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Effect of modifier concentration on the fracture behaviour of rubber-modified PMMA

NILESH SHAH
Rohm and Haas Co., Research Laboratories, PO Box 219, Bristol, PA 19007, USA

Izod fracture surfaces of blends of PMMA with various amounts of a rubber modifier were studied using scanning electron microscopy. Attention was focused on modes of crack initiation and propagation and on the role of the modifier in the fracture process. It was found that the impact strength of this class of materials increased monotonically with an increase in modifier concentration, at least up to 40 wt % modifier. Unmodified PMMA was studied to provide a basis for understanding the morphological features on the fracture surfaces of the rubber-modified blends. It was confirmed that PMMA fractures through the formation and rupture of crazes. This phenomenon was also found to occur in blends containing 10 wt % modifier. However, blends with 20 wt % modifier crazed only in the later stages of the fracture process, when the crack speed had exceeded some critical value. No evidence of crazing was found in blends with 30 and 40 wt % modifier loadings, although extensive plastic deformation was observed on the fracture surfaces.

1. Introduction

It is well known that brittle thermoplastics such as polystyrene and polymethylmethacrylate (PMMA) can be toughened by the addition of a rubbery phase. The resulting blend exhibits enhanced impact strength when subjected to standard tests such as the Notched Izod and Falling Dart tests. The toughening mechanisms for some polymers such as high impact polystyrene and acrylonitrile–butadiene–styrene have been discussed in some detail in the literature [1–4]. Although some understanding of the macroscopic mechanical behaviour of rubber-modified PMMA has been reported [5, 6], there is a dearth of information on the role of the impact modifier in the fracture process. The present work addresses the dependence of fracture behaviour in rubber-modified PMMA blends on modifier content.

Although rubber-modified PMMA has been analysed sparingly, the fracture behaviour of PMMA has been the subject of many previous papers. Hull and Owen [7] were among the first to present an interpretation of morphological features on fracture surfaces generated by the failure of thermoplastics such as polycarbonate, polystyrene, and polymethylmethacrylate. Their results showed that fracture is preceded by crazing and features such as the "mackerel" structure are caused by the biplanar fracture of craze fibrils. The authors also observed bands on the surface which they attributed to either a stick–slip fracture process or a cyclic perturbation in the craze fracture process. This could be caused by the interaction between the propagating crack front and a stress wave reflected from the end of the sample.

The classical picture of "mirror, mist, and hackle" structure in fractured PMMA was provided by Kusy and Turner [8] in their study of the effect of molecular weight on the fracture morphology developed on notched tension samples. Their work involved an extended discussion of the formation of "ribs" which constitute the hackle region. Again, the formation of these bands or ribs was attributed to stick–slip phenomena during crack propagation as well as to Wallner lines (formed by the interaction between the advancing crack front with the reflected stress waves).

Doyle [9] presented a detailed description of the mechanism of the biplanar fracture that results in the formation of the mackerel pattern. He showed that the craze undergoes fracture at the interface between the fibrils and the polymer bulk. The fracture is caused by a local increase in stress due to the propagation of interfacial stress waves initiated by previous fracture events. In a subsequent paper, Doyle [10] presented an explanation for the formation of bands on the fracture surfaces of PMMA. It was shown that above a certain crack speed, the craze preceding the crack front may undergo branching. At sufficiently high stress levels, some of the branch crazes undergo fracture causing the crack front to split into several parallel fronts that are not coplanar. This forms the leading edge of the band. However, the formation and fracture of the various branch crazes absorbs enough energy to decelerate the crack and reduce the driving force for the propagation of the branch cracks. This in turn promotes recombination of the cracks into a single front and corresponds to the end of the band. On recombination, the crack speed rises again and branching recurs. This process is cyclic in nature and is thus responsible for the banded appearance of the fracture surface.

In the area of rubber-modified PMMA, there have

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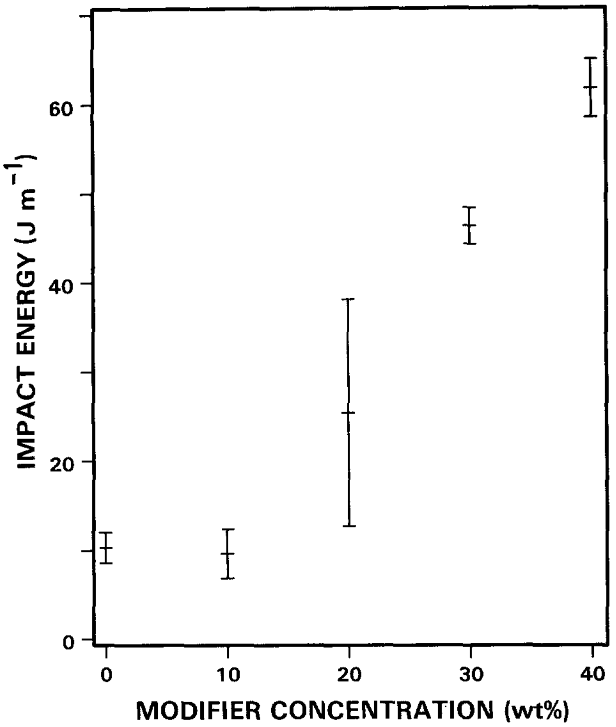

Figure 1 Variation of impact strength (in a Notched Izod test) with concentration of the modifier phase.

been two major attempts to investigate the role of the modifier in the fracture process. Bucknall *et al.* [5] studied the mechanical properties of pure PMMA and two samples of rubber-modified PMMA containing 27 and 36 vol. % of the rubber phase, respectively. By studying the volume changes during tensile creep measurements, the authors showed shear yielding to be the dominant mechanism of energy dissipation in the rubber-modified materials. Below $-5°$ C, Notched Charpy tests on the sample with 36% rubber showed that the surfaces were "rough and broken" like those of PMMA. As the test temperature was increased (between -5 and 23° C), a "flat area" was seen near the notch and at even higher temperatures ($>30°$ C), the entire fracture surface was flat. The changes in surface appearance correlated with transitions in the temperature dependence of impact

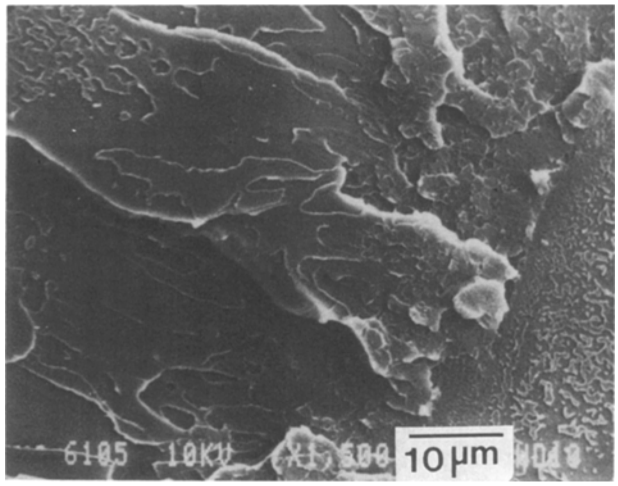

Figure 3 PMMA: Magnified view of the initiation zone of a band seen on the right-hand side of Fig. 2.

strength. The authors suggested that these transitions were associated with the appropriate T_g of the rubber phase at the applied strain rates.

More recently, Milios *et al.* [6] have studied the dynamic crack propagation behaviour of a series of rubber-modified PMMA samples with the help of the method of caustics. The authors concluded that the presence of the modifier increases the dynamic stress intensity factor at crack initiation. It was proposed that the modifier causes local shear yielding, which in turn blunts the pre-existing crack. However, once the crack starts, it propagates rapidly through the sample with an excess of energy, while the stress intensity factor decreases rapidly with the increase in crack length. One of the drawbacks of the method of caustics is that it is limited to the study of materials whose behaviour can be described by the formalism of linear elastic fracture mechanics. This limitation prevented its application to blends with modifier loadings in excess of 20 wt %.

In the present work, an appreciation of the role of the modifier has been obtained by analysing the morphological features of surfaces produced by the fracture of notched Izod bars.

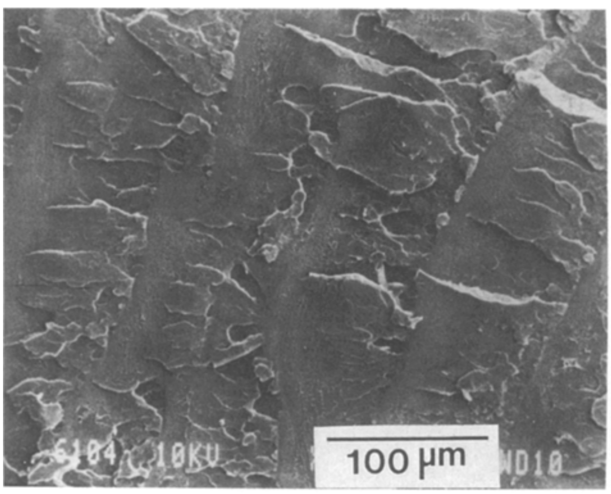

Figure 2 PMMA: Brittle bands near the notch. Crack propagated from bottom right-hand corner to upper left-hand corner.

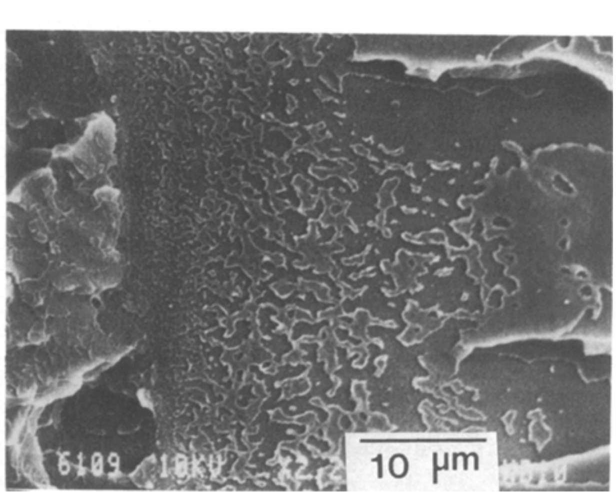

Figure 4 PMMA: Evidence of biplanar fracture of crazes near the end of a typical band.

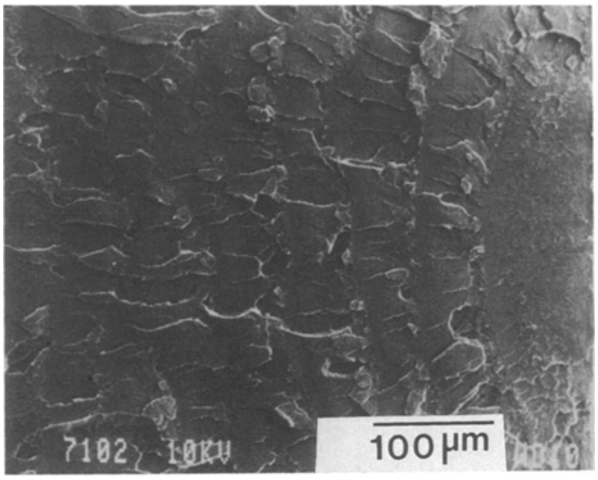

Figure 5 Blend with 10 wt % modifier: Formation of bands around a typical initiation zone.

2. Experimental procedure

Rubber-modified blends were prepared with 10, 20, 30, and 40 wt % modifier content in a medium molecular weight PMMA (with 4% ethyl acrylate as comonomer) matrix from Rohm and Haas Co. The unmodified matrix was used as a reference sample. The modifier (also from Rohm and Haas Co.) had a three-stage morphology, consisting essentially of a PMMA core, a crosslinked copolymer of butyl acrylate and styrene as the rubber stage and an outer stage identical to the core. The blends were prepared by melt-mixing the two phases on a two-roll mill at 230° C. Samples for testing were obtained by compression molding the blends into 3.17 mm thick plaques at 230° C, which were subsequently cooled at room temperature. The fracture surface were obtained by performing the Notched Izod test (ASTM D256) at 23° C on standard 3.17 mm wide bars (cut from the above plaques) with 0.25 mm radii notches.

For each sample, two sets of fracture surfaces were studied by scanning electron microscopy. Each set consisted of the two halves of a fractured Izod bar. In all the micrographs to be shown, the notch is on the right and hence, the crack propagated from right to left.

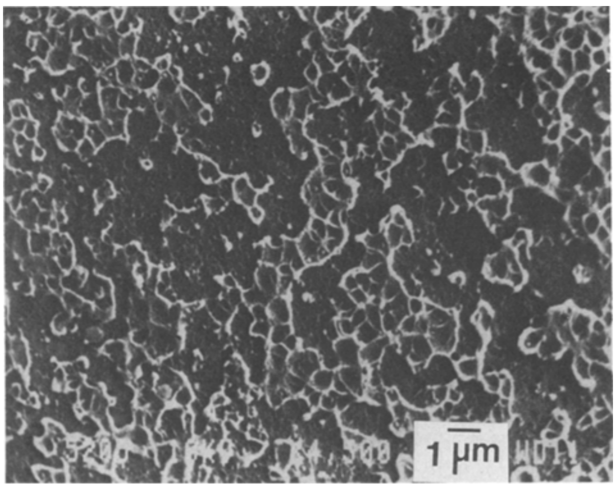

Figure 6 Blend with 10 wt % modifier: Mackerel structure showing the local plastic deformation around individual modifier particles.

3. Results and discussion

The impact strengths of the above blends are depicted in Fig. 1, where the error bars represent 95% confidence limits. The rise in impact strength shows the increase in ductility with the increase in modifier concentration up to 40 wt %.

A study of the fracture surface of PMMA was helpful in establishing a basis for understanding the morphology of the fracture surfaces of the rubber-toughened blends. Examination of the area next to the notch on fractured PMMA Izod bars shows that the crack initiates locally at one or more sites at the notch. The initiation sites can be identified by tracing the direction of crack propagation backwards to the notch. The crack propagates by the repeated generation and breakdown of crazes. This is clearly recorded on the fracture surface by a series of concentric bands which emanate from each initiation site. Fig. 2 shows a portion of the banded area seen close to the notch.

As explained by Doyle [10], the bands are formed by the initiation of branch crazes at high crack speeds and the subsequent rupture of these crazes accompanied by the deceleration of the crack. The existence of multiple co-existing fracture planes within each band appears to substantiate the view that the crack repeatedly splits into several branches and recombines during its progress. It should be noted that, at low magnifications, the left edge of each band appears to lie in a single plane while the right edge is multiplanar. This is consistent with the observation that the crack propagates from right to left with branch craze formation at the right edge and crack recombination at the left. Fig. 3 provides a closer view of the beginning of a band located on the right-hand side of Fig. 2. The end of the preceding band can be seen at the bottom right-hand corner of this micrograph. There is a large difference in depth between the plane of the preceding band and that of the band that occupies most of this micrograph. The presence of large planar ridges on the surface near the beginning of the latter band clearly shows that craze fracture occurred at one fibril–bulk interface or the other and that the location of the fracture plane did not oscillate rapidly between the two interfaces. The central portion of Fig. 4 is a view of the end of a typical band. There is a striking difference between the "mackerel" structure on this surface and the planar ridges in the previous figure. This shows that at the end of band, the crack shifts rapidly from one craze–bulk interface to the other as its speed increases until the point of craze branching (i.e. band initiation) is reached. The resulting fracture surface has "patches", as seen in the middle of Fig. 4, or a series of parallel steps oriented perpendicular to the crack propagation direction.

The next sample in this series is a blend containing 10 wt % of the rubber modifier. The impact strength of this material does not differ substantially from that of the unmodified matrix. On a macroscopic scale, the fracture surface of this sample has the same

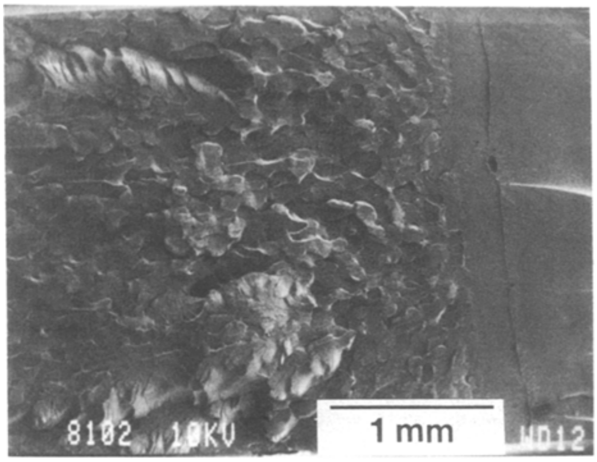

Figure 7 Blend with 20 wt % modifier: View of the entire width of the Izod fracture surface near the notch. Transition from an apparently smooth surface to a rougher surface.

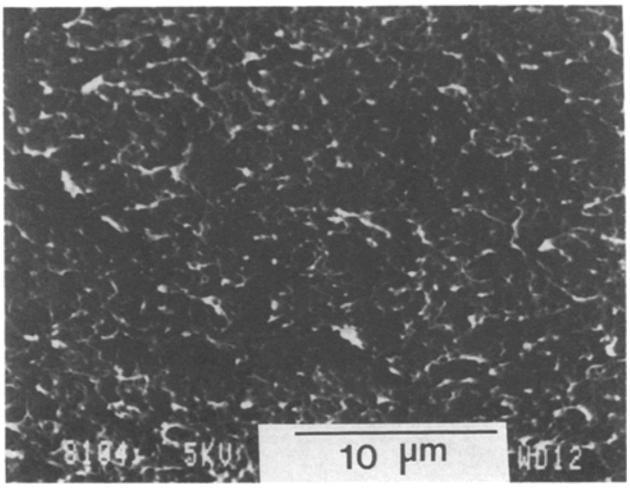

Figure 8 Blend with 20 wt % modifier: Detailed view of the deformation near the notch seen in Fig. 7. Note the orientation of the tips of the drawn and fractured matrix.

characteristics as that of the unmodified matrix. The surface is covered with brittle fracture bands whose orientation can be used to identify the crack propagation direction and the location of the initiation sites. Fig. 5 shows the features around one such initiation zone. From the orientation of the bands, it is clear that the main crack front propagates radially outward from the initiation site. In the event of more than one initiation site, the cracks propagate radially until either the various fronts impinge upon each other or the edges of the sample are reached. The average band width in this sample (10 wt % modifier) is smaller than that on the unmodified PMMA surface. This suggests that the presence of modifier helps to decrease the crack speed rapidly and thus facilitates early unification of the branch cracks prior to the formation of a new band. Unification is caused by the initiation of crazes from adjacent branch cracks and their propagation in a direction intermediate between the directions of these cracks. This direction is selected due to the high stress levels that are induced by the adjacent branch cracks. It was found that the uniformity of the bands decreases with increasing distance from the notch. It seems that as the crack increases in speed with the distance from the notch, the formation of branch crazes does not retard its progress enough to promote recombination of the resultant branch cracks.

Closer scrutiny of the bands in this sample reveals two additional facts. First, the structure of the bands and that of the minor crack fronts (formed by the fracture of the branch crazes) is essentially similar to that seen on PMMA surfaces. Second, the structure on the level of the "patches" left by the craze fracture process is substantially different from that seen in the unmodified matrix. This is clearly shown in Fig. 6, a view of the typical mackerel structure found in this sample. The modifier appears to have initiated some plastic deformation in the vicinity of each particle. This deformation is superimposed on what appears to be the usual mackerel structure. Thus, the modifier caused local deformation without inducing any substantial macroscopic morphological changes. This is in accordance with the results seen in the impact test. This micrograph clearly reveals the effect of single particles on the matrix as the concentration is low enough for the particles to be well separated.

The above observations show that crazing can occur even in a modified PMMA when the modifier loading is low. As is seen in Fig. 6, a large number of modifier particles are visible on the fracture surface. This is a natural consequence of the fact that the rubber particles cause stress concentration in the surrounding matrix when the sample is put under a tensile load. The high local stresses cause the matrix to undergo yielding at low applied loads and facilitate the drawing of the craze fibrils. When craze rupture occurs, the fibrils collapse around the rubber particles, leaving them exposed on the surface. From the locations of these particles on the surface, it appears that some of them were actually part of the fibril network.

Based on impact data, the first signs of any significant ductility are seen in the blend containing 20 wt % modifier. The standard deviation in the impact data is much greater than that in the data on the other blends in this study. These two observations combine to suggest that the fracture mechanism changes at or near this modifier concentration. The structure on the fracture surface seen in Fig. 7 further substantiates this conclusion. This is a view of the entire width of the fracture surface near the notch. The initially smooth texture changes to a rougher surface characteristic of brittle behaviour. It is clear that even on the rough surface, the edges of the facets are not as sharp as those seen on the previous surfaces.

It appears that the mode of crack initiation has changed dramatically with the increase in modifier concentration. Instead of radially propagating fronts initiated at one or more sites, the crack in this case appears to be composed of several fronts initiated on different planes all along the notch. The white, horizontally aligned features emanating from the notch are the junction lines that separate adjoining fronts. Although only one prominent junction line is seen near the middle of the notch, there are several small junction lines that are hinted at near the bottom of the

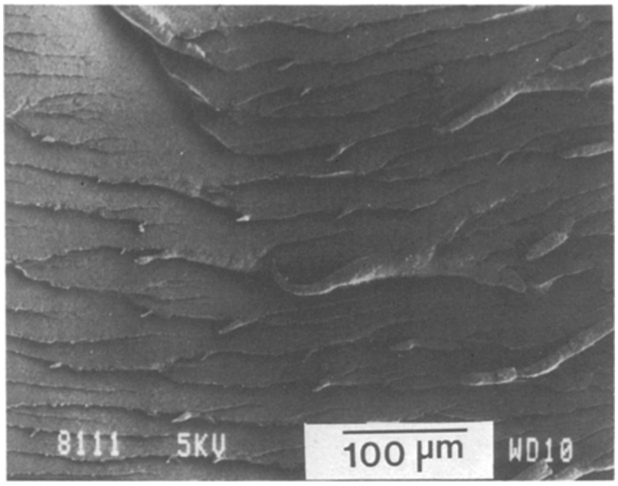

Figure 9 Blend with 20 wt % modifier: Propagation of several parallel crack fronts near the end furthest from the notch. The torn fibrils are all oriented away from the notch.

notch but are not clearly resolved at this magnification. Each of the crack fronts is itself planar except in the immediate proximity of the junction lines. Near these lines, adjacent fronts propagate towards each other although the overall propagation direction is away from the notch. The individual fronts finally coalesce into a single front near the vertical ridge. The velocity of the crack apparently increases rapidly after the formation of a uniform front because the surface texture changes dramatically very near the ridge.

From the above observations, it appears that the modifier content in this sample is sufficient to initiate substantial plastic deformation in the matrix in the early stages of the impact process. The resultant crack blunting prevents the early initiation of radially propagating crack fronts originating at heterogeneities on the notch. The cracks appear to have formed almost simultaneously all along the notch in independent fronts propagating perpendicularly to the notch (except near junction lines). Uniform initiation along the notch is suggested by the fact that the transition zone between the smooth and rough textures in Fig. 7 is approximately parallel to the notch. The

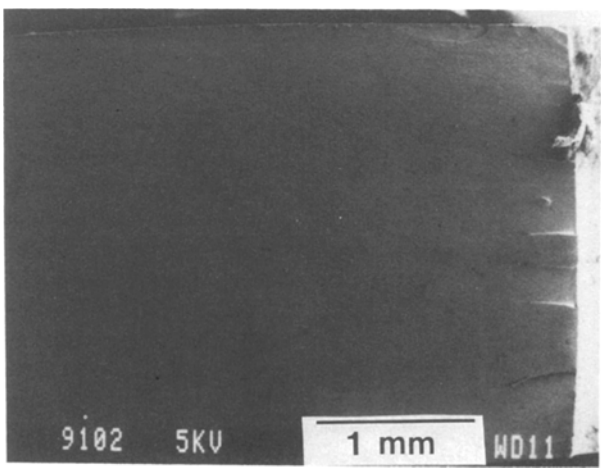

Figure 10 Blend with 30 wt % modifier: View of the entire width of the area near the notch. The smoothness of the surface is retained throughout the crack propagation process.

energy absorbed by plastic deformation in the early stages of the fracture process could be responsible for a major portion of the impact strength of this sample (also suggested by Milios *et al.* [6]). In that case, the size of the "smooth" region would correlate with the impact strength of the material. If this size varies from Izod bar to Izod bar, it would account for the large standard deviation in the impact strength of this particular blend.

Fig. 8 shows the details of the deformation around modifier particles in the area to the right of the vertical ridge seen in Fig. 7. The holes shown in the micrograph represent the positions occupied by particles that were removed by the fracture process. It seems that the crack propagates by fracturing the matrix around the particles. The particles are then distributed between the matching fracture surfaces and the surface should show both holes and particles. However, the particles are harder to see because the matrix relaxes from its elongated state and draws the particles into its surface layer. Even then some hints of particles are seen on the surface.

A large number of holes have the matrix drawn over them. The white areas are tips of the drawn and fractured matrix that is raised above the rest of the surface. The tips point away from the notch and in the crack propagation direction. It was found that the matrix on the matching fracture surface was also drawn away from the notch. This seems to eliminate the possibility that fracture occurred in a shear mode because neither surface shows stretched fibrils pointing towards the notch. Thus, fracture occurred through a tearing mechanism activated by the tensile stresses applied during the impact process.

A study of the region that underwent rapid fracture reveals that the crack front undergoes the splitting and recombination processes characteristic of brittle behaviour. However, this phenomenon is modified by the local energy absorption processes initiated by the modifier particles. It is found that the drawing of the matrix in this area is perceptible but not as extensive as that seen in the vicinity of the notch. The crack speed continues to rise with the distance from the notch as seen in Fig. 9. This is a view of the region furthest from the notch. The crack speed is high enough to cause the front to split into several parallel fronts. However, the splitting process does not absorb enough energy to slow the crack and thus recombination is not favoured. The torn fibrils point away from the notch, while those on the matching surface were found to point towards the notch. This seems to suggest that the fracture in this region occurred in a shear mode. Thus, the Izod bar fails in tension until almost the end where it fails in shear.

The fracture behaviour of the blend containing 30 wt % modifier resembles that of the above blend in its initiation characteristics. This is seen in Fig. 10. However, in contrast with Fig. 7, this surface retains its apparent smoothness at low magnifications until the end of the fracture process. The incremental amount of modifier suffices to keep the crack speed from increasing to the point where the material fractures in a brittle manner. On the scale of single

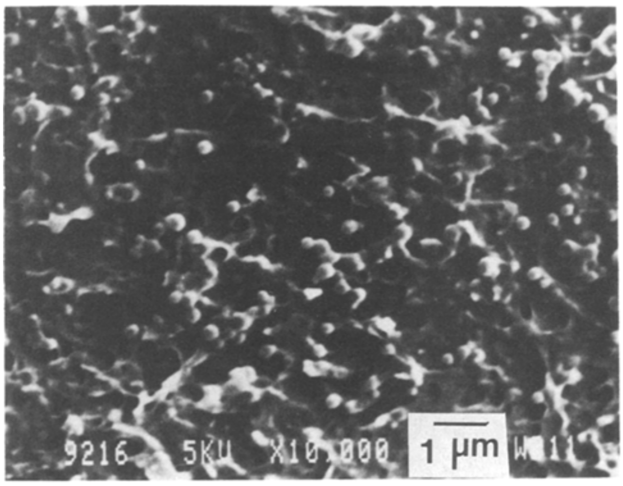

Figure 11 Blend with 30 wt % modifier: Deformation caused by the fracture process. The drawn matrix is seen along with some of the attached modifier particles.

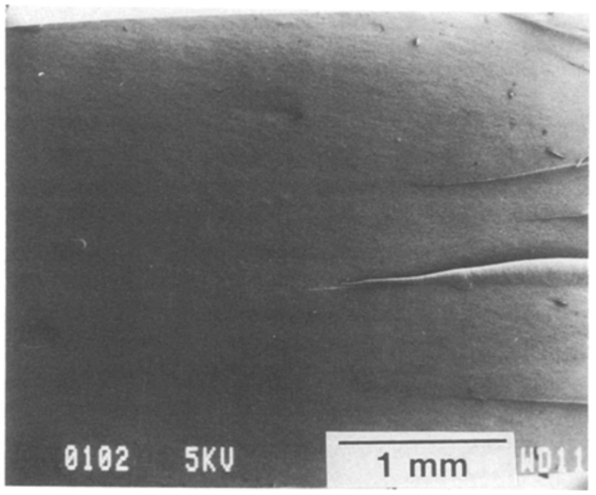

Figure 12 Blend with 40 wt % modifier: Region near the notch. Note similarity with Fig. 10 and the presence of parabolic features aligned with the direction of crack propagation.

particles, the deformation is similar to that seen in the previous blend except that it is more widespread as the number of particles is larger in the present case. Fig. 11 is a view of the deformation on the surface. The drawing of the matrix is clearly seen. In addition, this micrograph reveals the presence of nodules which could either be modifier particles attached to the matrix or the melted ends of fractured matrix fibrils [11].

The only other change seen by increasing the modifier concentration is the presence of a number of parabolic features on the fracture surface. Such a feature is said to be caused by the interaction of a radially propagating secondary crack front with the main crack front [12]. In this sample, the originating heterogeneity was found to be inorganic in most of the cases.

Increasing the modifier content to 40 wt % does not promote any change in the basic fracture mechanism. As seen in Fig. 12, the individual crack fronts emanating from the notch propagate even further before coalescing into a single entity. This is an indication that the blend absorbs more energy than any of the previous materials in the early stages of the propagation process. No substantial change was seen in the deformation around individual particles. Again, several parabolic features were seen on the fracture surface.

4. Conclusions

Crack initiation in PMMA and the blend with 10 % modifier occurs through the rupture of crazes created by the tensile stress fields imposed on the sample during the impact test. The propagation step involves the repetitive growth and failure of branch crazes nucleated at the tip of the existing crack front. The crack speed increases with the length of the crack but undergoes oscillations during the branching process. In the case of the rubber-modified blend, the modifier participates in the crazing process and promotes some local plastic deformation.

Increasing the modifier content to 20 wt % causes the first significant changes to occur in the fracture mechanism. In the initial stages of the propagation process, band formation is suppressed by the crack blunting caused by the plastic deformation around modifier particles. However, as the crack progresses, it accelerates and the strain rate increases. This in turn increases the yield stress of the matrix and reduces its ability to absorb energy. The crack speed increases further until brittle behaviour becomes dominant.

There is one other important difference between this blend and the previous materials. The initiation process changes from a localized phenomenon to one that appears to occur all along the notch. It is probable that the first step in the impact process is elastic and plastic deformation followed by widespread crack initiation in stress-concentrated zones in the root of the notch. The stress concentration may be due to material heterogenieties or those created by the notching process.

The improvement in impact strength with a further increase in modifier concentration may be attributed to an increase in the number of stress concentration sites and the related decrease in interparticle distance. The effect of the increase in the number of such sites is obvious. A decrease in the interparticle distance allows significant overlap between the stress concentration fields due to neighbouring particles. This in turn creates matrix zones where the stress concentration is even higher than that seen in the immediate vicinity of isolated particles, thus allowing yielding to commence at even lower applied stresses. These factors are influential in the promotion of increased plastic deformation, probably in the form of shear yielding.

From the above discussion, it is clear that crazing does occur in PMMA and rubber-modified blends with low particle concentrations. In blends with intermediate concentrations, crazing may be expected to occur only in the later stages of the fracture process when the crack speed reaches a critical value. In the blends with high modifier concentrations, no obvious signs of crazing are found although a significant amount of plastic deformation is seen on the surface.

The absence of crazing in these latter blends has also been reported by Bucknall *et al.* [5]

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