

Mechanism of Reinforcement in Rubber-Modified Polystyrene Systems Studied by Use of a Miniature Dart Drop Test

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Synopsis

A miniature dart drop test was used in a study of the mechanism of reinforcement in impact resistant rubber-modified polystyrene. A typical SBR-polystyrene system was diluted with varying amounts of polystyrene, and thin compression moldings were made from each blend. The impact-whitened areas were observed directly under the microscope and photomicrographs are presented. The whitening is caused by scattering of light from interfacial separation of portions of many rubber particles from polystyrene and by formation of a multitude of microcracks and/or crazes, starting at the partially separated particles. The absorption of energy by this mechanism can be very large. The driving force for the initial separation appears to be the triaxial tension under which the rubber particles exist, and this results from the higher volume shrinkage rate of rubber compared to that of polystyrene. Included also are photomicrographs taken of specimens after tensile stretching, and the mechanism derived from the impact case is extended to explain the increased elongation and corresponding whitening.

Introduction

Rubber-modified polystyrene products are sold in large volume, but relatively little fundamental work has been published on the reason why rubber particles give impact strength to a brittle polymer. Several comprehensive studies of these systems have appeared,¹⁻³ and they show that there is no general agreement on the mechanism. One approach is that of Schmitt and Keskkula⁴ in which they suggest that the rubber particles do not stop cracks from growing, as previously taught, but rather promote the growth of many energy-absorbing microcracks. Bucknall and Smith⁵ have recently used a similar explanation, but with the added idea that "crazes" rather than "cracks" develop. This paper will describe a specific approach which supports and extends the conclusions of Schmitt and Keskkula.

Their proposed mechanism was supported by a phase-contrast photomicrograph showing fine cracks in the polystyrene matrix radiating from the rubber particles. A valid criticism of this evidence (as well as for that in some of the other published works) is that it does not represent the actual impact situation because the specimen had been loaded in tension rather

than subjected to an impact blow. More important, the specimen was a microtomed slice, $2\ \mu$ thick, in which many of the rubber particles had been cut through, so that they were not in their normal state, i.e., surrounded entirely by the continuous polystyrene phase. To overcome these objections, thicker specimens and an impact type test are necessary. Thicker samples can be made easily, but overlapping of rubber particles interferes with the microscopical observation of fine structure. Another problem is that quite often the process of microtoming itself introduces cracks. The solution of these problems was accomplished by diluting the polystyrene-rubber system with polystyrene. In this way, overlapping of particles was minimized so that molded specimens of about 5 mils thickness could be tested and viewed directly without slicing thinner sections.

A miniature dart drop test was devised in order to subject each specimen to an impact blow. This test has been referred to by Turley.⁶ A test of this type has a more specific meaning than other types for the study of the mechanism of impact reinforcement. In many of the tests which have been used, the energy to fracture a specimen is measured and related to the mechanism. It is more logical that the test not break the specimen, because the important thing is what happens to the energy when an impact blow is sustained without producing fracture. In this respect, the purely nondestructive test of low energy, e.g., dynamic mechanical or dielectrical, may also not be adequate. If the mechanism of reinforcement does involve any kind of crazing or cracking or separation at interfaces, then the test used must produce these phenomena in order to be completely valid. This is not meant to imply, however, that other types of energy absorption or reflection mechanisms do not also play a part in the total mechanism.

The general approach for this study, then, consisted of diluting an impact grade polystyrene-rubber product with polystyrene, molding the blends into thin specimens, subjecting these to a miniature dart drop test, and observing the changes in fine structure under the microscope. The microscopical evidence indicates a dual reinforcement mechanism involving the absorption of energy by separation at interfaces and by crack and/or craze formation. Speculation about the forces behind these changes is included.

In the following discussion, the term crack rather than craze is used exclusively. The crazes which develop in many polymers when subjected to tensile forces have been shown to contain craze matter.^{7,8} Whether the same is true of the areas of reflected light developed under impact conditions cannot be determined from this study. Regardless of whether these areas contain craze matter or are true cracks, much energy would be absorbed by their formation so that the general mechanism remains valid. It is likely that both crazes and microcracks occur.

Experimental

An impact grade rubber-modified polystyrene made by polymerizing a rubber-styrene solution was chosen for the base material. It contained about 5% of a 70/30 butadiene-styrene copolymer, although the reinforcing

particles occupy nearly 25% of the volume of the system because they contain droplets of polystyrene. Clear polystyrene resin was mixed with this product so that the blends contained 10, 20, 30, 40, and 50% of the base plastic. An excellent way to blend small quantities (6-8 g.) of polymers is with the capillary melt viscometer described by Karam.⁹ Under heat and nitrogen, the charge was passed back and forth through the capillary opening any desired number of times. The thoroughness of mixing as a function of the number of passes was first determined by blending a few pellets of color concentrate into a polymer. A small amount of each blend and each of the base materials was compression molded into a thin sheet averaging about 5 mils in thickness.

The miniature dart drop test consisted at first of a 2-in. piece of No. 18 copper wire with rounded end dropped from a height of 8 in., a glass tube being used for a guide. Later, it was found that commercial sewing needles, which are available in many sizes, make inexpensive, very durable darts when dropped eye end down. An electromagnet encircling the glass tube at the top holds the needle until the switch is opened. To avoid repeated striking of the sample in one area, either the sample or the bottom end of the guide tube is moved quickly after the first bounce of the dart.

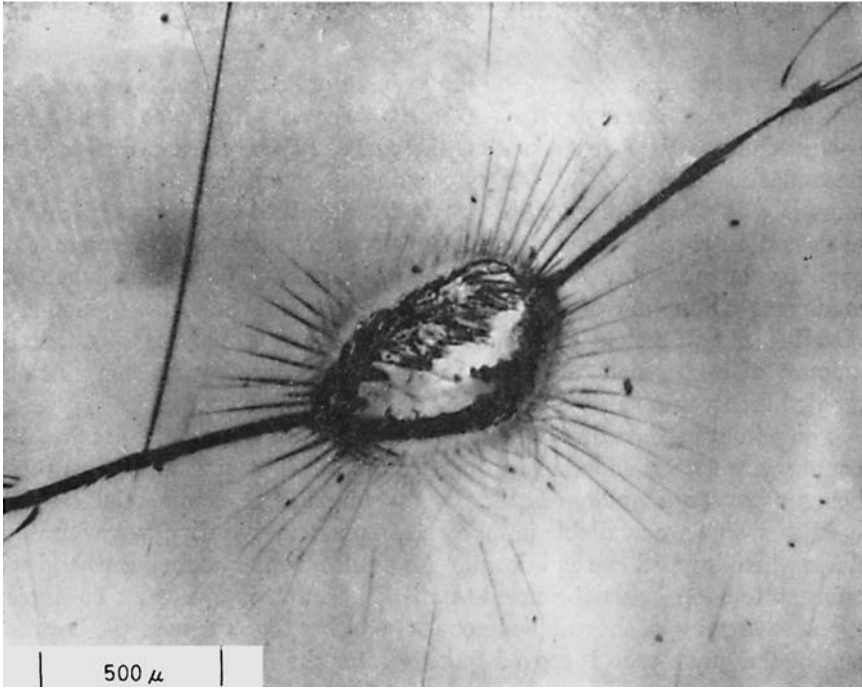
Each specimen was approximately a 1.5×1.5 cm. piece of the 5-mil thick sheet described above. A glass microscope slide was used to support the sample during the test; otherwise, the dart would sometimes penetrate the sample. This makes the test qualitative, but it could be refined quite easily to give a quantitative measure of impact strengths. For example, either the dart height or weight can be adjusted, and the specimen temperature can be controlled with relatively simple equipment.

The whitened areas around the impact zone of each sample was viewed under the microscope under ordinary lighting. Phase-contrast methods were not needed, because the cracks and interface separations were readily visible. These appear white against a dark background by reflected light, and dark against a light background by transmitted light. All the photomicrographs shown were taken by transmitted light because the features stand out more clearly than under reflected light, where glare often obscured the fine structure.

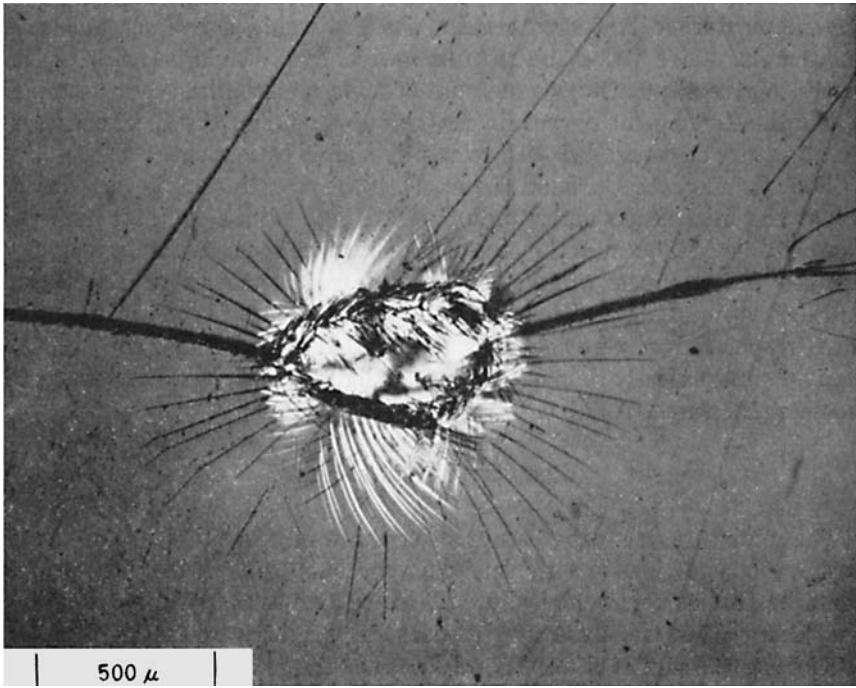
Results and Discussion

The miniature dart drop test used for this study was designed to apply an impact type blow to a thin polymer specimen so that the impact area could be studied microscopically. There was no attempt to measure the dart energy, but the same weight and drop height were used for all the specimens. This was chosen by trial so that the pure polystyrene sample developed rupture-type cracks, while the blends containing the higher amounts of rubber did not.

The polystyrene sample after impact is shown in Figure 1a. A rupture crack extends out from each end of the elongated impact area. These

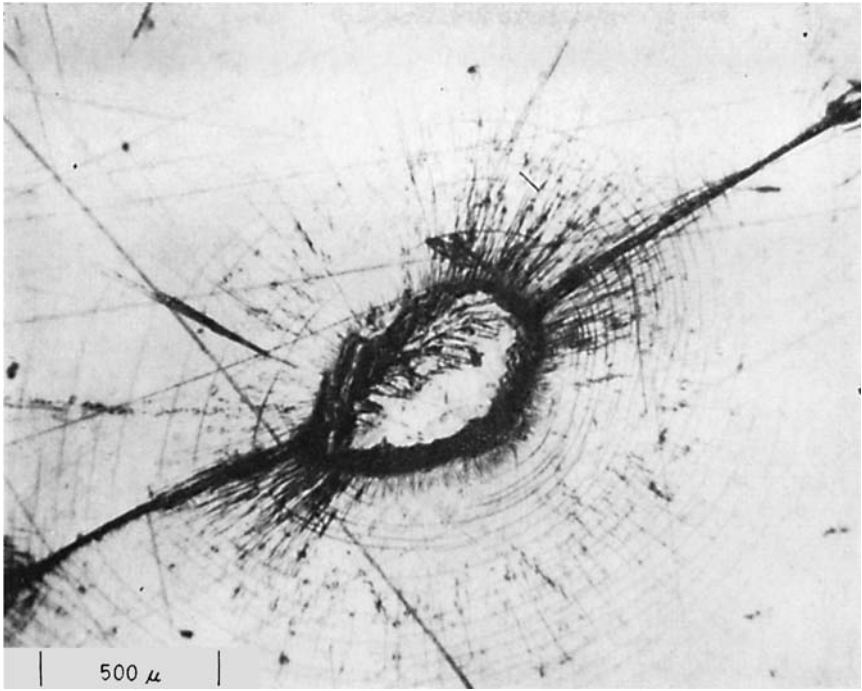


(a)

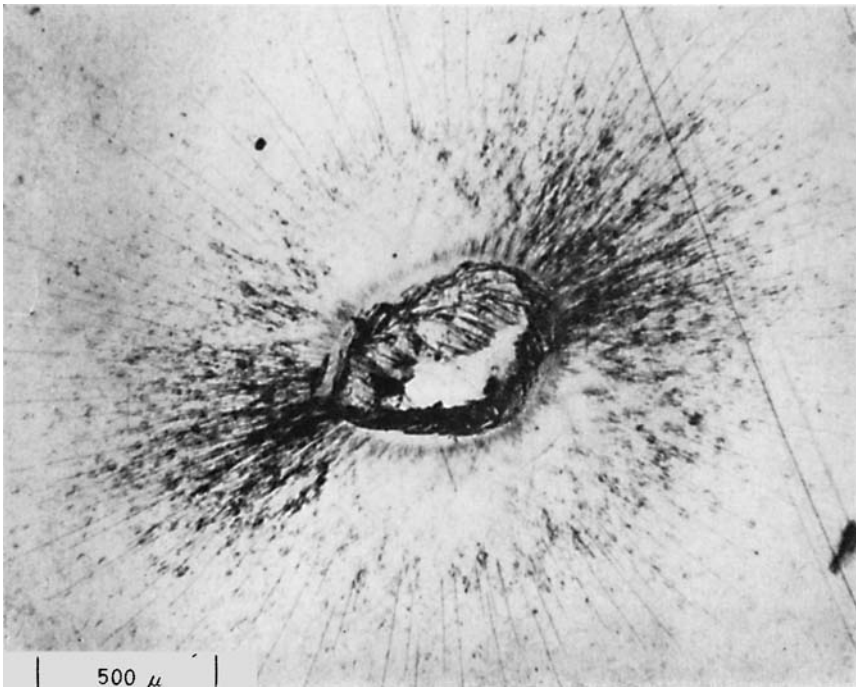


(b)

Fig. 1. Photomicrographs of the impact area on polystyrene: (a) by transmitted light and (b) under partly crossed polarizers.

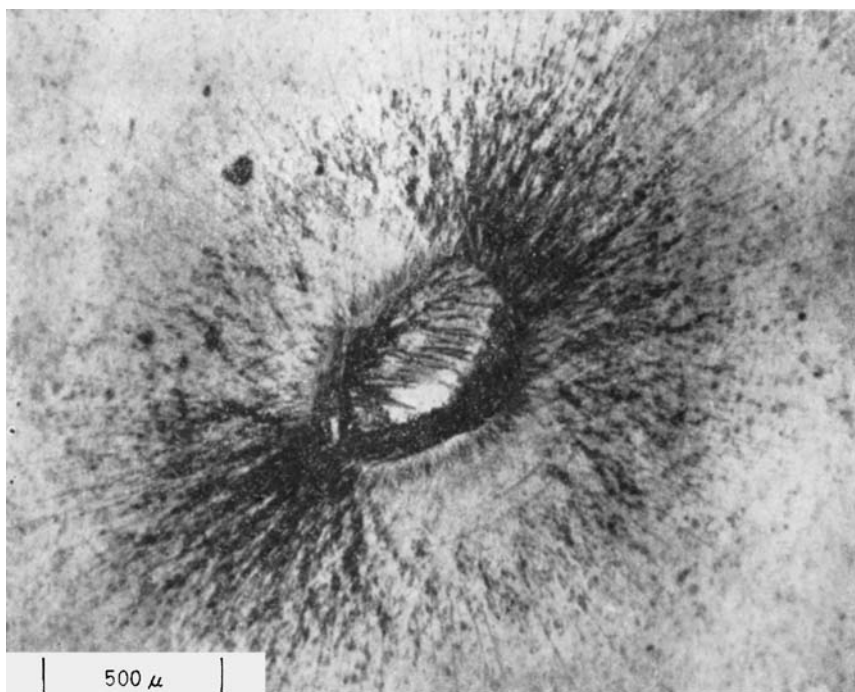


(a)

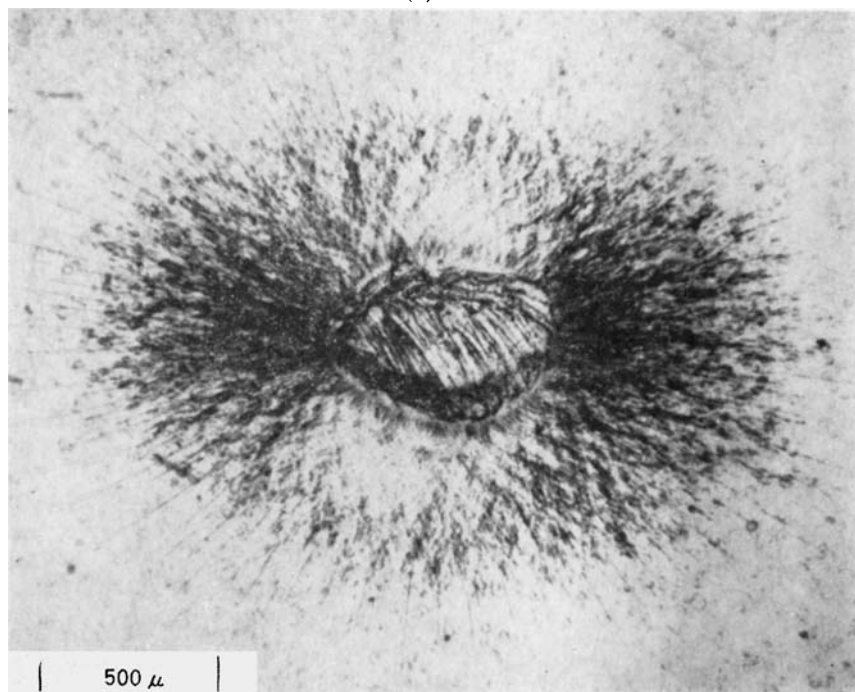


(b)

Fig. 2. Photomicrographs of the impact area on rubber-modified polystyrene diluted with polystyrene: (a) 10% and (b) 20% rubber-modified polystyrene.

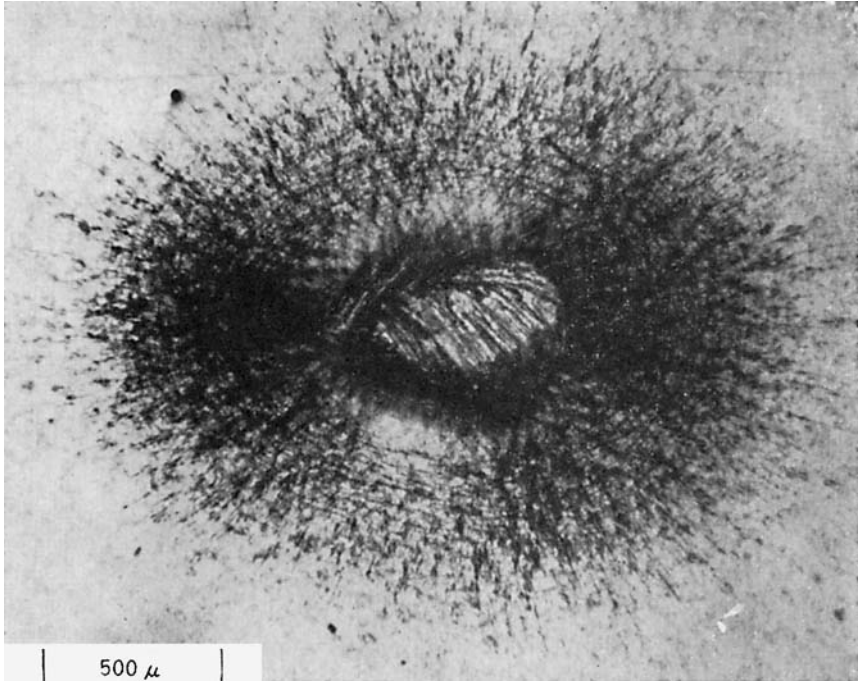


(a)

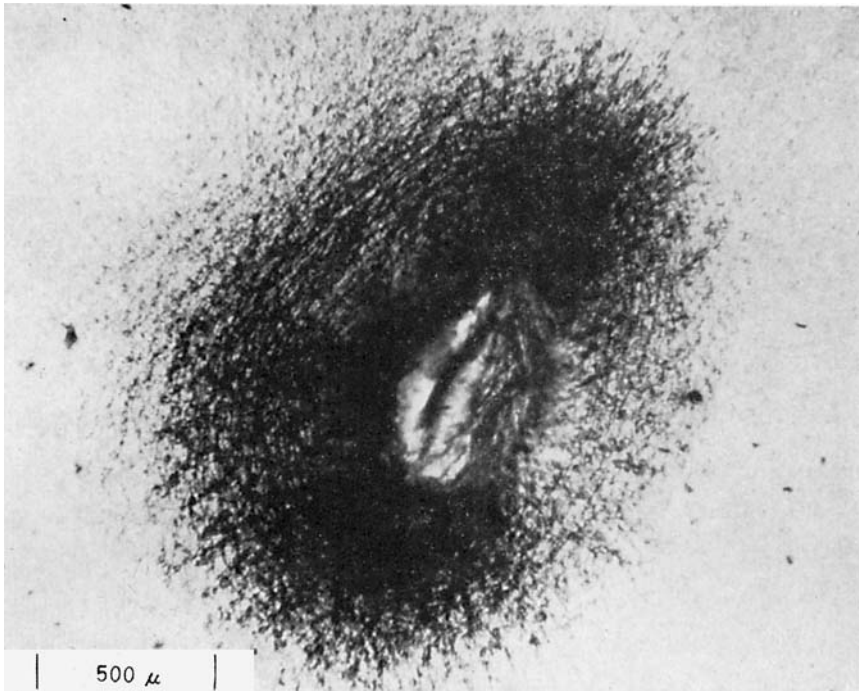


(b)

Fig. 3. Photomicrographs of the impact area on rubber-modified polystyrene diluted with polystyrene: (a) 30% and (b) 40% rubber-modified polystyrene.

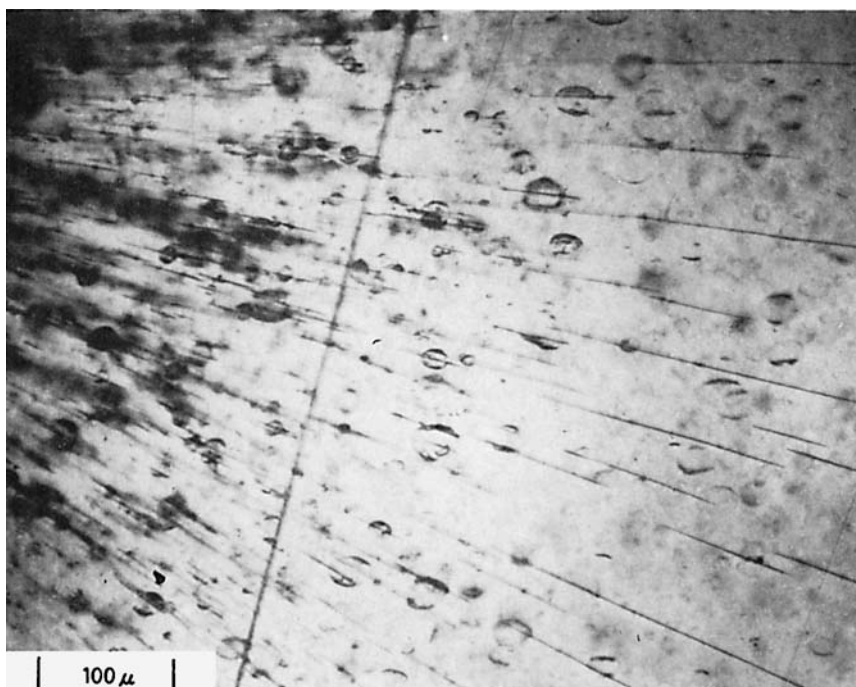


(a)

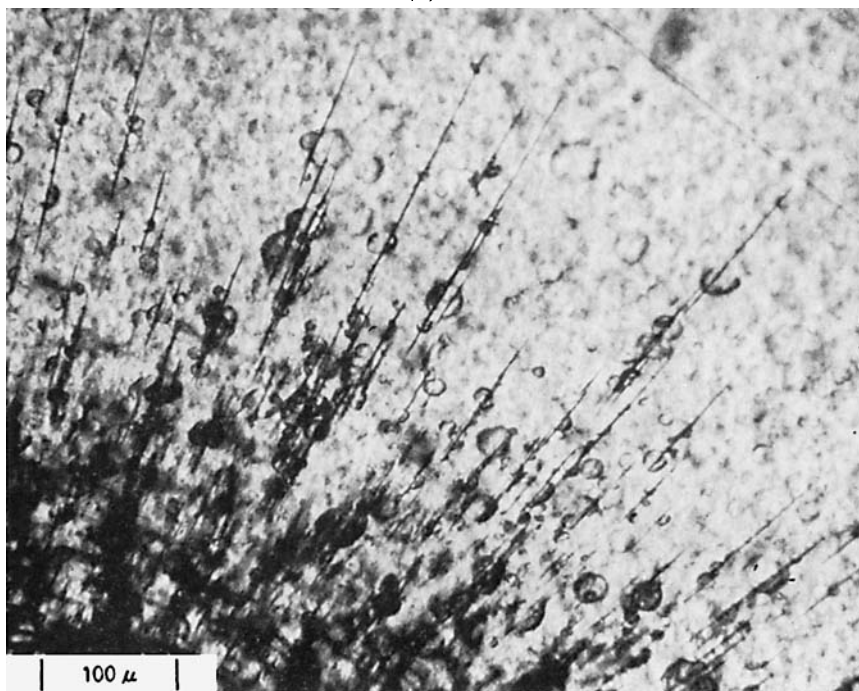


(b)

Fig. 4. Photomicrographs of the impact area on rubber-modified polystyrene diluted with polystyrene: (a) 50% and (b) 100% rubber-modified polystyrene.

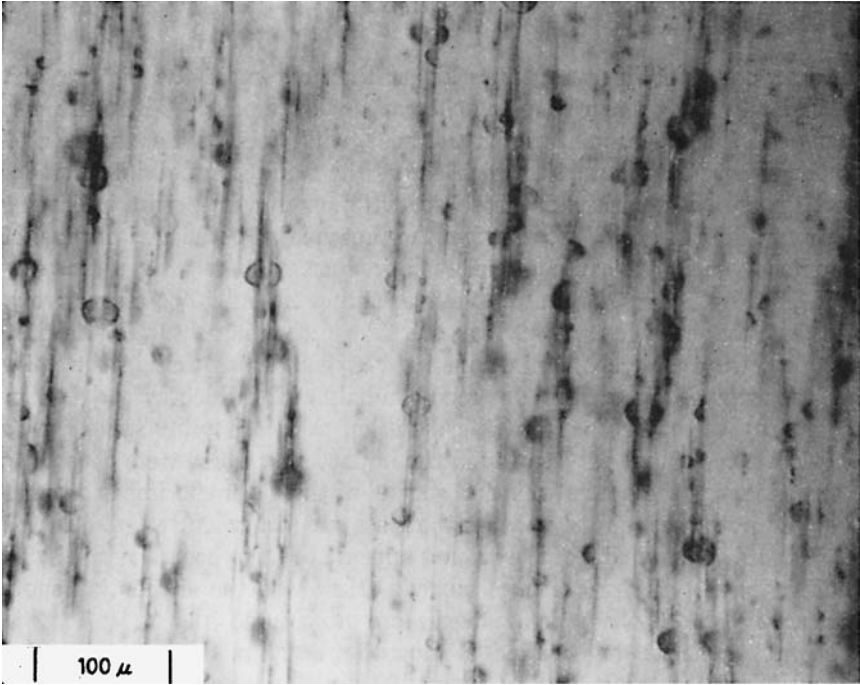


(a)

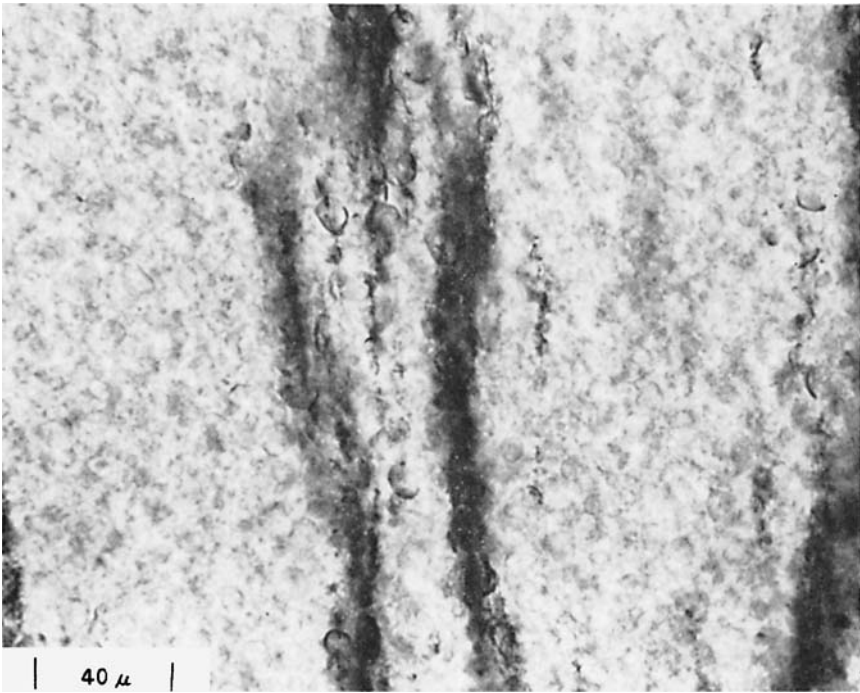


(b)

Fig. 5. Photomicrographs of the outer edge of the impact area on rubber-modified polystyrene diluted with polystyrene: (a) 20% and (b) 50% rubber-modified polystyrene.



(a)



(b)

Fig. 6. Photomicrographs of stretched specimens: (a) 10% rubber-modified polystyrene (SBR rubber) and (b) 100% rubber-modified polystyrene (polybutadiene).

cracks were actually many times longer than shown in the picture, and periodically along them were bunches of smaller cracks. There are also many short cracks around the impact zone, while fainter lines can be seen at the sides. In Figure 1*b*, which shows the same sample viewed under partially crossed polarized filters, these faint lines are very bright, indicating a strong birefringence. This shows the presence of unrelieved strains, of insufficient energy to cause a true crack or craze.

In Figures 2*a* and 2*b*, the samples containing 10 and 20%, respectively, of the rubber-modified polystyrene are shown after impact. In the 10% sample, a rupture crack again appears, very similar to that in the polystyrene sample. There are also many radial cracks which extend farther out than those of Figure 1, and, in addition, there are many spots. Also visible are concentric cracks around the impact area which were caused by a stretching by the dart of this and several of the other specimens because they did not lie completely flat on the glass support when tested. In the 20% sample, the energy of the impact appears to have been absorbed well enough that no rupture crack occurred. However, the cracks and spots observed in the 10% sample are even more prominent.

Figures 3*a* and 3*b* and 4*a* and 4*b* show the results of the impact test on the samples containing 30, 40, 50, and 100% rubber-modified polystyrene, respectively. The number of cracks increase progressively, but they become shorter, while the relative numbers of dark spots increase dramatically. To the unaided eye, or by reflected light microscopy, the amount of whitening also progressively increases.

The specimens containing 20 and 50% of the base rubber-modified polystyrene were photographed at higher magnification in order to observe better the fine features of this whitening effect. These pictures are shown in Figures 5*a* and 5*b*. Two features stand out, i.e., short radial cracks and rubber particles made visible by partial separation from the polystyrene. In the 20% sample, the longer cracks are farthest from the center, and do not appear to be associated with the separated rubber particles, but the shorter ones are. In fact, the shorter cracks appear to start at rubber particles which have partially broken from the matrix. There are also many rubber particles which have one or more small areas separated from the polystyrene with no visible crack associated with them. Similar features are seen in the 50% diluted specimen (Fig. 5*b*), but the overall density of partly visible or separated rubber particles is higher, while the number and lengths of the cracks are decreased. Also, each of the cracks appears to be associated with a partly separated rubber particle.

The series of photographs shown in Figures 1–5 show that separation of portions of the rubber particles, as well as crack formation, are associated with impacts on rubber-modified polystyrene. These phenomena probably are not only associated with, but are likely to be the main causes of the impact strength, because much more energy is absorbed than would be by one large rupture crack. The role of the rubber particle is to present a weakness to an applied force so that microseparations and microcracks

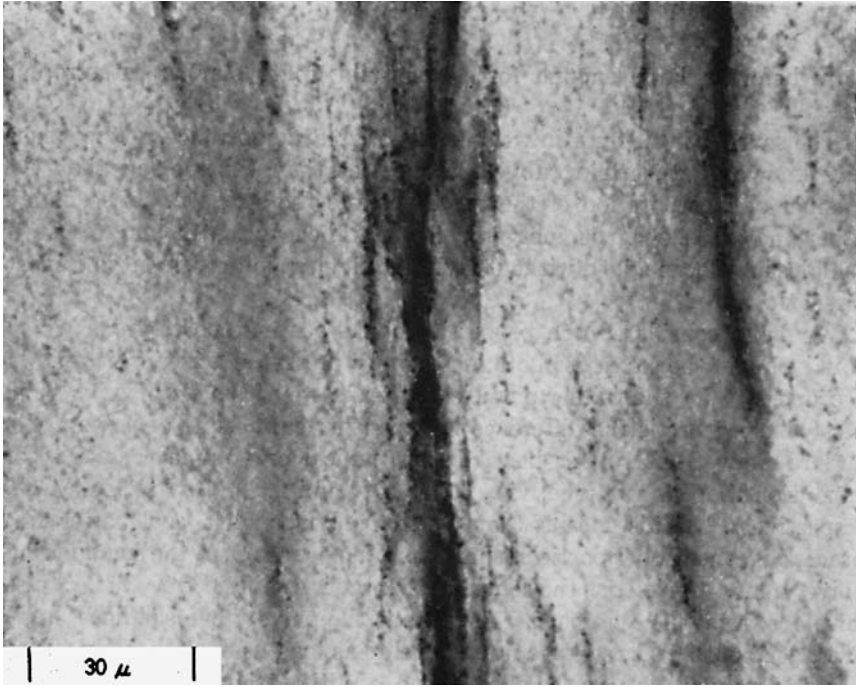
form before a large enough force can build up to start a catastrophic crack.

The source of this built-in weakness is of great importance. It is generally known that certain rubbers are better than others, and that the manner of incorporation of the rubber affects the strength. Also, many other materials such as inorganic fillers, other polymers and even air bubbles have been added without giving equivalent improvement in impact strength.

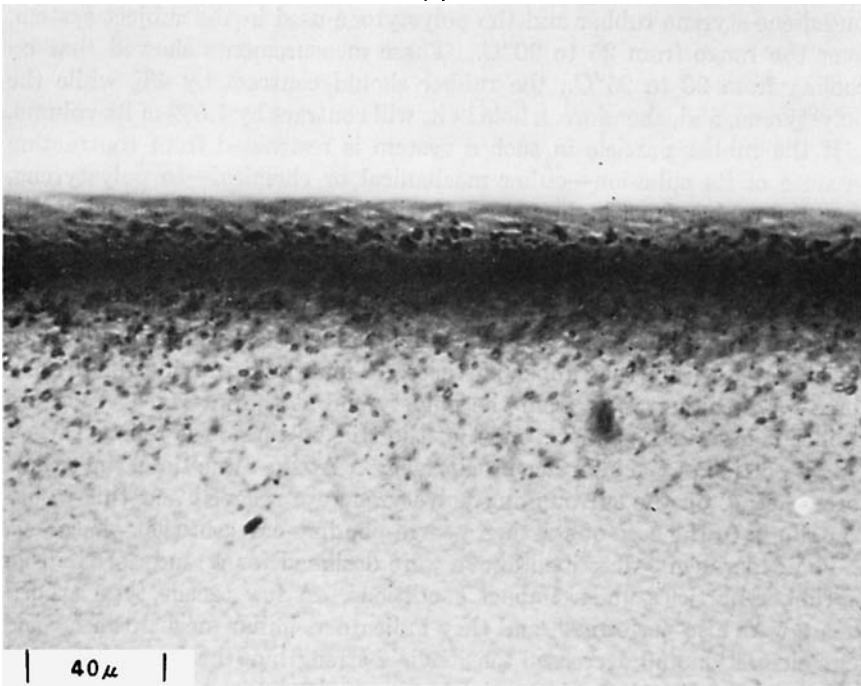
We have considered the properties of rubber and polystyrene which could explain the series of photomicrographs presented above which imply a propensity for the rubber particle to break away from its matrix. The most likely cause is the difference in expansion coefficients of polystyrene and rubber. SBR rubber has a larger cubical or volume coefficient of expansion than polystyrene, viz., 66×10^{-5} and 27×10^{-5} in.³/in.³/°C., respectively.¹⁰ This means that as the polymer melt cools after hot processing, the rubber particles shrink at a faster rate than the surrounding polystyrene. As long as the continuous phase is semifluid, very little stress develops from this difference. As soon as the polystyrene solidifies, however, at about 90°C., stresses must develop as long as the rubber particles remain firmly adhered to the polystyrene. With a standard mercury-filled dilatometer we measured separately the total volume expansion of the butadiene-styrene rubber and the polystyrene used in the subject system, over the range from 25 to 90°C. These measurements showed that on cooling from 90 to 25°C., the rubber should contract by 4% while the polystyrene, and, therefore, a hole in it, will contract by 1.5% of its volume.

If the rubber particle in such a system is restrained from contracting because of its adhesion—either mechanical or chemical—to polystyrene, then the rubber must be in a state of triaxial tension under normal conditions. The actual amount of this tension cannot be measured conveniently, but it might be calculated if the coefficient of volume extensibility were known for the rubber. A rough calculation from compressibility data and the contraction differences gives a possible value of several thousand psi of tensile force within the rubber particles. This would provide the driving force for breaking away from the polystyrene at the interface. Because rubber is not rigid at 25°C., most of the triaxial tension is relieved when only a portion of the interface breaks away. At the same time, the tensile forces acting on the surrounding polystyrene are relieved and this would contribute to the ease of starting a corresponding crack in that phase.

The experiments described above were designed for a study of the role of rubber particles under impact conditions. A few tensile type experiments were also performed, and they indicate a similar mechanism for the high elongation and decreased tensile yield strength of the rubber-modified polystyrene. Figure 6*a* shows the results of slowly stretching, in a small jig, the 10% rubber-modified system described earlier. Partly separated rubber particles associated with cracks are prominent. Similarly, Figure 6*b* shows the results of the same test applied to a system, undiluted, containing



(a)



(b)

Fig. 7. Photomicrographs of: (a) mechanically blended rubber-modified polystyrene, stretched and (b) cut edge of polyethylene-polyisobutylene blend.

polybutadiene as the rubber phase. The separation of portions of the rubber particles is very evident. No microcracks can be seen, although they could be present, but obscured.

In Figure 7a is the corresponding picture of another type of rubber-modified polystyrene. This sample was made by mechanically blending a crosslinked SBR-type rubber into polystyrene. The rubber particles are somewhat smaller, and their adhesion to the polystyrene phase is much less than in the system made by polymerizing a rubber-styrene solution. Separation of particles from the matrix appears to be, again, an important feature of the whitening. Figure 7b shows the cut edge of a polyethylene-polybutylene rubber mixture. This system has much improved tear resistance over the unmodified polyethylene. The dark spots are the result of phase separation of rubber from the continuous polyethylene.

For these latter examples, it is suggested that a mechanism similar to that proposed for impact reinforcement is involved. Thus, each rubber particle is prone to break away from its matrix because of triaxial tension forces built up by differences in contraction on cooling from the melt, but is prevented from doing so because of its adhesion to that matrix. When an excessive force is applied, separation occurs and an associated crack may start. This multiple stress relief mechanism prevents the building up of sufficient strain energy to promote catastrophic crack growth. An explanation of how multiple short crack formation can lead to high elongation is given by Nielsen.¹¹

Conclusion

The mechanism for the reinforcement of rubber-modified polystyrene as presented in this paper is not meant to be exclusive of others. It was pointed out in the earlier work⁴ that there must be several contributing mechanisms for the absorption and reflection of the energy of impact. However, a large amount of energy can be used up in making the multitude of phase separations and short cracks, so that this is likely to be the major contribution to reinforcement.

There are a number of other rubber-modified rigid polymer systems and the techniques of dilution and use of a miniature dart drop test might well be applied to them. Whitening of these materials on impact is quite common, so that the proposed mechanism may be fairly general. However, the small size of the particles in some systems (e.g., generally less than 1μ in the ABS polymers) is a limiting factor in the use of optical methods, and it is difficult to apply electron microscopy to these phenomena.

The author thanks Dr. Henno Keskkula for the many discussions and support of this approach, Mr. P. A. Traylor for the photography, and Professor E. H. Andrews, Queen Mary College, London, for the discussion and encouragement to publish.

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Received July 12, 1967

Resubmitted August 11, 1967