

Microstructure of Some Rubber-Reinforced Polystyrenes

HENNO KESKKULA and P. A. TRAYLOR,
The Dow Chemical Company, Midland, Michigan

Synopsis

An electron-microscope technique is presented to permit detailed examination of the fine structure of the rubber particles in reinforced polystyrenes. Several rubber-modified polystyrenes, prepared by different methods, have been examined by this technique, and the resulting photomicrographs compared with those of the previously used phase contrast method. Polymers produced by the agitated-solution process are examined in more detail. It is shown that the rubber particle fine structure is basically unaltered as the amount or type of rubber is changed or if the polymer is diluted by mechanically blending with polystyrene. It is characterized by the presence of numerous polystyrene occlusions within the particle.

INTRODUCTION

Phase-contrast microscopy has been used extensively for some time to identify and characterize rubber-modified polymers.¹⁻⁵ Even though its use has afforded many new insights into the morphology of high-impact polystyrene, phase-contrast microscopy does not permit sufficient resolution for detailed study of the inner structure of the reinforcing particle, nor is it particularly useful as the rubber particle diameter becomes less than 1 μ .

Accordingly, the purposes of this paper are to introduce an electron-microscopy technique which provides improved resolution and to indicate some of its applications. Since the undertaking of the majority of the present work, another electron-microscopy technique has been reported⁶ which also shows a major improvement over previous techniques.

EXPERIMENTAL

Phase-Contrast Microscopy

The method used in the present study has been reported earlier.¹ Dark-phase contrast microscopy shows those portions of the specimen having lower refractive index as lighter than the background. Accordingly, rubber will appear light and polystyrene dark in the phase-contrast photomicrographs presented in this paper.

Electron Microscopy

A molded polymer, usually prepared by compression molding, is carefully polished by cutting, or planing, with a glass knife. The polished surface is then exposed to a solvent vapor, e.g., boiling isopropanol. A short exposure causes the polystyrene at the surface to become more swollen and etched than the rubber phase. The differential response to the alcohol produces a surface which, when examined, reveals the details of the rubber particle to a high degree of resolution.

The specimen for viewing in an electron microscope is obtained by using a double replicating method of the solvent-vapor-treated surface. A thin coating of poly(vinyl alcohol) (PVA, Elvanol, Grade 51-05) is deposited from a 15% solution to form the first replica. After careful drying in a dust-free atmosphere, the replica is removed from the polymer surface and fastened face upwards onto a microscope slide. This replica is then moved into a metal evaporator where carbon and platinum are simultaneously evaporated over its surface, producing the final replica.

The carbon-coated PVA film is now carefully cut into 0.3-cm. square pieces and dropped onto the surface of a 60°C. water bath, with the PVA side resting on the water. After the PVA has been dissolved, a water rinse follows and the platinum shadowed carbon film is taken up on a specimen grid and dried before examination in the electron microscope.

DISCUSSION

There are principally two methods for preparing rubber-modified polymers.^{5,7,8} The first method involves polymerization of a monomer, e.g., styrene, solution of rubber. In this method, shearing agitation of the polymerizing mass is required, particularly during the phase inversion,⁹⁻¹² in order to achieve desirable morphology and mechanical and flow behavior.¹³ The second method involves an intimate mixture of a rubber or grafted rubber (emulsion, prepared separately or *in situ*) with a rigid polymer.

It is of some interest to examine the morphology of some of the rubber-reinforced polymers and to examine the rubber particle in some detail.

Mechanically Blended Polymers

The morphological difference between a mechanically blended rubber-polystyrene and a solution product was reported by Claver and Merz.² They observed that the particle size in a mechanical blend varied with the amount of thermomechanical working. Accordingly, a variety of particle sizes, shapes, and distributions can be obtained as different raw materials, and different amounts of shear are used during the mixing operation.

The rubber particles in mechanical blends of rubber and polystyrene (Fig. 1) appear to be solid and not to contain distinct rigid polymer occlusions. Such rubber particles tend to be irregular and seldom have a round cross-section.

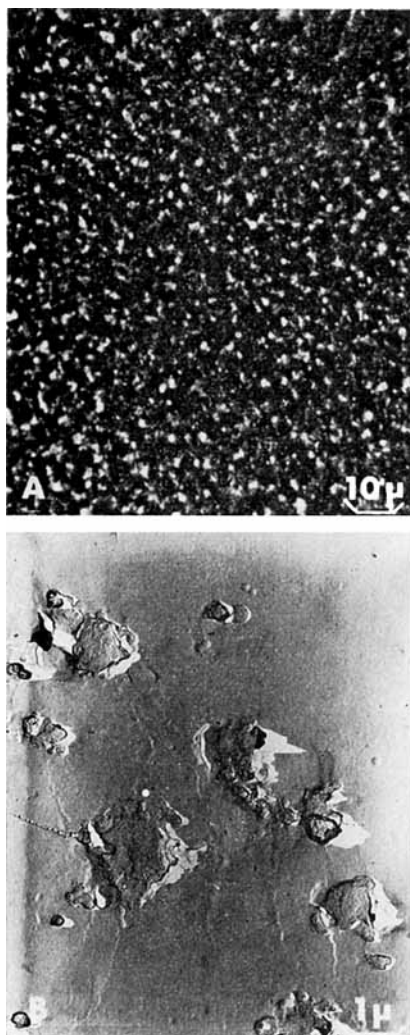


Fig. 1. Mechanically blended butadiene-styrene copolymer rubber and polystyrene: (A) phase-contrast photomicrograph (rubber phase white); (B) electron photomicrograph (rubber is the material which appears to project above the polystyrene background plane).

Emulsion-blended polymers would tend to give rise to more uniformly round particles, but without the distinct occlusions¹⁰ of the rigid polymer phase inside the rubber particles.

Polymer by Solution Process

Non-Agitated Polymerization. When a styrene solution of rubber is polymerized isothermally to completion without agitation, the resulting polymer is one which swells without completely dissolving in the common solvents.¹³ Such a product can be sufficiently masticated to give moldings

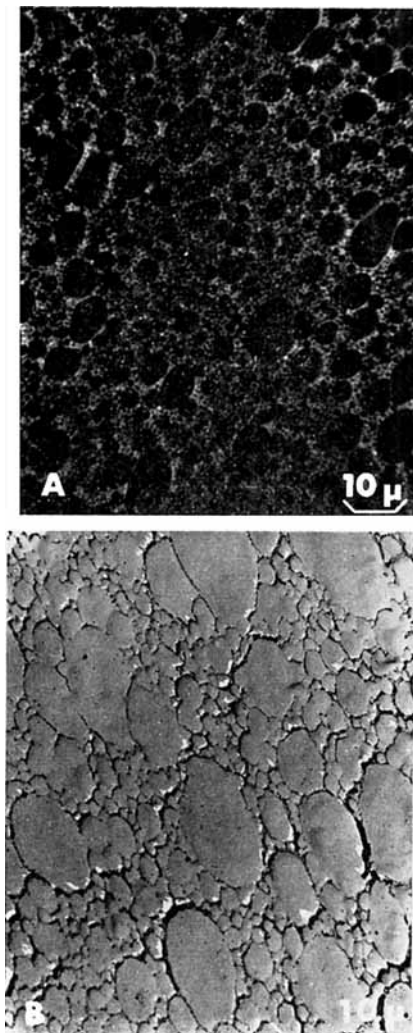


Fig. 2 See caption, p. 2365.

and extrusions. However, these fabricated pieces contain blemishes and imperfections which make such a product undesirable from a commercial point of view.

The photomicrographs shown in Figure 2 (A, B) permit one to see that in the absence of agitation phase inversion has not occurred, resulting in an interwoven rubber-polystyrene network, which cannot be expected to behave as a true linear thermoplastic polymer. As one starts to polymerize styrene in the presence of dissolved rubber, phase separation takes place early in the polymerization.^{9,10} As the polymerization continues without agitation, more and more polystyrene is formed in the rubber solution. The growth of the interwoven network structure will

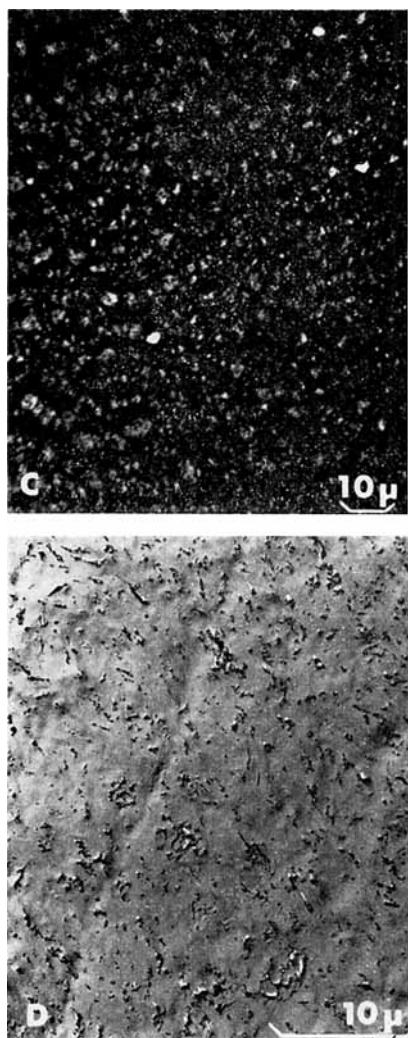


Fig. 2. Non-agitated solution polymer: (A), (B) polymer before mechanical mixing; (C), (D) polymer after mastication; (B), (D) electron photomicrographs.

continue until all of the styrene is used up (Fig. 2A, 2B). Usually in polymerization of this type sufficiently high temperatures are used towards the end so that the rubber phase becomes crosslinked and thus insoluble.

When such a polymer is masticated after complete conversion, the rubber membranes throughout the polymer are torn into smaller fragments. The tearing of the rubber network is random and will depend on the specific shearing conditions used. However, the attainment of a uniform product has not been possible. Apparently, as the mastication continues, the material becomes more fluid and gives rise to less shear, which in turn is responsible for a less efficient tearing of the rubber struc-

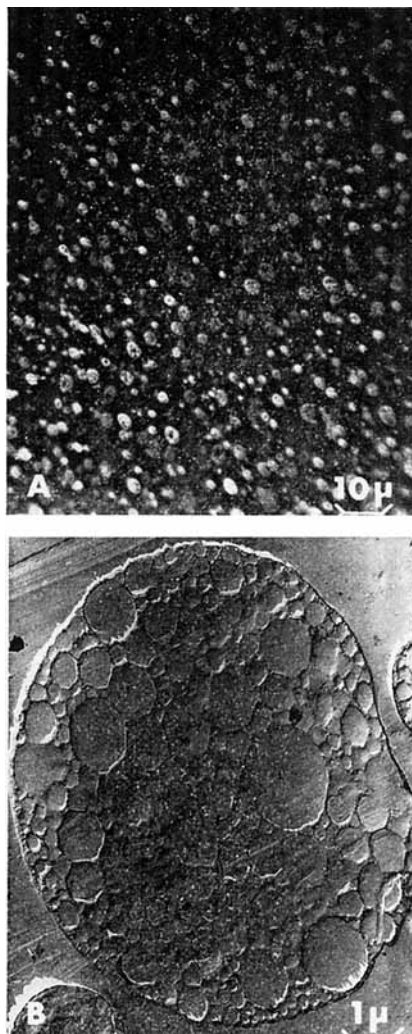


Fig. 3. See caption, p. 2367.

ture. Figures 2C and D show the general background of the torn rubber. No uniformly round particles can be observed, such as those shown in Figure 3. Actually, no particles which cause blemishes are shown as they are macroscopic aggregates, visible to the naked eye.

Agitated Polymerization. The mechanism of rubber particle formation in a polymerizing solution has been reported.¹⁰ Studies of the effect of rubber concentration, rubber type, polymerization conditions, etc., have not been available in the literature. In the following section, a qualitative morphological picture is presented to show the effect of rubber concentration in styrene. Also presented are experiments on two different types of rubbers which have been considered.

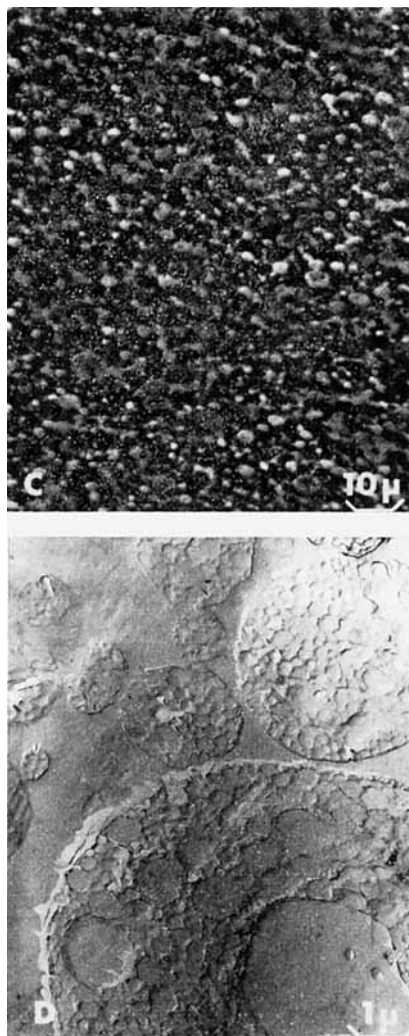


Fig. 3. Agitated solution polymers: (A), (B) 5% polybutadiene in polystyrene; (C), (D) 16% polybutadiene in polystyrene; (B), (D) electron photomicrographs.

Photomicrographs of two solution-polymerized products obtained with the employment of shearing agitation during polymerization are shown in Figure 3. The polymer depicted in Figure 3A contained 5% rubber and the one in Figure 3C had 16% of the same rubber. Both phase-contrast photomicrographs show a wide distribution of particle sizes. The larger particles ($>5 \mu$) contain occlusions of polystyrene which are readily visible. The small particles, however, present a less clear picture. Apparently the limited resolution of the light microscope is responsible for this situation. The corresponding electron photomicrographs (Figs. 3B and 3D, respectively) indicate the lack of any fundamental difference

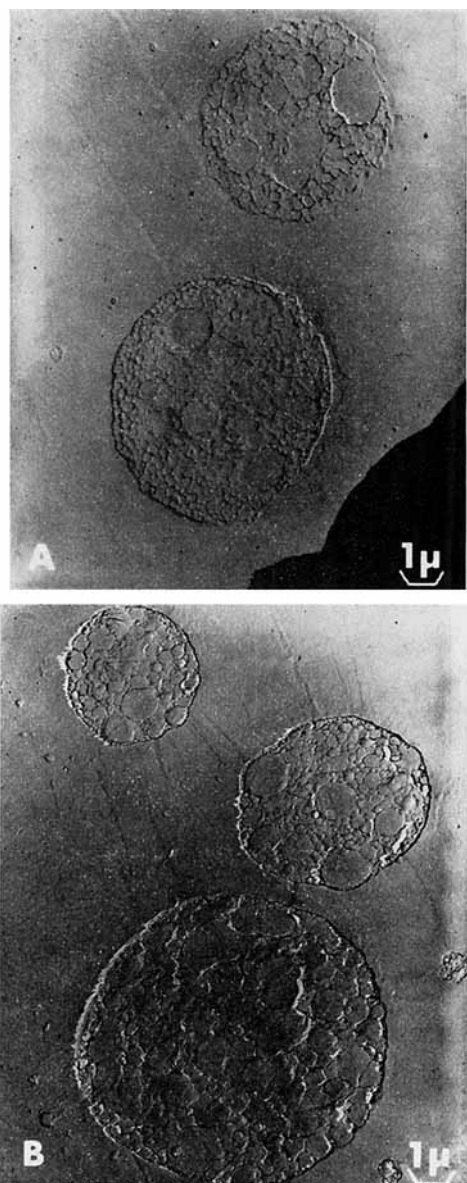


Fig. 4. See caption, p. 2369.

between the rubber particles in these products. They all show similar interior details.

To know the particle morphology at very low rubber concentration would be of interest. The particles obtained from a reinforced polystyrene containing only about 1% of two different elastomers, polybutadiene and butadiene-styrene copolymer rubber, are shown in Figures 4A and 4B. Again, there appears to be no fundamental difference in the internal

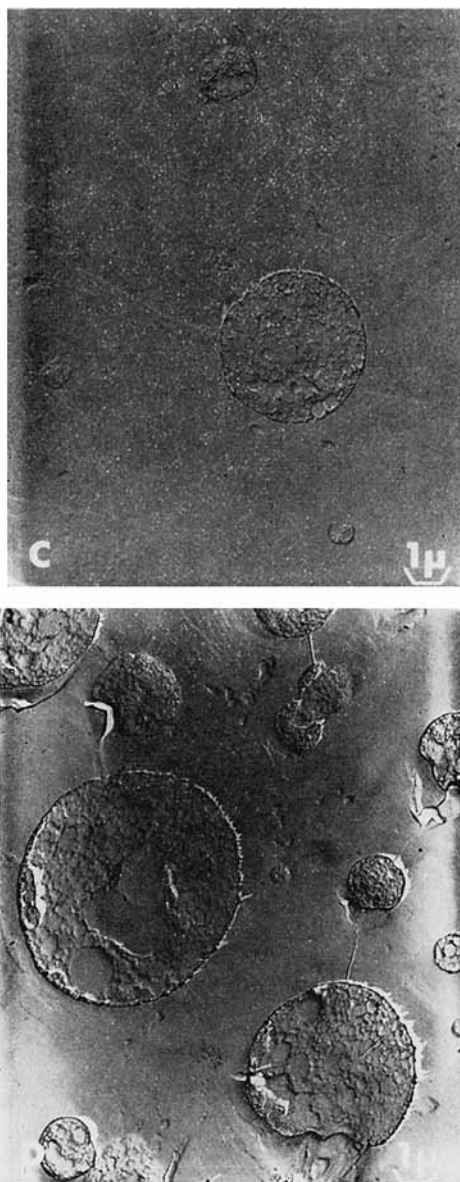


Fig. 4. Agitated solution polymers: (A) 1.5% butadiene-styrene copolymer in polystyrene; (B) 1% polybutadiene in polystyrene; (C) 16% polybutadiene containing polymer diluted to 1% rubber by mechanical mixing with polystyrene; (D) same as C, except dilution to 5% rubber. All electron photomicrographs.

details. Figure 4C depicts a rubber particle from the product which was obtained by mechanically masticating an appropriate ratio of a 16% rubber-containing product and polystyrene to yield a material containing only 1% rubber. On scanning a large area in the electron micro-

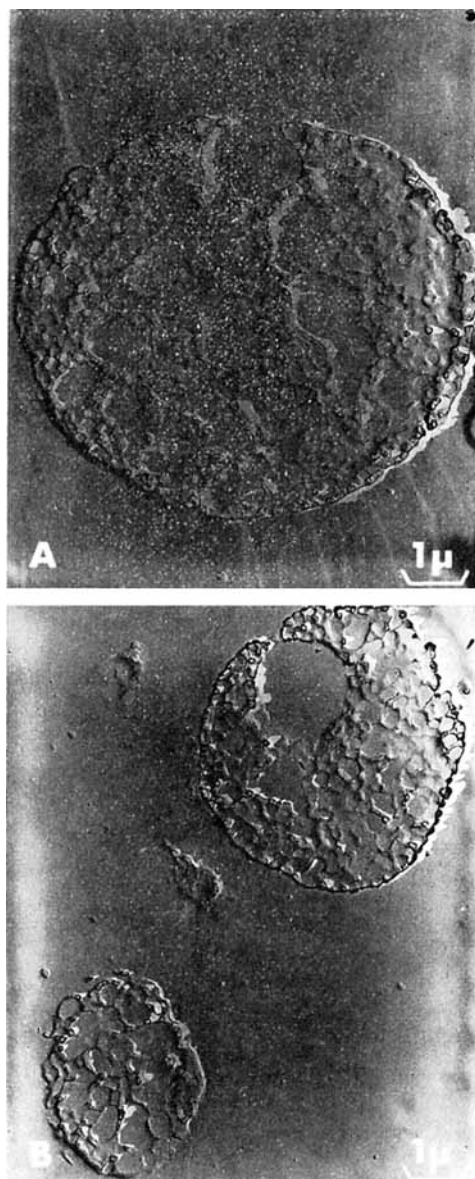


Fig. 5. See caption, p. 2371.

scope, it was concluded that the rubber particle size or size distribution did not appear to be altered and that the inner structure of the particles was also not changed from the original product. Figure 4D represents a similar specimen in which the dilution with polystyrene was carried to a 5% rubber level.

It is noted that the inner structure of the particles does not change upon mastication. Also, it has previously been reported that in the case of

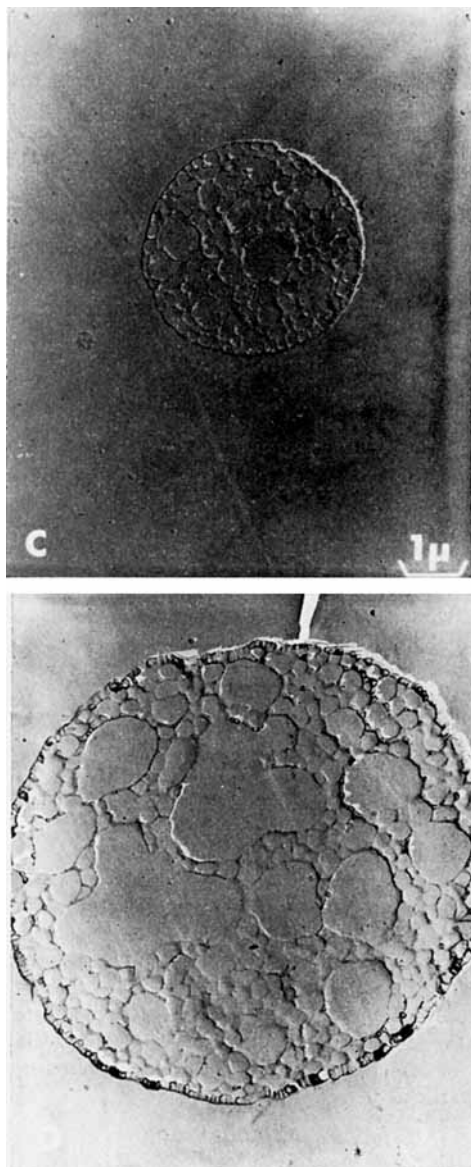


Fig. 5. Typical rubber particles from the 1.5% butadiene-styrene copolymer containing polystyrene. The sample was scanned to show the different types of particles present. All electron photomicrographs.

solution-made polymers no change in the rubber particle size is observed after mastication.²

Finally, Figure 5 presents some detailed inner structure of rubber particles obtained from a product containing 1.5% butadiene-styrene copolymer rubber and prepared with shearing agitation. It is concluded

that even though different shapes of rubber particles are possible within one product, the basic inner structure remains the same, and that the described electron-microscope technique provides a marked improvement in the examination of the fine structure of these particles in comparison with the previously reported phase-contrast technique.

The authors wish to thank B. A. Kozakiewicz for supplying several polymers for study. Thanks are also due to Dr. R. F. Boyer, Dr. S. G. Turley, and Dr. G. E. Molau for their valuable comments and reading the manuscript. The authors are also indebted to The Dow Chemical Company for permission to publish this work.

References

1. P. A. Traylor, *Anal. Chem.*, **33**, 162 (1961).
2. G. C. Claver, Jr. and E. H. Merz, *Offic. Dig. Federation Paint Varnish Prod. Clubs*, **28**, 858 (1956).
3. N. E. Davenport, L. W. Hubbard, and M. R. Pettit, *Brit. Plastics*, **32**, 549 (1959).
4. A. J. Staverman, *Proc. Roy. Soc. (London)*, **A282**, 115 (1964).
5. R. N. Haward and J. Mann, *Proc. Roy. Soc. (London)* **A282**, 120 (1964).
6. K. Kato, *J. Electron Microscopy (Japan)*, **14**, 220 (1965); *Polymer Eng. Sci.*, **7**, 38 (1967).
7. D. J. Angier and E. M. Fettes, paper presented to the Rubber Division, 150th American Chemical Society Meeting, Miami, Fla., May 1965.
8. Brit. Pat. 899,999 (June 27, 1962).
9. G. E. Molau, *J. Polymer Sci. A*, **3**, 1267 (1965).
10. G. E. Molau and H. Keskkula, *J. Polymer Sci. A-1*, **4**, 1595 (1966).
11. B. W. Bender, *J. Appl. Polymer Sci.*, **9**, 2887 (1965).
12. Brit. Pat. 1,005,681 (Sept. 29, 1965).
13. J. L. Amos, J. L. McCurdy, and O. R. McIntire, U.S. Pat. 2,694,692 (Nov. 16, 1954).

Résumé

Une technique électronique microscopique est présentée en vue de détailler la structure fine des particules de caoutchouc dans le polystyrène renforcé. De nombreux polystyrènes modifiés au caoutchouc, préparés par diverses méthodes, ont été étudiés par cette technique et les photomicrographies résultantes ont été comparées à celles obtenues précédemment par contraste de phase. Les polymères produits par le processus d'agitation en solution sont examinés en plus grand détail. On montre que la structure fine des particules de caoutchouc est fondamentalement non-altérée si la quantité ou le type de caoutchouc est modifié, ou si le polymère est dilué par mélange mécanique avec du polystyrène. Elle est caractérisée par la présence de nombreuses occlusions de polystyrène au sein de la particule.

Zusammenfassung

Ein elektronenmikroskopisches Verfahren zur detaillierten Untersuchung der Feinstruktur von Kautschukpartikeln in verstärkten Polystyrolen wird beschrieben. Einige kautschuk-modifizierte, nach verschiedenen Methoden dargestellte Polystyrole wurden nach diesem Verfahren untersucht und die erhaltenen Mikroaufnahmen mit den früher nach der Phasenkontrastmethode erhaltenen Aufnahmen verglichen. Eingehender werden die nach dem Prozess der "bewegten Lösungen" erzeugten Polymeren untersucht. Es wird gezeigt, dass die Feinstruktur der Kautschukteilchen bei Änderung von Menge oder Type des Kautschuks oder bei Verdünnung des Polymeren durch mechanische Vermischung mit Polystyrol im wesentlichen unverändert bleibt, Sie wird durch die Anwesenheit zahlreicher Polystyrolokklusionen im Teilchen charakterisiert.

Received April 6, 1967

Prod. No. 1636