer particles

Figure 4a shows deformation in a $0.3\ \mu\text{m}$ thick sample containing 45 vol % two-layer particles, again indicating widespread cavitation. It is difficult to identify craze structure in the matrix since the particle density is high. In *Figure 4b*, on the other hand, which contains 15 vol % of particles, the deformation mechanism is more clearly identifiable as crazing in regions where there are relatively few particles. The density of craze nucleation is correspondingly lower in this sample than for the higher particle content.

Microtomed films containing three-layer particles

The differences between the three-layer particle modified PMMA and the two-layer particle modified PMMA are readily apparent from *Figure 5*. The rubber shell initially shows cavitation around its whole circumference, but the voids are separated by ligaments of rubber linking the glass outer shell/matrix to the glass inner core. As deformation continues there is widespread crazing in the intervening matrix regions, with several narrow crazes being initiated at each rubber particle. The particles are then incorporated within the deformed regions of matrix, becoming highly elongated, and there

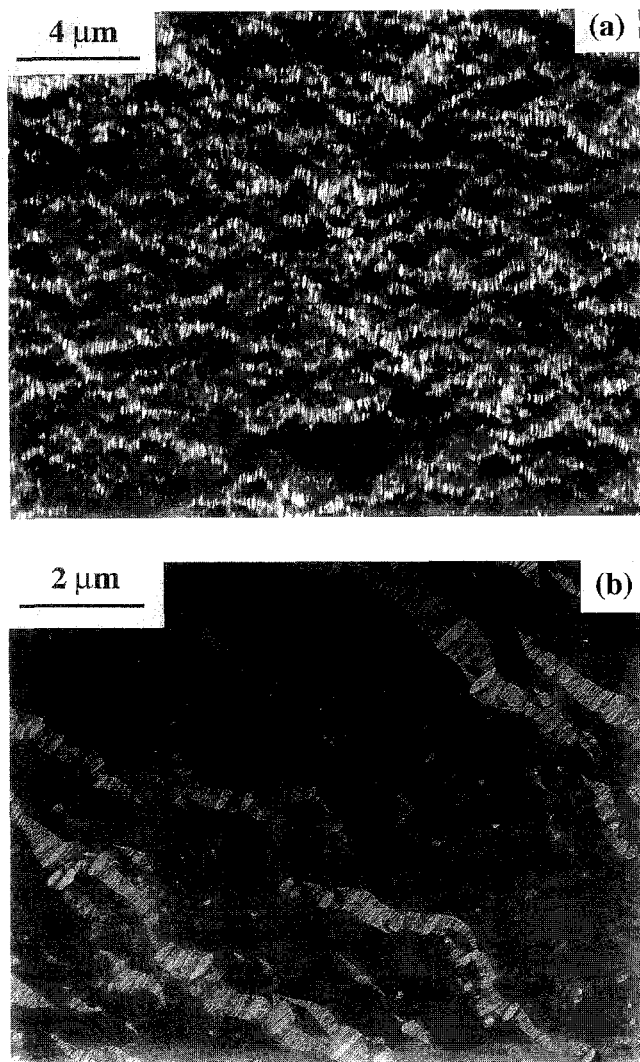


Figure 4 Deformation in a $0.3\ \mu\text{m}$ microtomed film containing two-layer particles: (a) 45 vol % particles; (b) 15 vol % particles

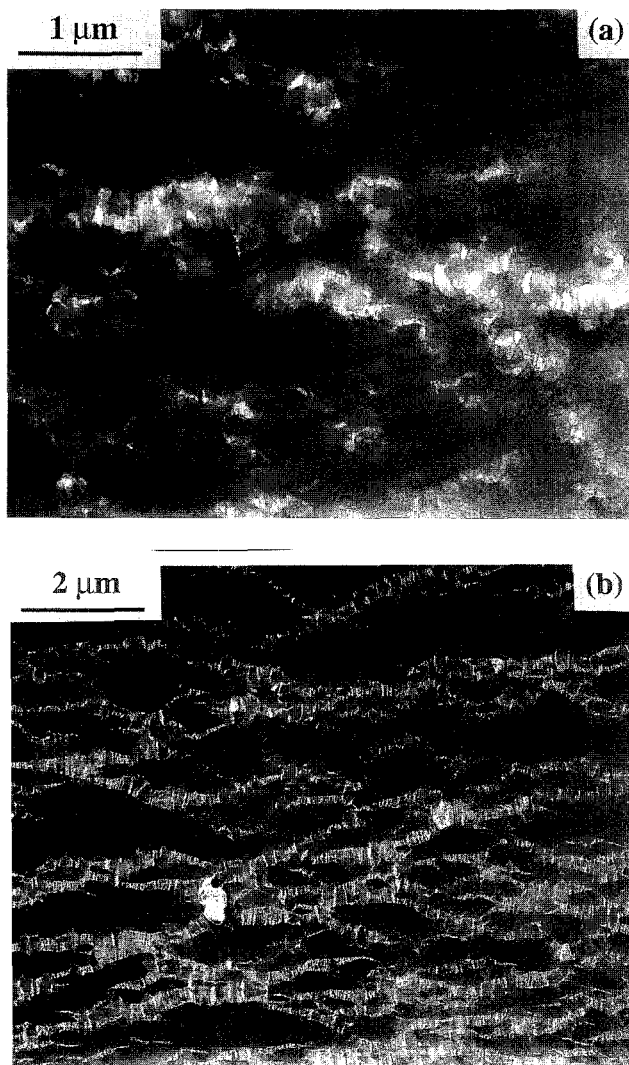


Figure 5 Deformation in a $0.3\ \mu\text{m}$ microtomed film containing three-layer particles: (a) deformation onset; (b) large deformation

is no coarse cavitation—the sifter mechanism referred to earlier also appears ineffective, presumably owing to the presence of multiple crazes at each particle. The overall density of crazing/shear deformation nevertheless appears similar to that in the 45 vol % two-layer core-shell particle modified PMMA.

CONCLUSIONS

We believe the usefulness of thin film methods for the TEM observation of deformation in rubber modified PMMA to be demonstrated, providing confirmation of the role of crazing in these materials. It must of course be remembered that the stress state in a bulk sample may be very different to that in the thin film geometry, which will have an important bearing on the respective strains at which cavitation and widespread matrix deformation take place (which may in turn influence the competition between crazing and homogeneous shear deformation for a given set of test conditions).

The important result here is the observation of sharply contrasting mechanisms of craze-particle interaction in the two- and three-layer particle modified PMMAs. In the two-layer systems, the particle cavitation results in the presence of large voids in the crazes. One anticipates that the load bearing ability of individual crazes will be diminished by the presence of the voids, and also their capacity to absorb energy as they widen. In the three-layer system, on the other hand, there is no coarse voiding within the crazes. We think this may be highly significant in view of the higher room temperature fracture energies and stress intensity factors observed over a wide range of testing rates for three-layer particle modified PMMA. Moreover, compact test specimens of the two-layer systems show a tough-brittle transition with increasing test speed at about 1 m s^{-1} , which is absent for the three-layer system up to the highest test speeds (10 m s^{-1}). If this tough-brittle transition is due to the nucleation of unstable secondary cracks ahead of the main crack-tip, as has been suggested in ref. 14, the

improved craze stability in the three-layer system which may be inferred from the present results provides a plausible explanation for the superior high speed performance of this latter.

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