Some Aspects of the Microstructure of Polyblends of Poly(vinyl chloride) and Butadiene–Acrylonitrile Copolymer Rubber with and without Talc Fillers

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To supplement some interesting observations of the effect of conditions and filler loadings upon tensile behavior of the poly(vinyl chloride)–acrylonitrile–butadiene copolymer rubber (PVC/NBR) system,[1] this type of polyblend was examined microscopically to determine whether differences in rupture energy calculated from tensile data might be related to significant variations in microstructure. A phase microscope is inadequate for this system because structural details here are smaller than the resolving power of optical microscopes. Hence, a replica technique was adopted and an RCA-EMU electron microscope was used.

Test bars were cut from a thick sheet recovered from the two-roll compounding mill. The test strips were cooled in liquid nitrogen and fractured by impact. Two different types of surface were obtained parallel and perpendicular to the calendering direction. Fracture surfaces were wetted with a 15% aqueous solution of polyvinyl alcohol. Specimens were left to dry and after 24 hr. a thin film (negative replica) was stripped off the specimen. The poly(vinyl alcohol) (PVA) negative replica was fixed on a glass cover-slip with the replica side up. The glass plates were put into an RCA evaporator and a thin layer of silicon monoxide was evaporated at a vacuum (0.5 × 10⁻⁴ mm. Hg). This silica replica was then shadowed at an angle of 1–5 with chromium.

The double replica obtained was put into distilled water, chromium side up. After the PVA had dissolved, the residual positive replica was captured and placed on a grid, dried, and transferred to the sample chamber of the electron microscope. The same replica technique was used also on microtome cut sections and on fracture surfaces of tensile test-bar specimens fractured on the Instron machine. Magnification on the viewing screen of the microscope was 2855×, and every print was enlarged to increase magnification to about 11,000×.

Results

1. Effect of mixing temperature (mixing time = 10 min., PVC/NBR ratio = 70/30).

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Fig. 1. Polyblend: PVC/NBR = 70/30. Mixing temperature: 275°F. Mixing time: 10 min. Replica: on cut section.
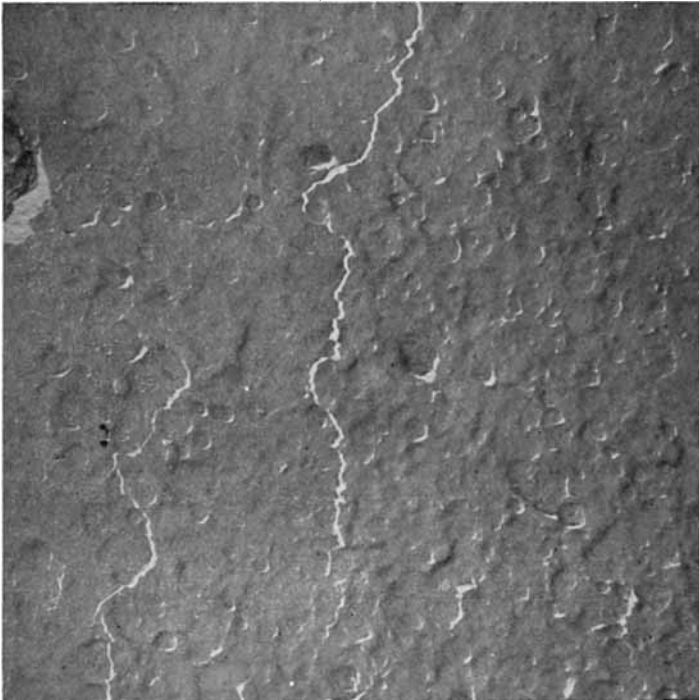

Fig. 2. Polyblend: PVC/NBR = 70/30. Mixing temperature: 275°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.
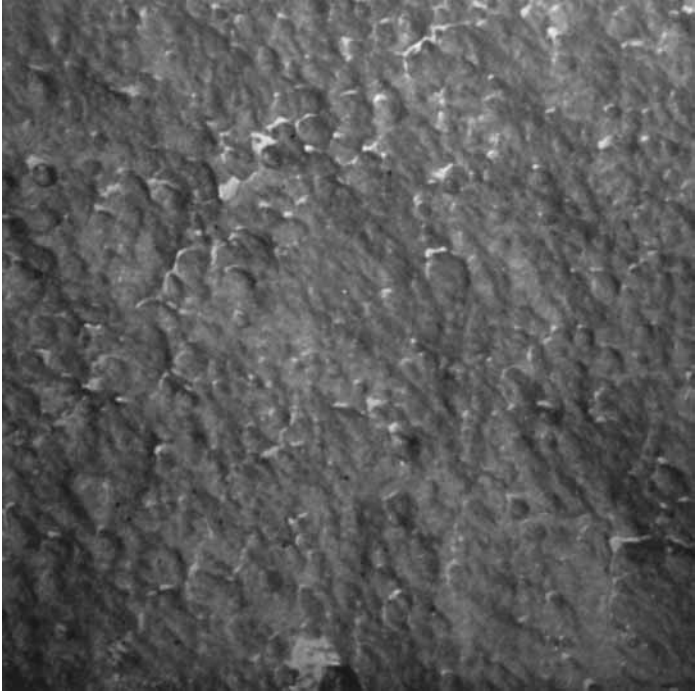
Fig. 3. Polyblend: PVC/NBR = 70/30. Mixing temperature: 275°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.

Fig. 4. Polyblend: PVC/NBR = 70/30. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cut section.
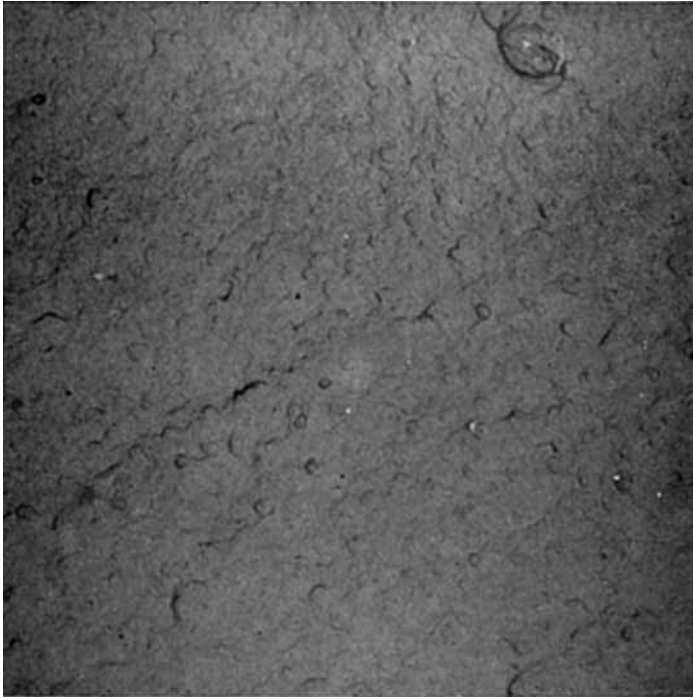
Fig. 5. Polyblend: PVC/NBR = 70/30. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.
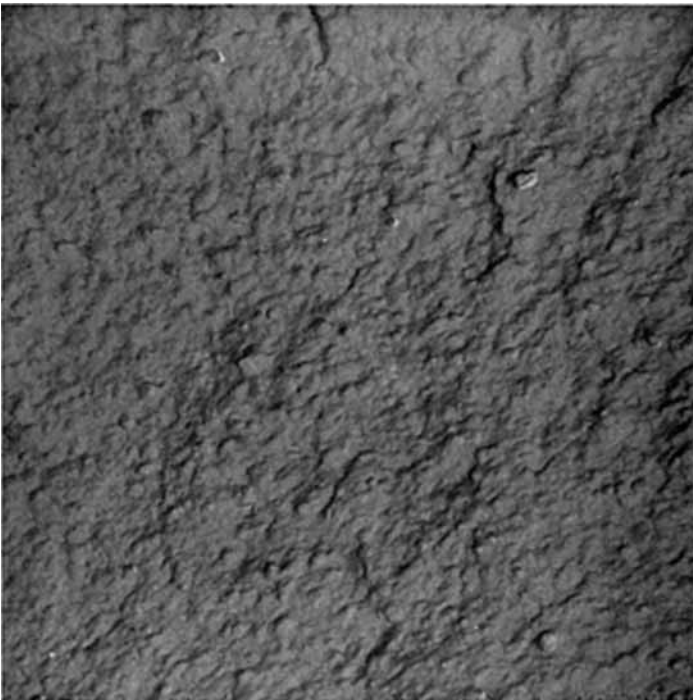

Fig. 6. Polyblend: PVC/NBR = 70/30. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction
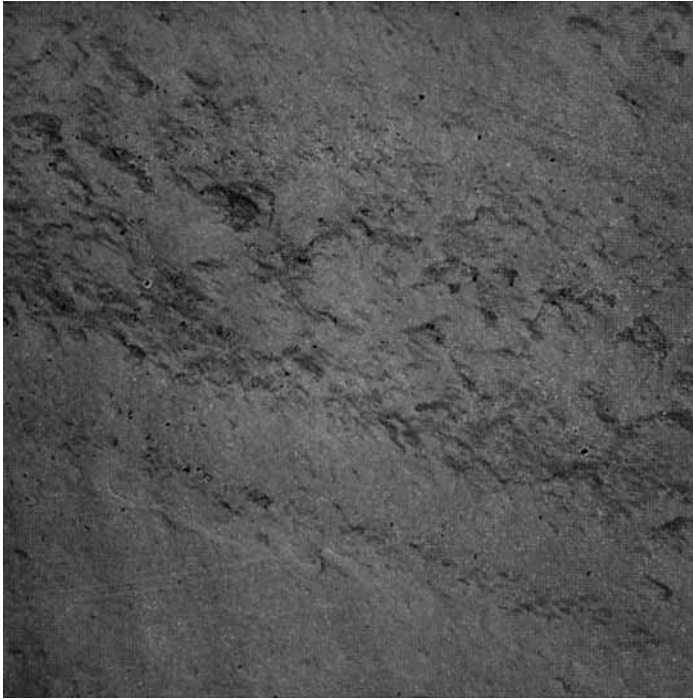
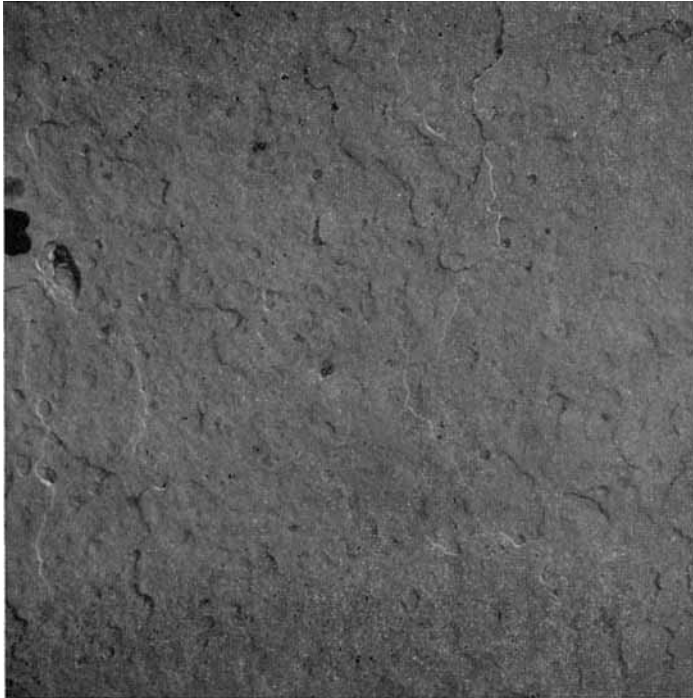Fig. 7. Polyblend: PVC/NBR = 70/30. Mixing temperature: 330°F. Mixing time: 7 min. Replica: on cut section.

Fig. 8. Polyblend: PVC/NBR = 70/30 Mixing temperature: 330°F. Mixing time· 7 min. Replica: on cold fracture section parallel to the calendering direction.
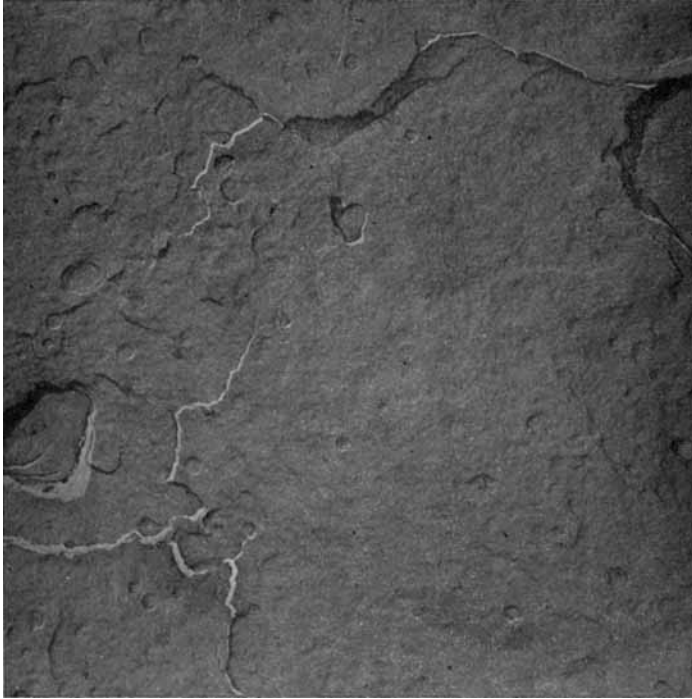
Fig. 9. Polyblend: PVC/NBR = 70/30. Mixing temperature: 330°F. Mixing time: 7 min. Replica: on cold-fracture section perpendicular to the calendering direction.
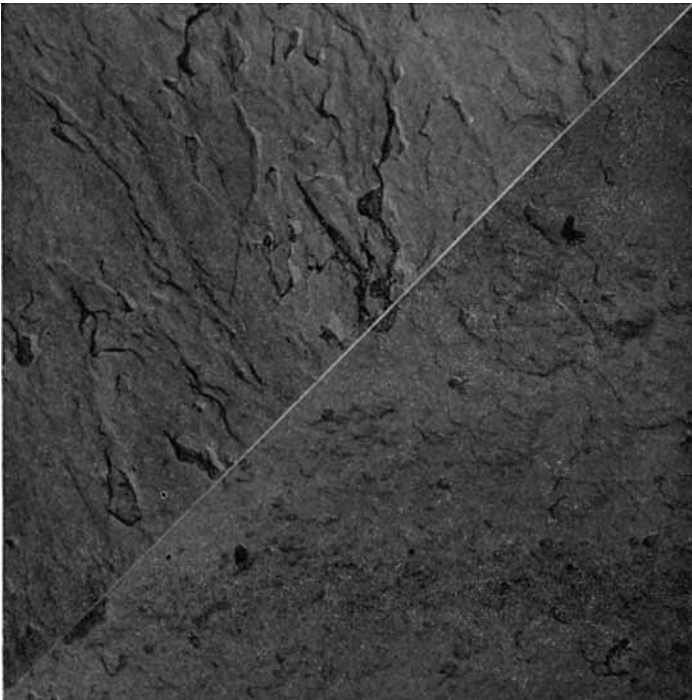

Fig. 10. Polyblend: PVC/NBR = 70/30. Mixing temperature: 300°F. Mixing time: 2 min. Replica: on cut section.
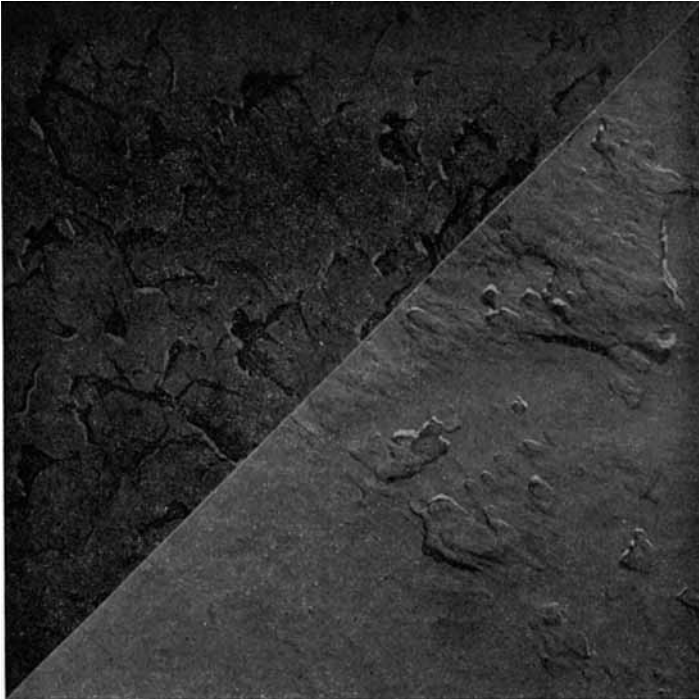
Fig. 11. Polyblend (upper): PVC/NBR = 80/20. Mixing temperature: 300°F. Mixing time: 2 min. Replica: on cut section.

Fig. 12. Polyblend (lower): PVC/NBR = 80/20. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cut section.

Fig. 13. Polyblend PVC/NBR = 80/20. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.

Fig. 14. Polyblend: PVC/NBR = 80/20. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.

Fig. 15. Polyblend: PVC/NBR = 95/5. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cut sections.

Fig. 16. Polyblend: PVC/NBR = 95/5. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.
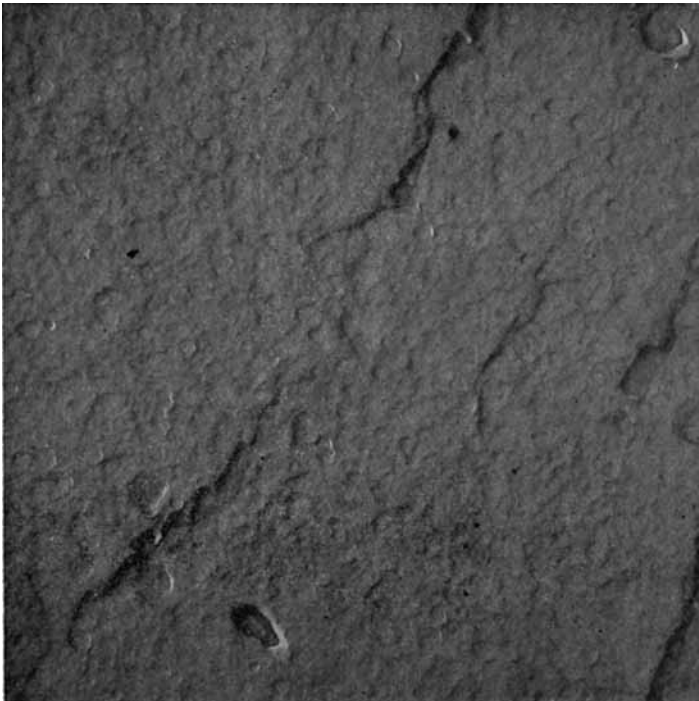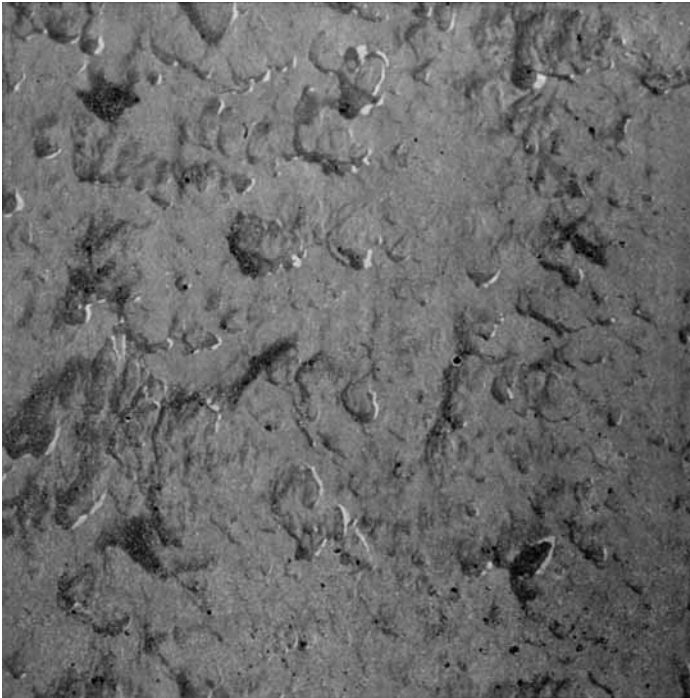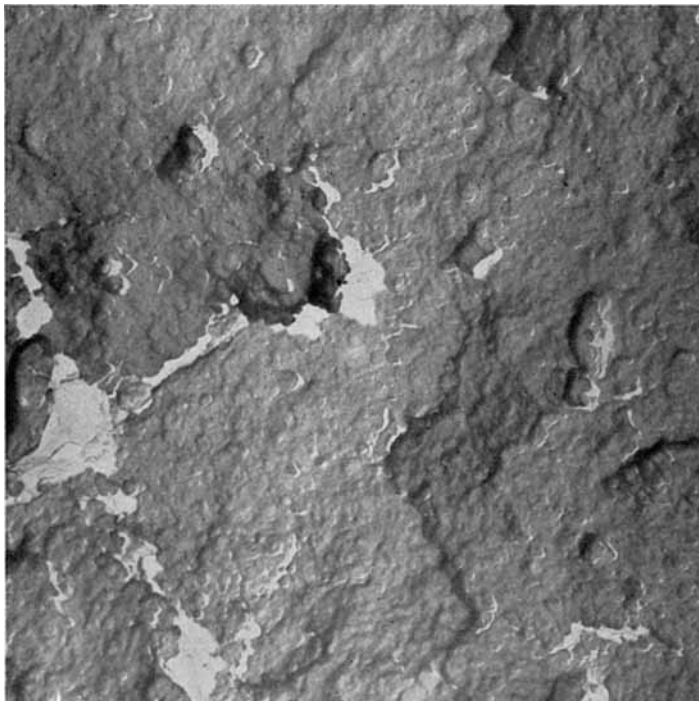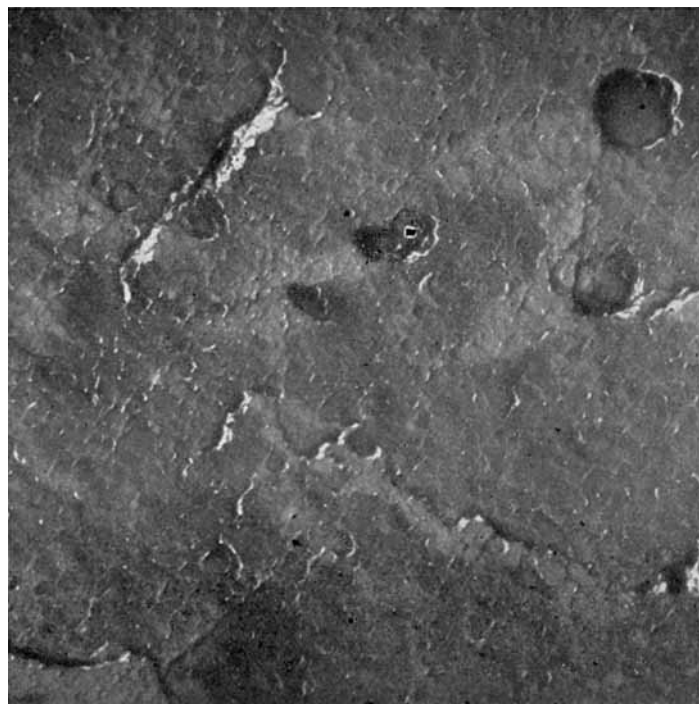

Fig. 17. Polyblend: PVC/NBR = 95/5. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.
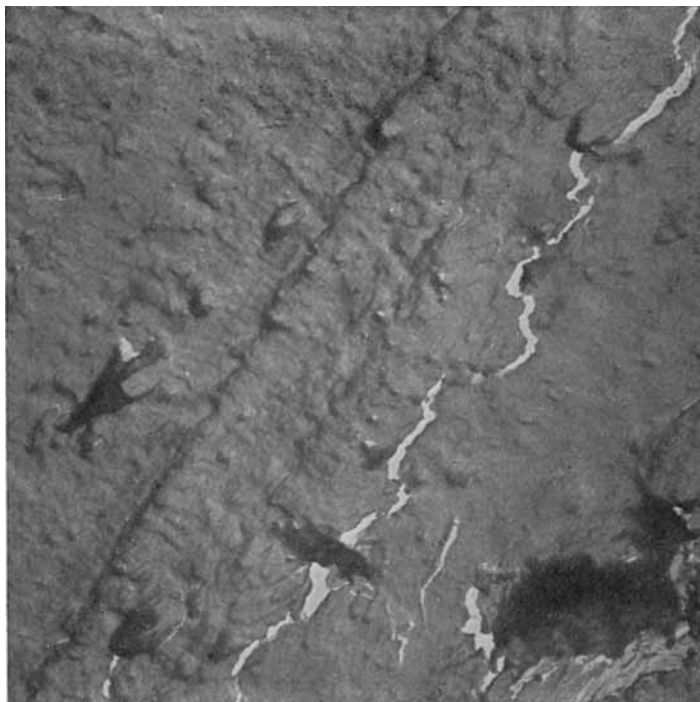
Fig. 18. Polyblend: PVC/NBR = 88/12.   Mixing temperature: 300°F.   Mixing time: 10 min.   Replica: on cut section.

A. Mixing temperature 275°F. (Figs. 1–3).   Structure is coarse.   Good correlation between cut surface pattern (Fig. 1) and fracture surface pattern (Figs. 2,3).   Rubber spots are present but not in an evenly distributed or a typical pattern.   Stress–strain curves show plasticized behavior.[1]

B. Mixing temperature 300°F. (Figs. 4–6).   Structure becomes finer in comparison with the preceding one.   Fracture surface pattern (Figs. 5, 6) is like that of microtome cut surface (Fig. 4).   Both cut and broken surface patterns are sharper and finer than from specimens processed at 275°F. Stress–strain curve shows higher rupture energy,[1] which leads one to expect better impact resistance.[2]

C. Mixing temperature 330°F. (Figs. 7–9).   These patterns are very sharp and fine.   The structure becomes more homogeneous and looks degraded;   tensile rupture energy is lower.   The compound processed at 275°F. is undermixed, and that at 330°F. is overmixed.   A PVC/NBR polyblend has high tensile rupture energy and, by inference,[2] good impact properties only for optimal degrees of mixing which are clearly distinguishable in replicas of either cut or fracture sections.

2. Effect of mixing time (mixing temperature = 300°F.), PVC/NBR ratio = 70/30).

A. Mixing time 2 min. (Fig. 10).   Cut surface pattern clearly shows presence of two phases.   Rubber is dispersed in an almost pure PVC phase.

Fig. 19. Polyblend: PVC/NBR = 88/12. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.

Stress–strain curves show a low energy of rupture. This tensile behavior is commonly found in plastics having poor resistance to falling weight impact.[2]

B. Mixing time 10 min. (Figs. 4–6). Rubber is much more dispersed. Stress–strain curve is typical of plastics which show high impact behavior.

When the mixing time is varied at the mixing temperature of 300°F. and the PVC/NBR is adjusted to 80/20, then at a mixing time of 2 min. we obtain a structure like that in Figure 11. Presence of two phases is evident, and the stress–strain shows characteristics which should correlate with poor impact behavior.[2] When mixing time is increased to 10 min. at 300°F. we obtain structures as shown in Figures 12–14. Rubber is well dispersed; fracture surface patterns are similar to those shown by Figures 4–6. Stress–strain curves are characteristic of expectations for high impact behavior.

To study the effect of varying the PVC/NBR ratio at constant mixing temperature of 300°F. and constant mixing time of 10 min., we obtained the following.

At PVC/NBR ratio 95/5 the results shown in Figures 15–17, that is, a very coarse structure and large black spots. Brittle behavior is indicated by tensile test for these specimens.

At 88/12, we obtain Figures 18–20, again we have a coarse structure with big black spots, and also brittle behavior is suggested by tensile tests.

At 80/20, we obtain Figures 12–14. Here the rubber is well dispersed and the fracture surface shows how a PVC/NBR compound has to be mixed to give good tensile and impact properties.

At 70/30, we obtain results shown in Figures 4–6. This is the characteristic structure of high-rubber compositions which develop high impact resistance at the expense of diminished modulus.[2]

In conclusion, a low rubber content composition (less than 10% of rubber) has a coarse structure pattern, undermixed or nonmixed rubber particles generally being present.

Fig. 20. Polyblend: PVC/NBR = 88/12. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.

A high rubber content composition has a more uniform structure with only occasional undermixed rubber particles.

Our interpretation suggests that at optimal mixing in PVC/NBR polyblends there exist two continuous phases in an interwoven or tangled arrangement, which resembles an array of mixed coarse fibers more than it does a dispersion of discrete rubber particles in a continuous matrix of PVC. The frequent appearance of rubber streams in the cut surfaces seems to suggest this structure.

Effect of Fillers

At low rubber contents, PVC/NBR 95/5, we have Figures 21 and 22, and for the ratio 88/12, Figures 23 and 24. At these rubber contents, the introduction of a low amount of filler changes the general pattern of structure, as shown in Figures 16, 17, 21, and 12. Filler-loaded compositions become more brittle and show a fracture pattern more characteristic of brittle fracture.[1] Comparisons between Figures 18 and 25 for cut surfaces without and with filler, respectively, suggest that filler-loaded compositions become less plastic and show a higher contrast of phase heterogeneity.
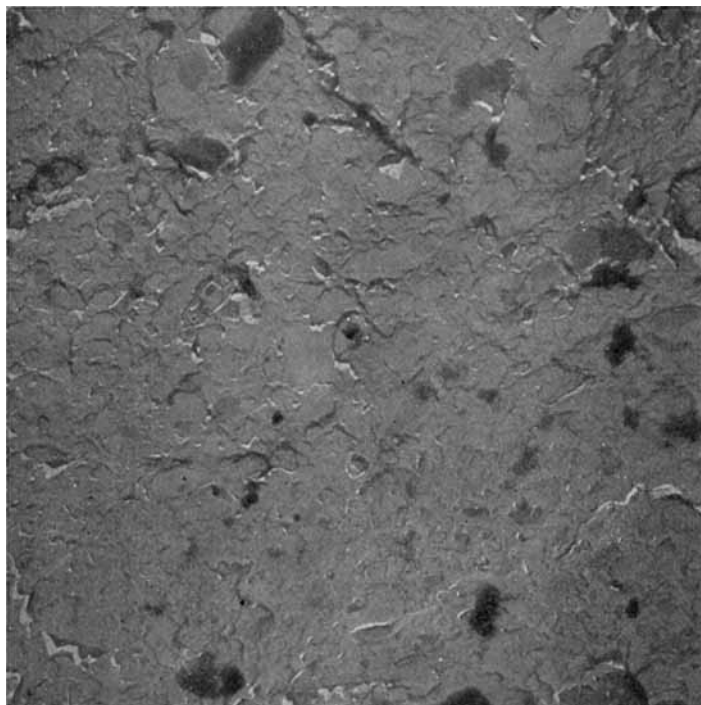

Fig. 21. Polyblend: PVC/NBR = 95/5. Mistron vapor: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.

Figures 19 and 20 (fracture pattern without filler) and Figures 23 and 24 (fracture pattern with filler) show the same differences. Tensile tests indicate that compositions without fillers are more rigid and brittle. Figure 23 shows that at a low rubber content, filler particles such as of the platy mica type, can be oriented by the milling process. The fracture pattern at low temperature seems to follow the filler-plastic interphasal regions. It doesn't appear as if the filler distribution is now confined only to the rubber phase, where it was introduced by milling before mixing of the filled
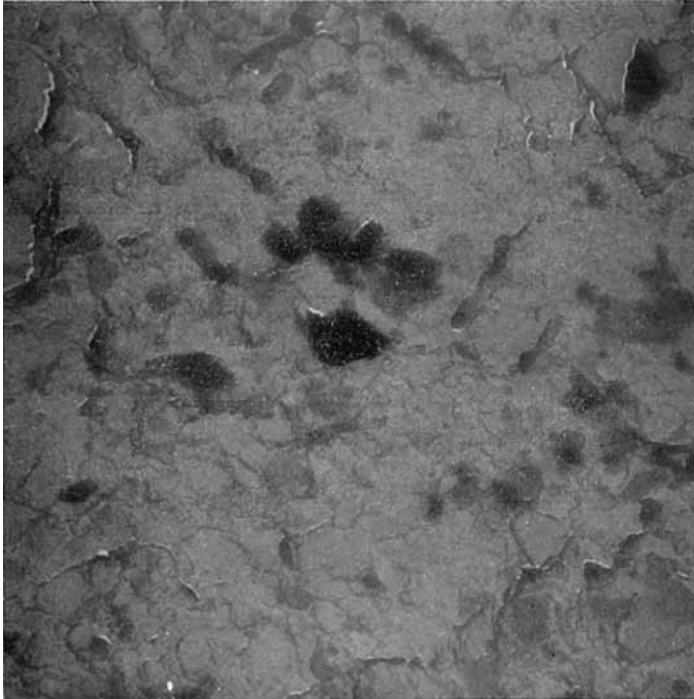
Fig. 22. Polyblend: · PVC/NBR = 95/5. Mistron vapor: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.

Fig. 23. Polyblend: PVC/NBR = 88/12. Mistron vapor: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.
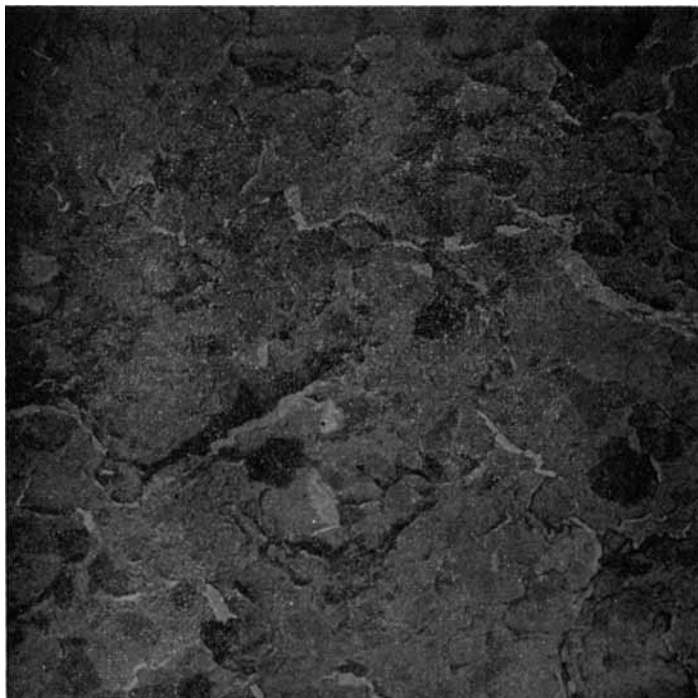
Fig. 24. Polyblend: PVC/NBR = 88/12. Mistron vapor: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.
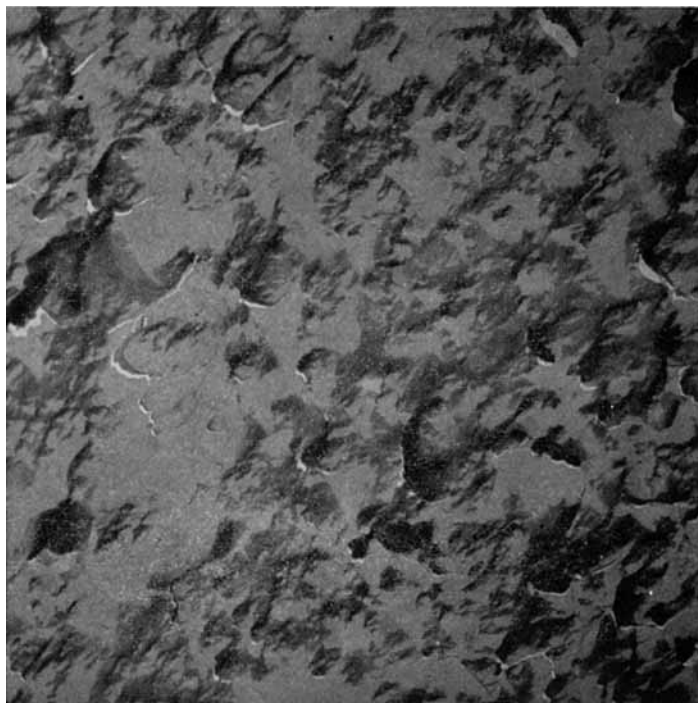

Fig. 25. Composition: PVC/NBR = 88/12. Mistron vapor: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cut surface.
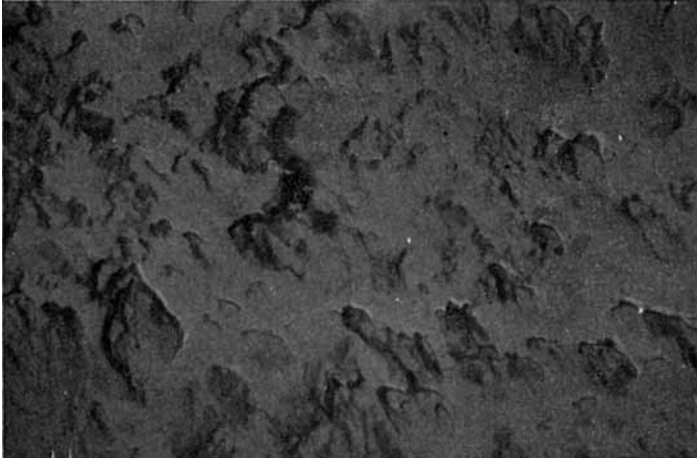
Fig. 26. Polyblend: PVC/NBR = 70/30. Platy filler: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cut section.
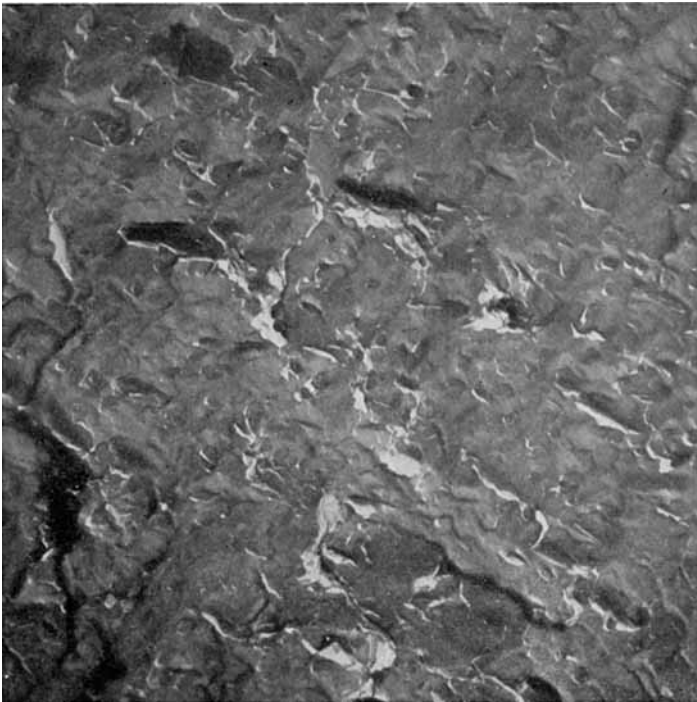

Fig. 27. Polyblend: PVC/NBR = 70/30. Platy filler: 5%. Mixing temperature; 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpendicular to the calendering direction.
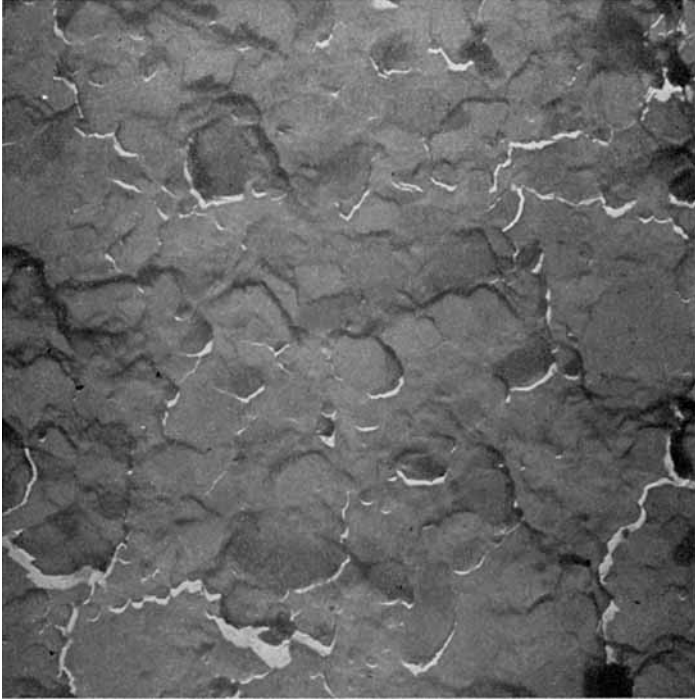
Fig. 28. Polyblend: PVC/NBR = 70/30. Platy filler: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.

Fig. 29. Polyblend: PVC/NBR = 70/30. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cut section of a prestrained specimen.

rubber with the PVC. At high rubber contents, (PVC/NBR 70/30) Figures 4–6 and 26–28 show the difference caused by filler loading in cut and cold-fracture sections.   Figures 4 and 26 show a very different pattern. The latter shows higher contrast in texture and less homogeneity of the
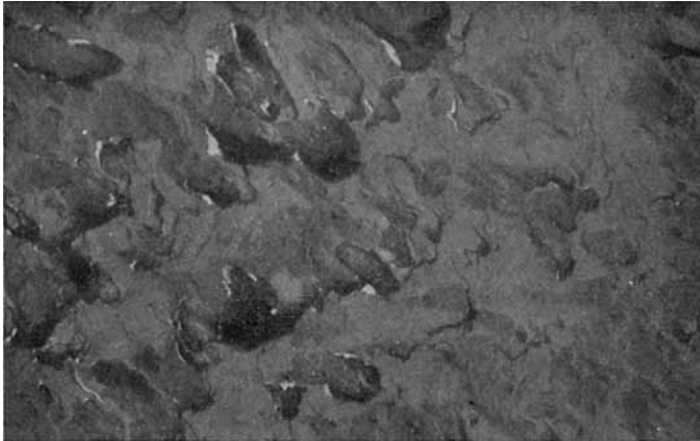

Fig. 30. Polyblend: PVC/NBR = 70/30. Platy filler: 5%. Mixing temperature: 300°F.   Replica: on cut section of a prestrained specimen.
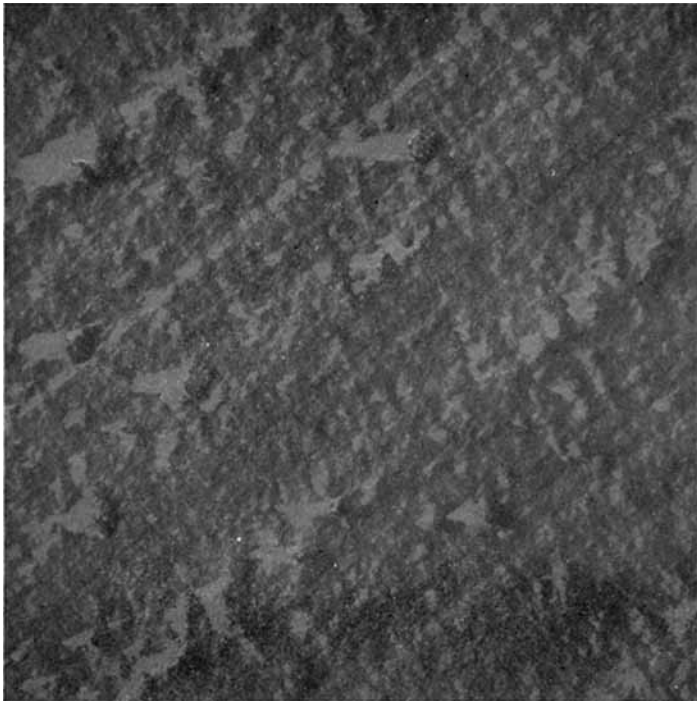

Fig. 31. Polyblend: PVC/NBR = 88/12. Mixing temperature: 300°F. Mixing time: 10 min.   Replica: on cut section surface of a prestrained specimen.

loaded composition compared with the fineness and uniformity typical of the unfilled plastic. Figures 6 and 28, when compared, show that the milling process seems to orient the platy particles and the polyblend system seems to behave as a uniform matrix with respect to distribution of the filler. From Figures 23 and 28, it also appears that the strength of filler-to-polymer bonds in the polyblends of high rubber content seems to be greater than in rubber-deficient systems. In Figure 23, a polyblend of rubber content of 12%, the breaking process seems to involve the filler–polyblend interphase. By contrast with 30% of rubber, the breaking
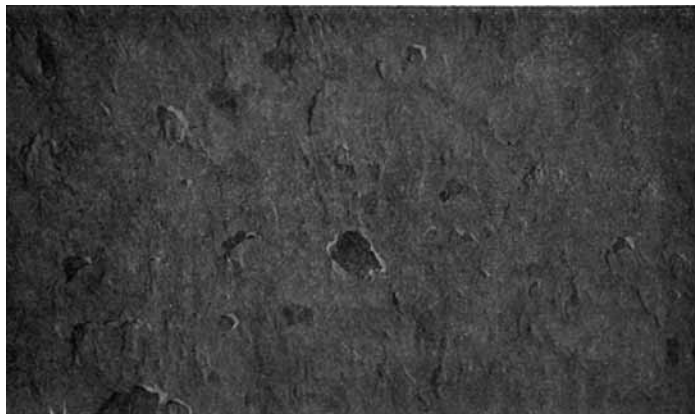

Fig. 32. Polyblend: PVC/NBR = 88/12. Mistron vapor: 5%. Mixing time: 10 min. Replica: on cut section of a prestrained specimen.
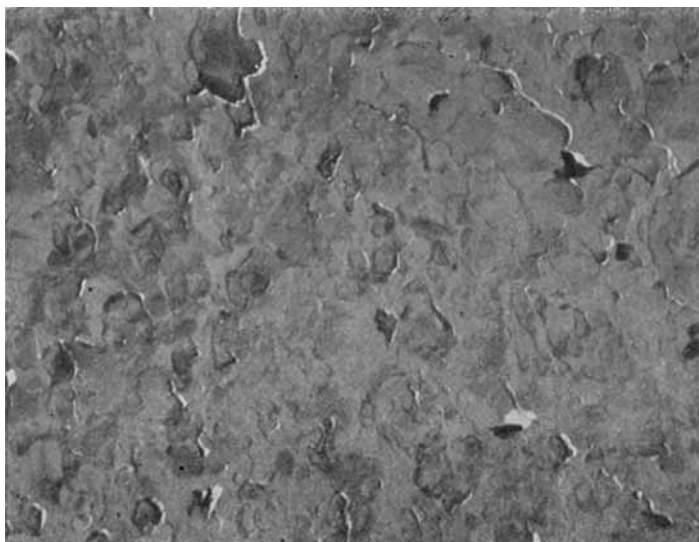

Fig. 33. Polyblend: PVC/NBR = 70/30. Mistron vapor: 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section of a prestrained specimen.

process seems to take place randomly in the plastic matrix rather than at or near the filler system.

The PVC/NBR system changes structure after being strained. This is shown more clearly at high rubber contents (70/30 without fillers, Fig. 29, and with fillers, Fig. 30). Replicas of cut surface of these filled or un-filled polyblends show quite different patterns: the filled composition is much coarser than the unfilled plastic. At low rubber content (88/12) without filler (Fig. 31) and with filler (Fig. 32), other effects are evident. Figures 28 and 33 show the difference between two patterns of the same loaded composition before and after stretching on the Instron machine. Straining beyond yield point seems to destroy the filler–polymer bonds and to convert the system to a higher degree of structure owing partly to the orientation of the rubber and partly to some disintegration of the struc-tural aggregates of filler particles.

Conclusions

Results of this microscopic evaluation may be summarized as follows.

1. There is an optimal mixing degree, not too coarse and not too fine, which provides the best tensile behavior and impact resistance. The optimal condition is microscopically distinguishable from other mixtures.
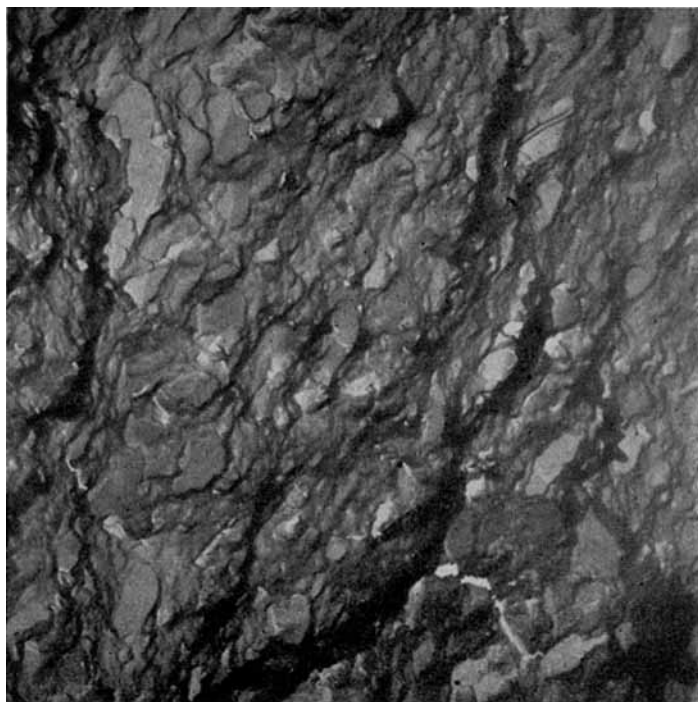

Fig. 34. Polyblend: PVC/NBR = 70/30. Mistron M-25: 5%. Mixing tem-perature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section perpen-dicular to the calendering direction.

TABLE I
Some Data about the Material Used

(a) PVC: B. F. Goodrich Chemical Company, Cleveland, Ohio. Resin type: 103 EP. Specific viscosity (in 0.4% solution of nitrobenzene at 30°C.): 0.45. Particle size: 100% through 42 mesh.

(b) Rubber: B. F. Goodrich Chemical Company,' Cleveland, Ohio. Rubber type: carboxylic nitrile rubber, Hycar 1071. Acrilonitrile content: high. Mooney viscosity: 45–50.

(c) Fillers: Sierra Talc and Clay Company, South Pasadena, Cal. (1) Mistron vapor. Surface area: 20 m.²/g. Particle shape: platy. (2) Mistron M-25. Surface area: 25 m.²/g. Particle shape: acicular.

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2. At low rubber contents the presence of large rubber particles is rather common. Poor distribution of the rubber may be a reason for the brittleness of such compositions. Proper mixtures are difficult to make when rubber content is dropped below optimal loads, and the structure differs also in kind as well as in degree from the preferred structure.

3. PVC/NBR systems, when properly prepared, have a structure suggesting a fibrous interweaving of two continuous phases. When undermixed, the situation tends toward the rubber phase dispersed in discrete and noninterlocked domains in a continuous matrix of PVC.

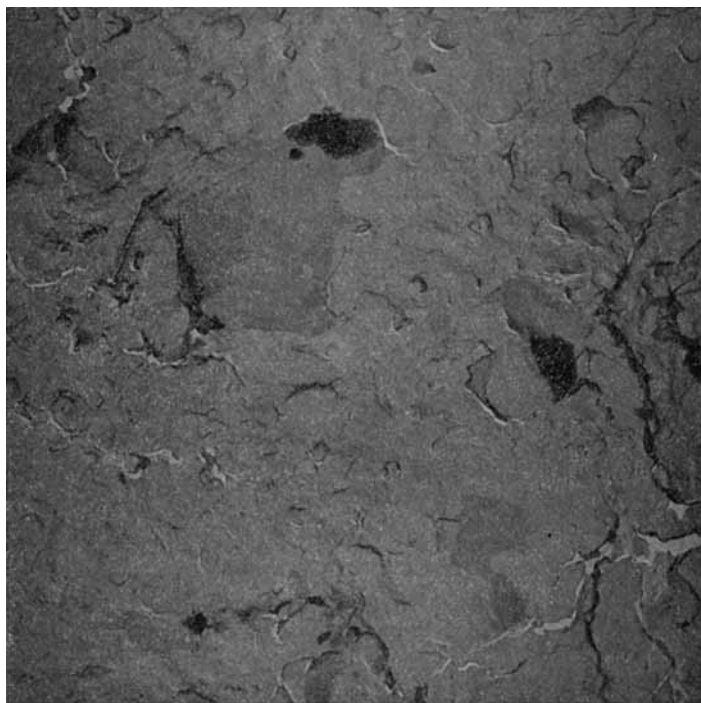Fig. 35. Polyblend: PVC/NBR = 70/30. Mistron M-25 = 5%. Mixing temperature: 300°F. Mixing time: 10 min. Replica: on cold-fracture section parallel to the calendering direction.
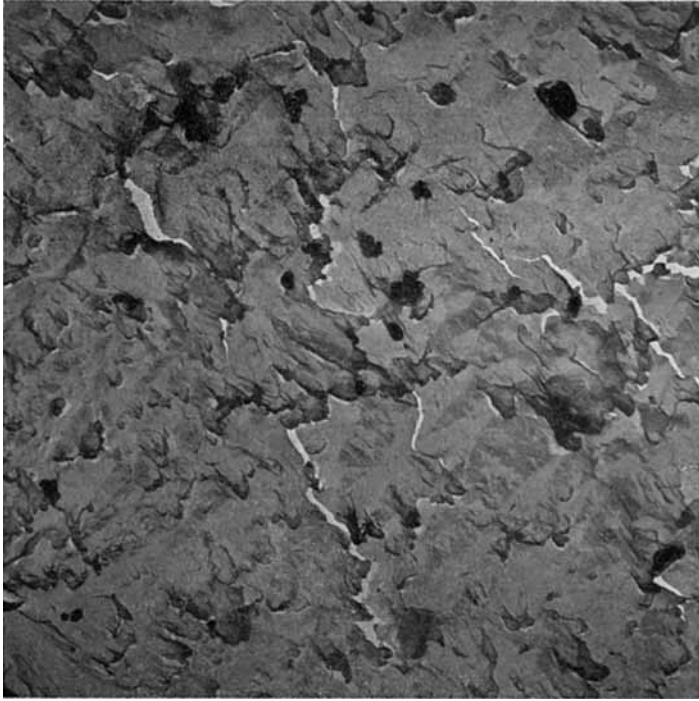
Fig. 36. Polyblend: Geon 8700 (B. F. Goodrich Chemical Company). Replica: on cut section of an extruded pipe.
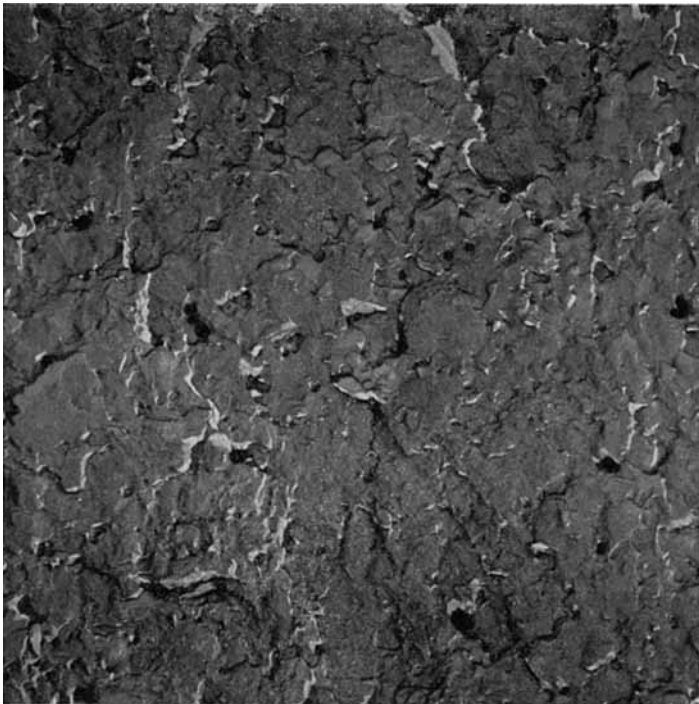

Fig. 37. Polyblend: Geon 8700 (B. F. Goodrich Chemical Company). Replica: on cold-fracture section of a milled specimen.
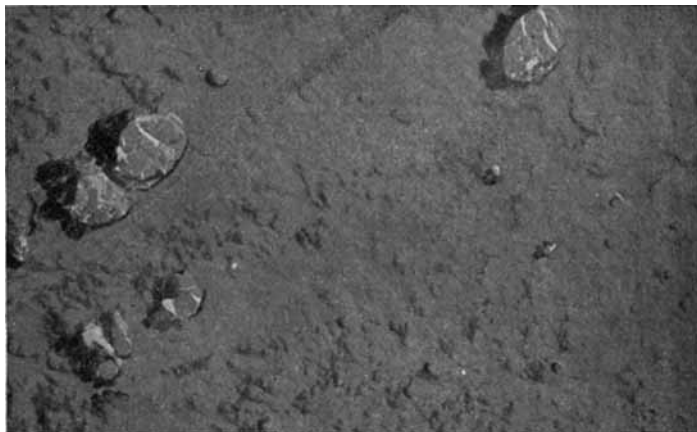
Fig. 38. Polyblend: Chemigum N-8 + Pliovic S-50 (The Goodyear Tire and Rubber Company). Replica: on cut section.

4. The addition of filler to the PVC/NBR systems causes development of a coarser, more heterogeneous structure with no indication that the filler prefers one or the other of the polymer phases. The cold-fracture and cut-structure then shows that where the rubber content is low the fracture path in the system follows the polymer–filler interphase more than it does at higher rubber contents where strength of the polymer–filler bond is higher and the fracture path tends to be random in the polymer matrix. For this reason it is difficult to distinguish a clear-cut separation of polymer phases.

In general, the introduction of filler seems to create a new type of régime with respect to the fracture mechanism.

Figures 36–38 are shown to give a comparison of similar polymers fabricated in usual ways with structures observed in the mill sheets of composition of Figures 1–35.

References

1. Lee, C. C., W. Rovatti, and E. G. Bobalek, *Preprint Booklet 22, No. 2, paper No. 52*, p. 287. Presented before the Division of Organic Coatings and Plastics Chemistry, at the 142nd meeting of the American Chemical Society, Atlantic City, September, 1962.

2. Evans, R. M., and E. G. Bobalek, *SPE J.*, **16,** 76 (1960); *SPE Trans.*, **1,** 93 (1961).

Synopsis

Fracture and microtome sections of polyblends, prepared from varying proportions of poly(vinyl chloride) and an elastomer (with and without talc fillers) and with the use of different conditions of mixing, were examined with the electron microscope. In general, the structures observed in cut and in fracture sections were very similar when taken from the same polymer at the same reference planes with respect to direction of process-induced orientation. Optimal tensile behavior seems to occur when the degree of mixing establishes a structure resembling a fibrous interweaving of continuous do-

mains. Undermixing or overmixing seems to establish more random dispersions of more or less large and discrete particles of rubber in a continuous poly(vinyl chloride) phase. Introduction of fillers changes the microstructure of the fracture patterns. Particularly in polymers containing talc fillers, the influence of prior strain history on microstructure is very evident. Thirty-eight figures are shown to demonstrate how differences in composition, mixing process, and strain history can alter the microstructure produced by fracture or cutting of the plastic.

Résumé

Les coupes et sections microtomiques de mélanges préparés à partir de proportions variables de chlorure de polyvinyle et d'un élastomère (avec ou sans talc comme charge) mélangés dans différentes conditions, ont été examinées au microscope électronique. En général les structures des surfaces de cassure ou de coupure sont très semblables pour un même polymère suivant les mêmes plans de référence compte tenu de la direction de l'orientation induite. Le meilleur comportement à la tension semble exister dans le cas ou le degré de mélange forme une structure ressemblant à un tissage fibreux de domaines continus. Mélanger trop peu ou trop aurait pour effet d'établir plus de dispersion de particules statistiques ± grandes et discontinues de caoutchouc dans une phase continue de chlorure de polyvinyle. L'introduction de remplisseur change la microstructure des réseaux de la cassure. L'influence des tensions subies antérieurement sur la micro-structure est très claire particulièrement dans les polymères contenant du talc comme chanrge. Trenté-huit figures sont produites pour démontrer comment les différences de composition, de procédés de mélange et des tensions antérieures peuvent altérer les microstructures produites par coupure ou cassure des plastiques.

Zusammenfassung

Bruchstellen und Mikrotomschnitte von Polymermischungen mit verschiedenem Anteil an Polyvinylchlorid und einem Elastomeren (mit und ohne Talk als Füllstoff), die unter verschiedenen Mischungsbedingungen erhalten worden waren, wurden unter dem Elektronenmikroskop untersucht. Im allgemeinen waren die an Schnitt- und Bruch-stellen beobachteten Strukturen beim gleichen Polymeren und an der gleichen Bezug-sebene in Hinblick auf die Richtung der verarbeitungs-bedingten Orientierung sehr ähnlich. Optimales Zugverhalten scheint bei einem Mischungsgrad aufzutreten, der zu einer Struktur mit faserartiger Verwebung kontinuierlicher Bereiche führt. Zu geringe oder übermässige Mischung scheint eher eine statistische Dispergierung mehr oder weniger grosser, diskreter Kautschukteilchen in einer kontinuierlichen Polyvinylchlorid-phase zu bewirken. Einführung von Füllstoffen ändert die Mikrostruktur der Bruch-bilder. Besonders bei Polymeren mit Talk-Füllstoffen ist der Einfluss der Verformungs-Vorgeschichte auf die Mikrostruktur recht augenfällig. Achtunddreissig Abbildungen zeigen den Einfluss von Zusammensetzungsunterschieden, des Mischungsvorganges und der Verformungsvorgeschichte auf die durch Bruch oder Schnitt des plastischen Stoffes entstehende Mikrostruktur.