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Homogeneity of Natural and Synthetic Rubber Compositions

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Natural rubber is unsurpassed by any synthetic rubber in terms of many important physical properties; for example, tensile, tear strength and low heat build-up. However, like all elastomers, natural rubber is deficient in one or more respects. As a consequence, rubber technologists endeavour to overcome the poor performance of an elastomer in a particular area and achieve the best compromise in properties through blending with a second rubber. Thus, in most rubber products, natural rubber finds application as a blend with a second elastomer. In view of this fact, a study of the homogeneity of natural and synthetic rubber blends is important.

Thermodynamics indicates that the entropy to be gained by mixing polymer molecules is very small because of the small number of molecules involved resulting from their high molecular weight. Hence, an almost insignificant positive free energy of interaction is enough to overcome this small entropy of mixing. Thus, two polymers do not have to be very dissimilar before they are insoluble in each other and lead to the existence of discrete zones or heterogeneity upon mixing. With this in mind, the question arises as to the homogeneity of blends of NR and various synthetics. If heterogeneous, what influence, if any do structural features such as molecular weight have on zone size or shape? Further, what is the distribution of filler particles between the separate zones and how are performance characteristics affected?

The present paper is one of a series investigating blend homogeneity of natural rubber with some of the principal synthetic elastomers. The particular objective was the determination of filler distribution between separate polymer phases as influenced by molecular feature and processing variations.

EXPERIMENTAL PROCEDURES

The procedures employed for polymer blend analysis were essentially the same as those outlined in the previous work by HESS *et al.* (1967). All pure gum blends were examined both by phase contrast microscopy, and by electron microscopy. The specimens for optical analysis were prepared by means of frozen sectioning on a Leitz Sledge Microtome.* Sections were cut to a thickness of about 0.5–1 micron. Electron microscope specimens were prepared by microtoming embedded blocks of each blend vulcanisate. The samples were embedded in a mixture of 50 parts butyl/methacrylate, 40 parts methyl/methacrylate, and 10 parts styrene. Benzoyl peroxide (1 part) was added as a polymerisation catalyst. This embedding mixture is slightly different than that used previously in that it contains a higher percentage of butyl/methacrylate.

The embedding mixtures containing the samples were allowed to polymerise overnight at a temperature of 65°C. All embedded specimen blocks were first pared down using glass knives. The final sections for microscopic analysis were then cut on an LKB Ultrotome** equipped with a diamond knife.

Filler Distribution Studies

Studies on filler distribution were carried out by electron microscopy, using the embedding technique. All specimens were examined in either a Phillips EM-75 or EM-100 Electron Microscope *** operating at 40 kV. Because of the lower inter-zone contrast on many of the blends containing high filler loadings, attempts were made to improve contrast by operating the electron microscope at still lower

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voltages in the range of 15–20 kV. Some improvement in contrast was obtained but the greater operational difficulty at lower voltages nullified any real advantages. Hence, all of the work included in this paper was carried out at 40 kV., which generally produced good inter-zone contrast on sections cut to a thickness of about 500–1000Å.

Compounding

All stocks were mixed on a mill using a variety of procedures which included the preblending of the raw polymers, blending of separate masterbatches containing filler and letdown of one polymer-filler masterbatch with another polymer, as well as solution and latex masterbatching. All samples for microscope analysis were based on 30-minute cures using dicumyl peroxide. Typical recipes and mixing procedures are shown in the Appendix.

Blend compounds containing filler were examined at both 20 p.h.r. and 40 p.h.r. loadings. At the higher loading, inter-zone contrast was often quite weak with NR/SBR blends. Contrast was enhanced in these stocks by using a curative imbalance between the two polymer phases. Most of the curatives were first added to the SBR phase (10–1 ratio to NR), care being taken to keep mixing temperatures well below those needed to cross-link the compound. Systematic studies on a large number of both pure gum and filled compounds did not indicate any significant change in polymer zone size or filler distribution as a result of the curative imbalance. These studies also included extensive work on NR/BR blends which show much higher inter-zone contrast, even at the higher filler loadings. The curative imbalance had no bearing on the microscope results, other than the enhancement of contrast. For the evaluation of vulcanisate properties, however, it was necessary to mix duplicate batches, one of which contained curatives added in the normal manner.

Contrast Mechanism

The mechanism for contrast in the electron microscope between the separate phases in a polymer blend can be based on the following variables:

1. Atomic structure;
2. Density;
3. Swelling differential in the embedding medium; and
4. Stability under electron bombardment.

In dealing with blends of natural rubber with SBR and BR, items 3 and 4 are the most important factors. Natural rubber generally shows higher swell in the methacrylate mixture and subsequently is thinned in the electron microscope when substantial amounts of the polymerised methacrylate evaporate under electron bombardment. Hence, the SBR and BR components of blends with natural rubber appear dark in the electron microscope because they are thicker. The contrast is further enhanced when the curative imbalance between the separate polymer phases is employed.

It is absolutely essential that the mechanism for producing contrast between the separate polymer phases be independent of the presence of the filler particles. With the embedding technique, this condition is satisfied. The sections are quite uniform in thickness initially, and contrast is subsequently produced by the combined effect of the degradation by the electron beam and evaporation under vacuum. This produces relatively well defined zone boundaries with minimum influence by thickness artefacts. In earlier work using frozen sections, which were swollen after microtomy, thickness artefacts were a serious problem. The contrast mechanism with frozen sectioning is still based in part on a polymer swelling differential, but the thickness gradation from one polymer phase to another is much more gradual. Hence, zone boundaries are more diffuse and there is a much larger region of confusion around the polymer interfaces. Furthermore, there is more tendency for the filler particles to restrict the swelling action. Thus, highly pigmented regions in either polymer phase tend to show up dark. This problem has been pointed out by MARSH *et al.* (1967). When the filler particles cause areas in both phases to appear as dark zones, electron microscope studies on distribution are no longer possible.

As a further test of the contrast mechanisms put forth in this paper and in the previous work, the authors have carried out a large number of experiments in which it was attempted to introduce zones in a single polymer. Included in these experiments were individual compounds of natural rubber, poly-butadiene, and SBR–1500, wherein separate masterbatches were blended with and without filler. The curative imbalance technique was also applied. In no instance did these experiments succeed in producing light and dark zones in a one-phase system. Thus, within the limits of good microtoming technique and the ability to visually detect contrast differences between the two polymer phases, the interpretation of results with the embedding technique appears to be valid. Nevertheless, good sampling is still an important consideration. In the studies to-date, over 3000 samples have been microtomed and examined in the electron microscope and over 7000 electron micrographs have been taken.

Measurements on Filler Distribution

Determinations of filler distribution were carried out by measuring the size and frequency of the particles contained in each of the separate polymer phases. For prints on which the inter-zone contrast was high, a transparent mesh was superimposed over the micrograph. Distribution was then determined from the per cent area covered by the filler particles in each phase. Where inter-zone contrast was low, the mesh tended to interfere with the visual observation of the zone boundaries. In these instances, the prints were measured by counting, taking unto consideration both the size and frequency of the filler particles contained in each phase. Although they cannot be considered highly quantitative, the measurements do aid greatly in numerically representing the observed differences among the various compounds which were studied.

In carrying out these measurements, it was also necessary to set up certain rules of interpretation for determining whether a given filler aggregate was located in one polymer phase or the other. Particles at or near the zone boundaries are the most difficult to assess. The location of these particles was based on the outlines of the dark zones (*e.g.*, BR or SBR in blends with NR), which generally appear as the disperse phase because of their lower swell. For a particle to be counted in the dark phase, two-thirds or more encapsulation by the zone was stipulated. In studying the tendency for filler particles to transfer from one polymer to another, this level of encapsulation was also required to indicate a definite migration effect.

RESULTS AND DISCUSSION

NR/BR Systems

Studies on heterogeneity and filler distribution effects in NR/BR blends represented the first application of this new electron microscope technique (Hess *et al.*, 1967). This system proved particularly fruitful and the results are worth reviewing:

Pure gum NR/BR: Shown in *Figure 1* are NR/BR blends of these proportions: 75/25, 50/50 and 25/75, respectively. Mixing of the compounds was carried out for 2 minutes in a B Banbury. This was followed by a 4-minute mill mix to add the curatives—dicumyl peroxide. The size and shape of the polymer zones are typical of Banbury mixes. With 25% BR, the zones are somewhat streaky in appearance. A mesh configuration characterises the 50/50 blend, while the 25% NR stock exhibits more or less spheroidal zones of the natural rubber phase. Additional mixing in the Banbury produced no significant reduction in zone size.

An important factor in determining polymer blend heterogeneity is polymer viscosity. A good illustration can be seen in *Figure 2.* Shown here are 50/50 blends of natural rubber with polybutadienes of varied viscosity. The viscosity measurements were made on a Brabender Plasticorder equipped with temperature and shear rate controls. It can be seen that, as the viscosity or molecular weight of the polybutadiene is raised, the zone size increases considerably.

Carbon black studies: The effect of carbon black addition on inter-zone contrast in

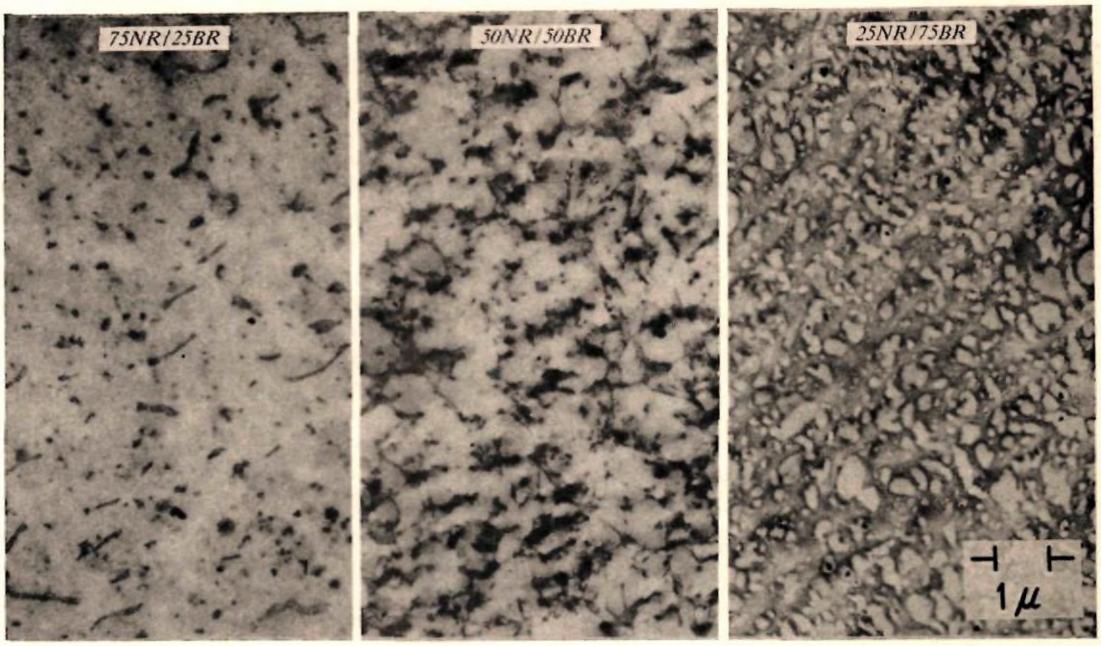

Figure 1. NR/BR blends of 75325, 50/50 and 25/75 proportions (Mixing: 2 min in Banbury).

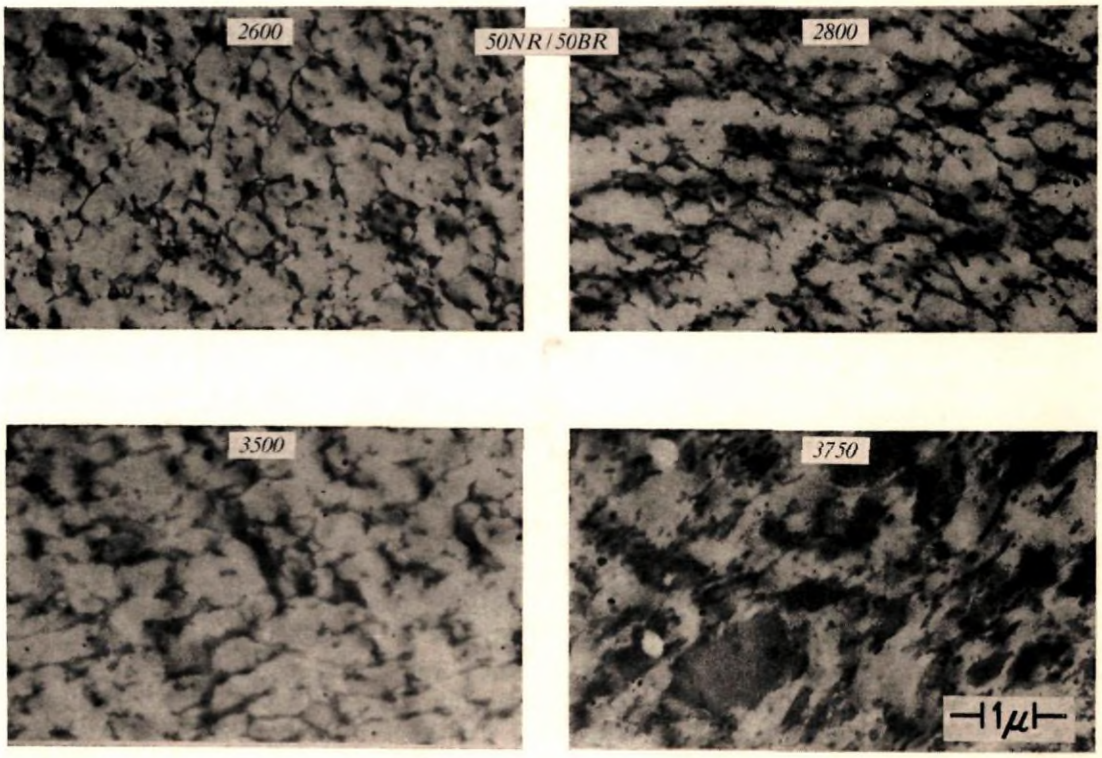

Figure 2. Effect of BR viscosity on zone size (Blend: 50 NR/50 BR; Viscosity units: M–GM torque).

NR/BR blends is illustrated in *Figure 3*. Shown here are blends of varying proportions, each containing 20 p.h.r. of an ISAF carbon black. Mixing procedures were varied. In the 75 NR/25 BR and 50 NR/50 BR blends, the elastomers were first pre-blended on a mill. The ISAF was then added. In the 25 NR/75 BR blend, 80 p.h.r. of black was first added to the NR, and this stock was then cut back to a 20 p.h.r. loading with BR. The important considerations illustrated in this *Figure* are:

1. The inter-zone contrast and definition of zone boundaries are relatively unaffected by black addition.
2. The stocks exhibit the characteristic zone shape and frequency shown in *Figure 1* for pure gum NR/BR blends.
3. The presence of carbon black is easily detected in either polymer phase.

Black distribution may, therefore, be readily determined by measuring the relative frequency of particles in each of the two phases.

Figure 3 indicates the tendency of carbon black to preferentially locate in the BR zones of a 50 NR/50 BR blend. In addition, the distribution of carbon black can be varied by changes in the mixing technique. These tools for controlling carbon black distribution were refined and used to prepare 50/50 blends differing widely in carbon black distribution. Carbon black content of the BR phase varied from 7 to 95%.

Mixing techniques utilised in this study included hydrosolution masterbatching, conventional dry mixing, and occasionally blends of stocks prepared by these different mixing procedures. A small quantity of N-Methyl-N,4-dinitrosoaniline (0.1%) was employed to fix a high carbon loading in the NR phase. The compounds employed in this study all contained 40 p.h.r. ISAF in 50/50 blend of NR/BR and approached the composition of a typical truck tread. Light microscope dispersion analysis revealed carbon black dispersion essentially equivalent for the various stocks

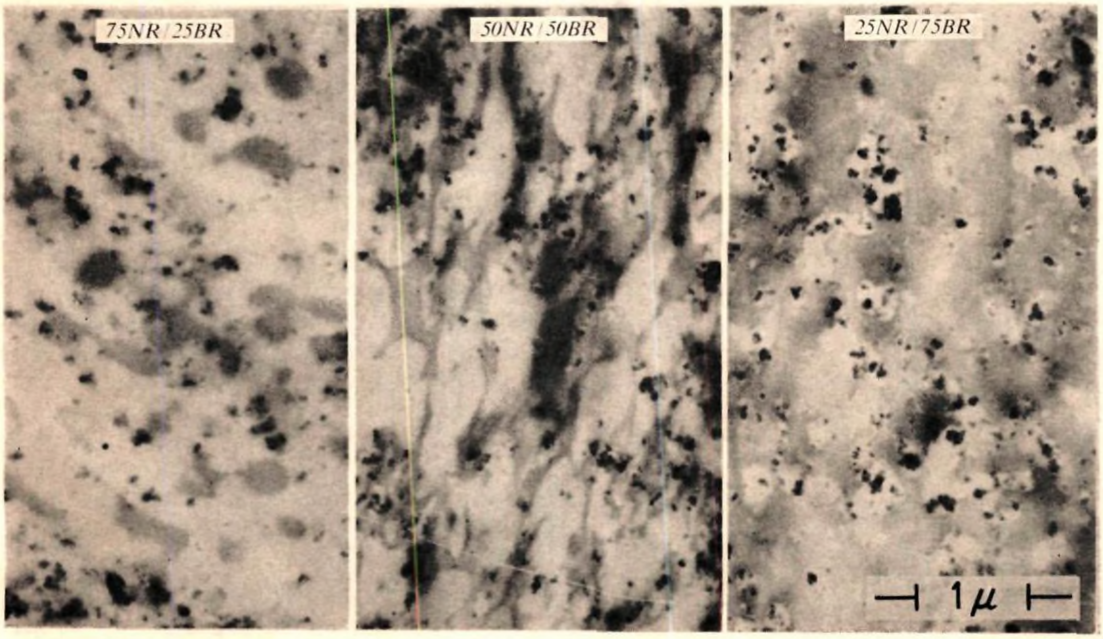

Figure 3. Black loaded NR/BR blends of varied proportions (20 p.h.r. ISAF carbon black).

studied. The total heat and mechanical history of each stock were held within narrow limits. The exception in this regard was the promoted stock which underwent a milling cycle at 310°F.

Vulcanisates were prepared using a conventional sulphur cure system. They were analysed for carbon black distribution via the electron microscope as well as for conventional performance characteristics such as tensile strength, tear strength, hysteresis, and roadwear. The roadwear tests were carried out in formal statistical designs using quadrant treads under severity conditions yielding an average wear of 60–70 miles/mil for a maximum test duration of 12 000 miles. The vulcanisate property data and roadwear results, as a function of carbon black distribution in the BR phase are plotted in *Figures 4* and *5*.

Figure 4 shows the effect of carbon location in the BR phase on hysteresis as defined by the following tests: Goodyear-Healy rebound, Goodrich heat build-up, and phase angle measured in the Monsanto rheometer. These tests were consistent in indicating a minimum energy loss when approximately 60% of the carbon was in the polybutadiene phase. This distribution function is equivalent to a 48 p.h.r. ISAF-loaded polybutadiene. Carbon black distribution changes in the direction of increased loadings in either the NR or BR phase resulted in higher hysteresis stocks.

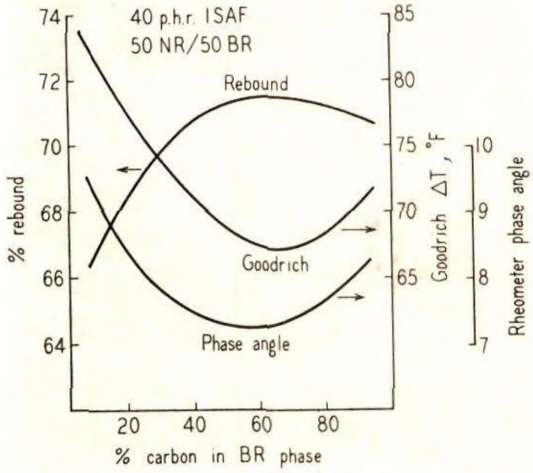

Figure 4. Effect of carbon distribution on hysteresis.

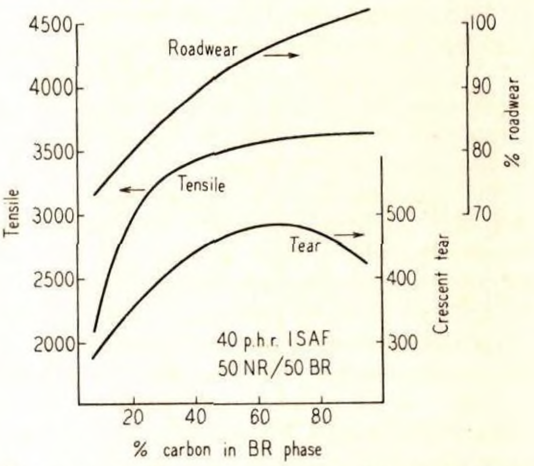

Figure 5. Effect of carbon distribution on vulcanisate properties.

Varied carbon distribution results in well-defined effects on tensile, tear and roadwear as indicated in *Figure 5*. Abrasion resistance increases significantly with increasing percentages of the carbon in the BR phase. Tensile strength of the blend is also dramatically determined by carbon black distribution. Vulcanisate tensile strength decreases rapidly as the major portion of the black locates in the NR matrix. The reverse situation with nearly all of the black in the polybutadiene phase acts to maximise tensile values. The finding is consistent with (1) the recognised need for BR for carbon black reinforcement to develop optimum mechanical properties, and (2) the ability of natural rubber to exhibit an alternate mechanism of reinforcement; *i.e.*, crystallisation under stress. The data in *Figure 5* also indicate Crescent Tear to be influenced by carbon distribution. Crescent Tear values are maximised when 60% of the carbon is in the polybutadiene phase.

PURE GUM BLENDS OF NR WITH OTHER ELASTOMERS

The zone size in pure gum blends is a useful means of assessing the relative compatibility of different elastomers. The factors which affect the zone size include variations in polarity, viscosity, mixing procedure, and filler content. Small zone size is favoured by a similarity in structure and viscosity. High mixing shear also produces intimate blending.

Pure gum blends of natural rubber with six different synthetic elastomers are shown in *Figures 6* and *7*. *Figure 6* represents optical phase contrast micrographs on frozen sections, and *Figure 7* shows electron micrographs of embedded specimens. For both sets of micrographs, the natural rubber appears as the light phase in all instances except the chlorobutyl and EPDM blends. Here, the natural rubber is represented by the dark phase for both the light microscope and electron microscope. It can be seen that nitrile and chlorobutyl produced the least compatible blends. Because of the very coarse zone size, this is shown much more clearly in the phase contrast micrographs. As would be expected, the most compatible blends are with polybutadiene and SBR. Comparing these two systems, the SBR blend is characterised by somewhat smaller zone size.

Carbon Black Distribution

Carbon black distribution in these six blend systems varies quite widely as shown in *Figure 8*. The polymers were first thoroughly preblended and then compounded with a 40 p.h.r. loading of ISAF carbon black. In only the chlorobutyl and EPDM blends is there a strong preference for the carbon to locate in the natural rubber phase. Presumably these results are attributable to the large difference in unsaturation in these two blend com-

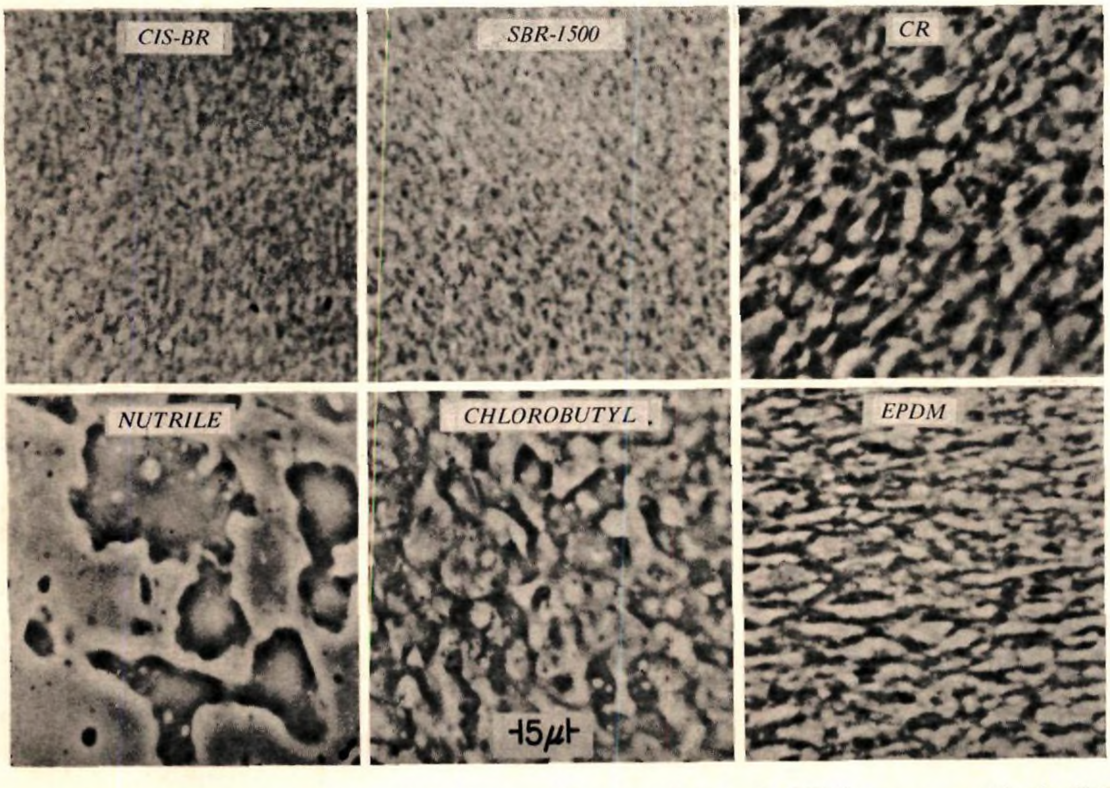

Figure 6. Relative compatibility of NR with different polymers in 50/50 pure gum blends (LM phase contrast—frozen sections).

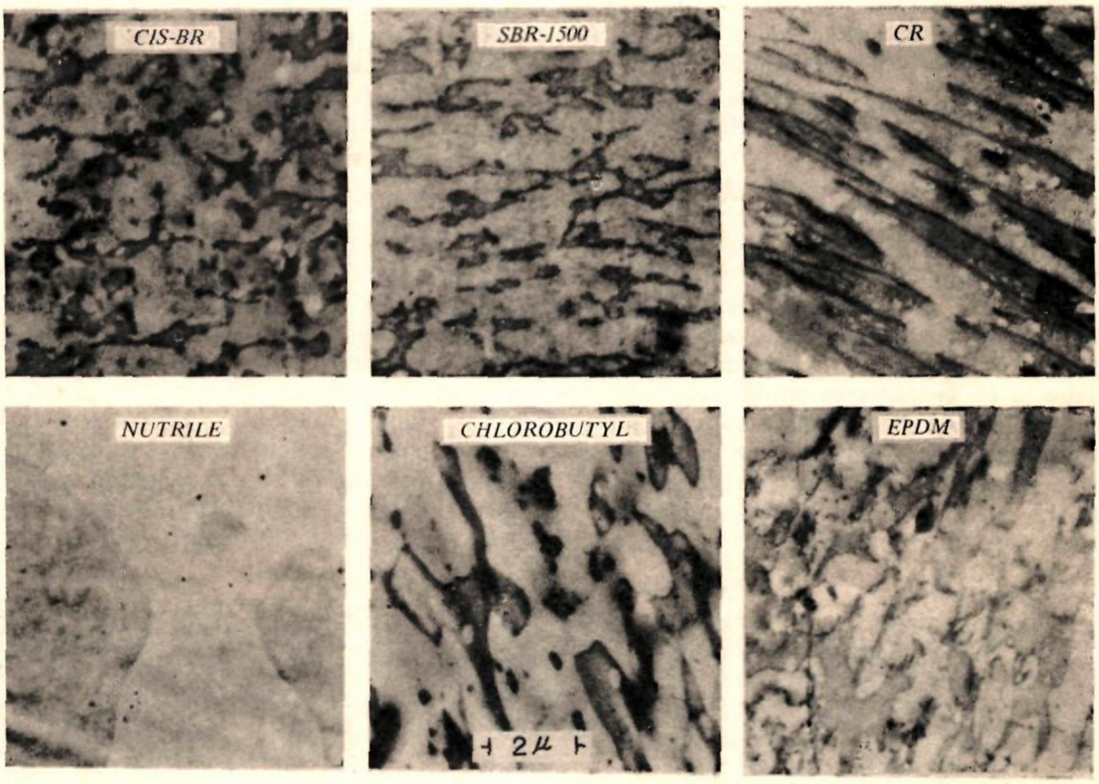

Figure 7. Relative compatibility of NR with different polymers in 50/50 pure gum blend (EM—embedded specimens).

binations. For the other four systems there is an equally strong tendency for the natural rubber phase to be low in carbon black content. These results may be attributable to viscosity and polarity effects, as well as the varied manner in which different polymers tend to wet carbon black. Polybutadiene in particular has been shown to be very strong in this latter respect (HESS AND FORD, 1963), but the fundamental reasons are not completely defined at the present time.

NR/SBR Blends

The relative compatibility of natural rubber with different types of SBR is illustrated by electron microscopy in *Figure 9*. This comparison includes SBR 1500, SBR 1712, SBR 1712 coagulated from the latex, high styrene SBR, carboxylated SBR, and solution SBR. The most compatible blends are those contain-

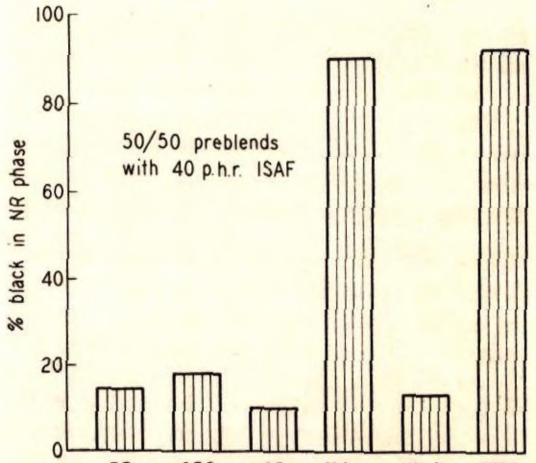

Figure 8. Carbon black distribution in blends of NR with different elastomers.

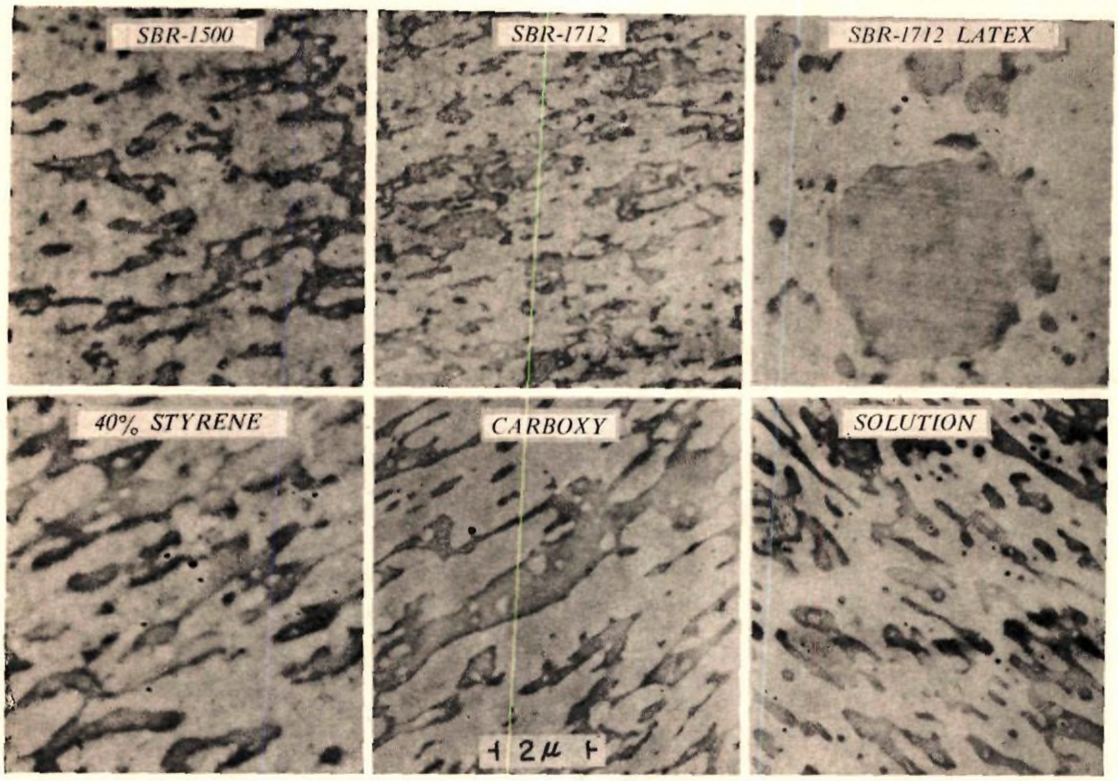

Figure 9. Relative compatibility of NR with different SBR's in 50/50 pure gum blends

ing the SBR 1500 and 1712. Very large zone size was shown with the SBR 1712 latex due to its very high viscosity. Relatively large zone size was also shown with the high styrene and carboxylated SBR. These results would appear to be attributable to differences in molecular structure rather than simple viscosity effects.

Viscosity and Mixing Effects on Zone Size and Carbon Black Distribution

Further studies on the effects of viscosity variations in NR/SBR blends are illustrated in *Figure 10.* Four different blends encompassing Mooney viscosity differences from 50 to 90 for both polymers are compared. Both blends with the high Mooney SBR are very heterogeneous and lumpy, regardless of the initial NR viscosity. With SBR of Mooney viscosity fo 50 (SBR 1500) varying the NR viscosity from 90 to 50 by means of pre-mastication produced a slight increase in SBR zone size.

Carbon black distribution in preblends of the above four polymer combinations are illustrated microscopically in *Figures 11* to *14* and shown graphically in *Figure 15*. Preblends containing the lower Mooney SBR indicated a strong SBR preference for the carbon black. The SBR black preference was substantially reduced when separate masterbatches of each polymer containing equal parts of black were blended. For these stocks, some transfer from NR to SBR was indicated. This appeared to be higher for the stock containing pre-masticated NR with an initial Mooney viscosity of 50. Transfer from NR to SBR was also indicated when all the black was added to the natural rubber and then cut back to a 40-part loading with SBR. Little or no black transfer

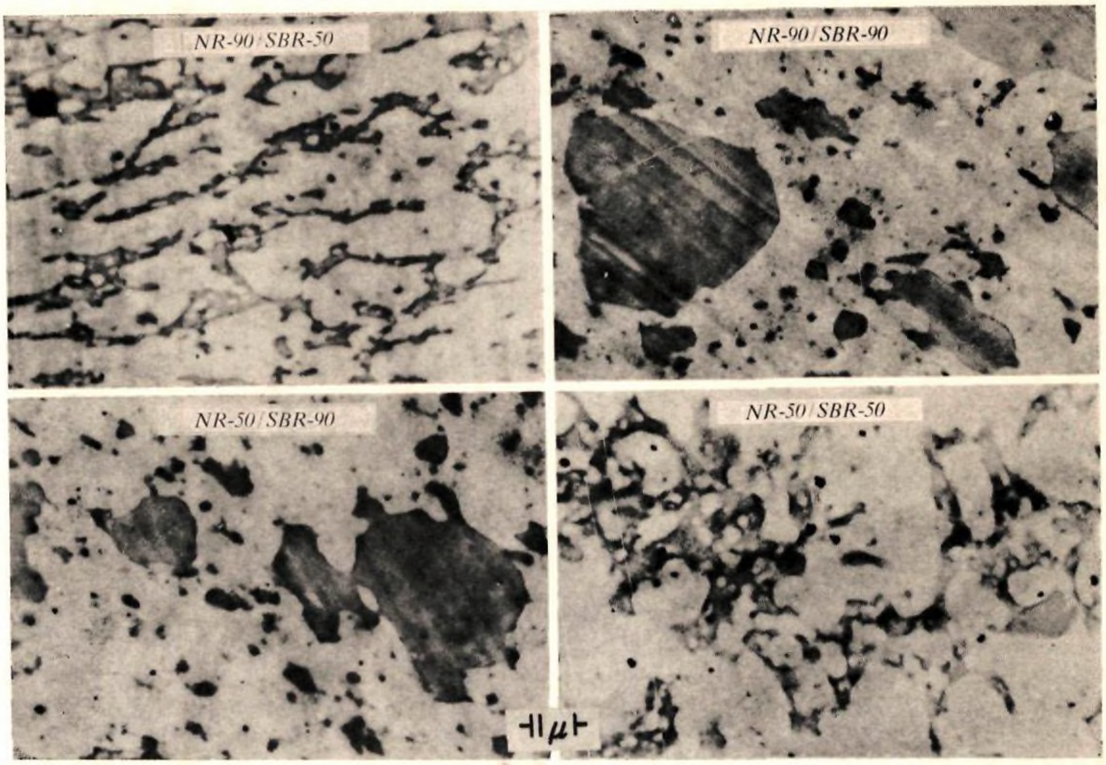

Figure 10. Mooney viscosity variations in 50/50 pure gum NR/SBR blends (EM—embedded specimens).

was observed when the NR black masterbatch was first given a mild heat promotion (0.1 part elastopar). It can also be seen that zone size is somewhat larger for both blends in which all of the black was added to the natural rubber first. The transfer of pigment from NR to SBR is restricted when the latter is the more viscous phase and efficient blending cannot occur.

For both blends containing the very high Mooney SBR, the tendency toward coarse, lumpy SBR zones prevailed even in the black-loaded compounds. Many of the larger SBR zones remained essentially unpigmented in the final mixes. For the preblend and separate masterbatch compounds there was a tendency for relatively equal distribution of black between the two separate polymer phases. When the black was first added to the natural rubber, there was little tendency for transfer to the SBR phase, with or without promotion. These results further illustrate that the transfer of pigment from one polymer to another is first dependent upon achieving an intimate mix. This was not achieved in either instance with the very high Mooney SBR and, hence, the transfer of black was minimal.

Distribution with Different SBR's

Carbon black distribution in four SBR/NR combinations containing 40 p.h.r. ISAF are illustrated in *Figure 16*. Shown here are blends containing SBR 1500, SBR 1712, high styrene SBR, and solution SBR. An SBR black preference is indicated in all four compounds in which the carbon black was added to the preblended elastomers. This preference was weakest for the SBR at the 40% styrene level.

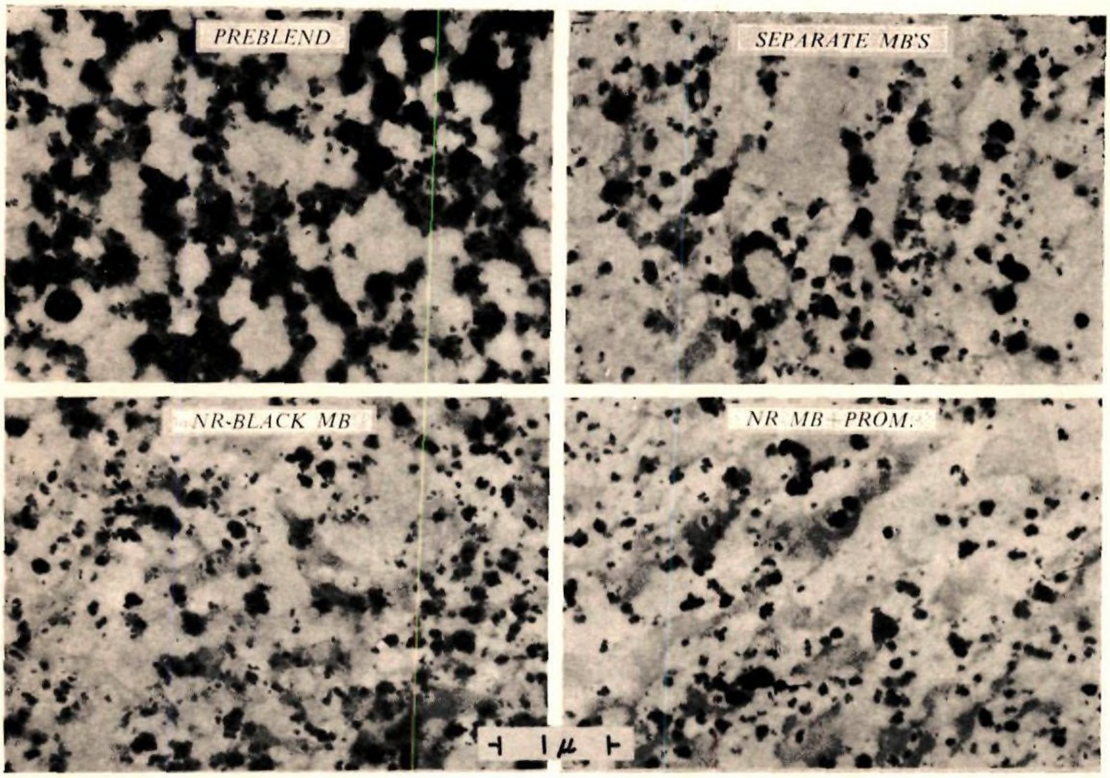

Figure 11. Carbon black distribution in preblends of NR/SBR illustrated microscopically [NR (ML–90)——SBR (ML–50); 50/50 blend + 40 p.h.r. ISAF].

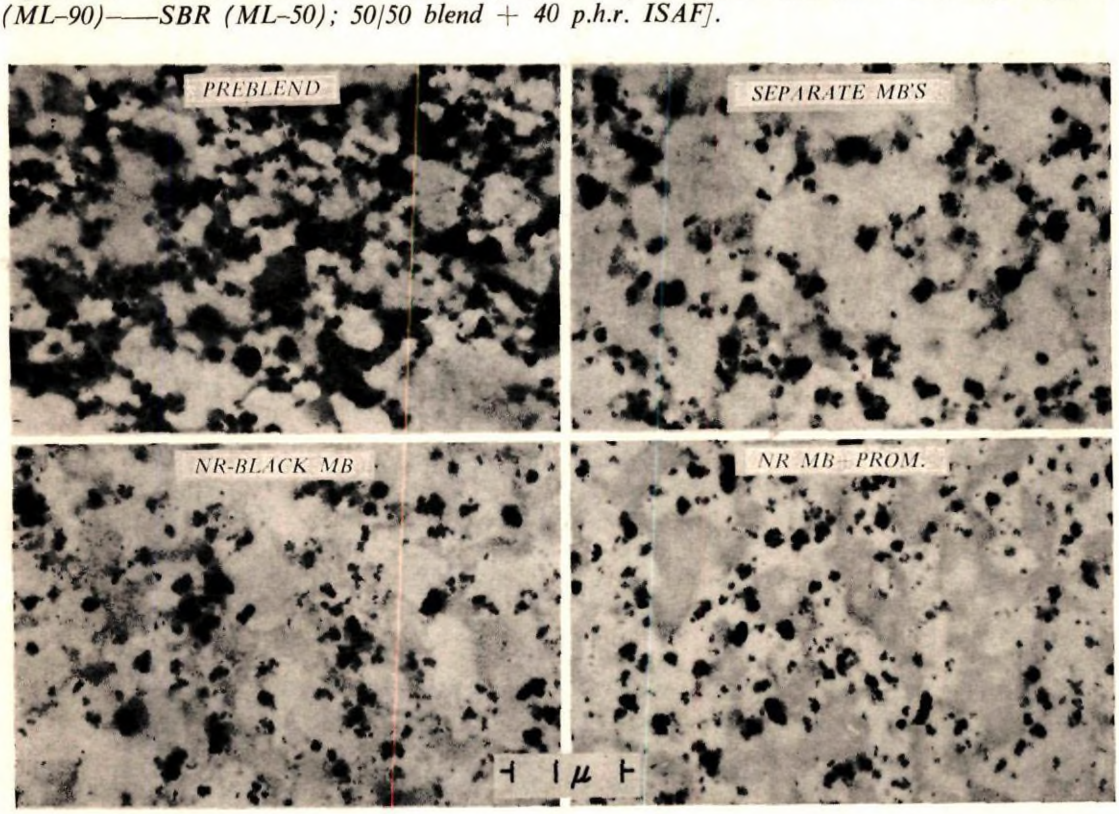

Figure 12. Carbon black distribution in preblends of NR/SBR illustrated microscopically [NR (ML–50)——SBR (ML–50); 50/50 blend + 40 p.h.r. ISAF].

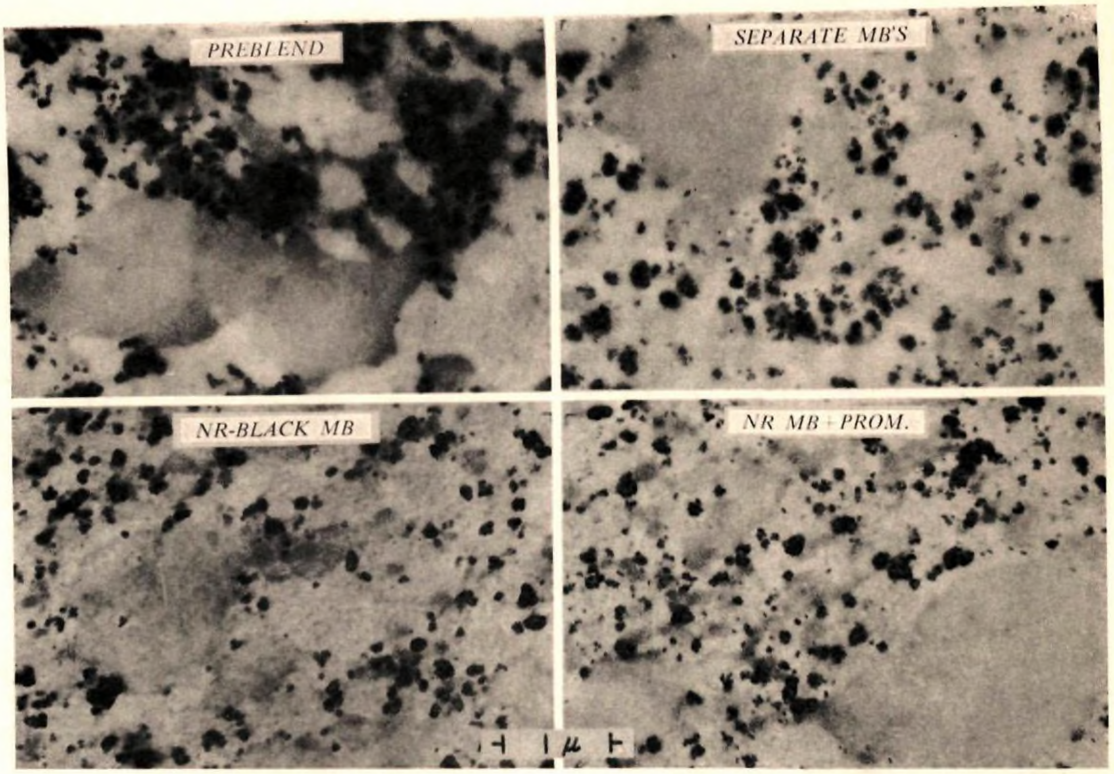

Figure 13. Carbon black distribution in preblends of NR/SBR illustrated microscopically [NR (ML–90)——SBR (ML–90); 50/50 blend + 40 p.h.r. ISAF].

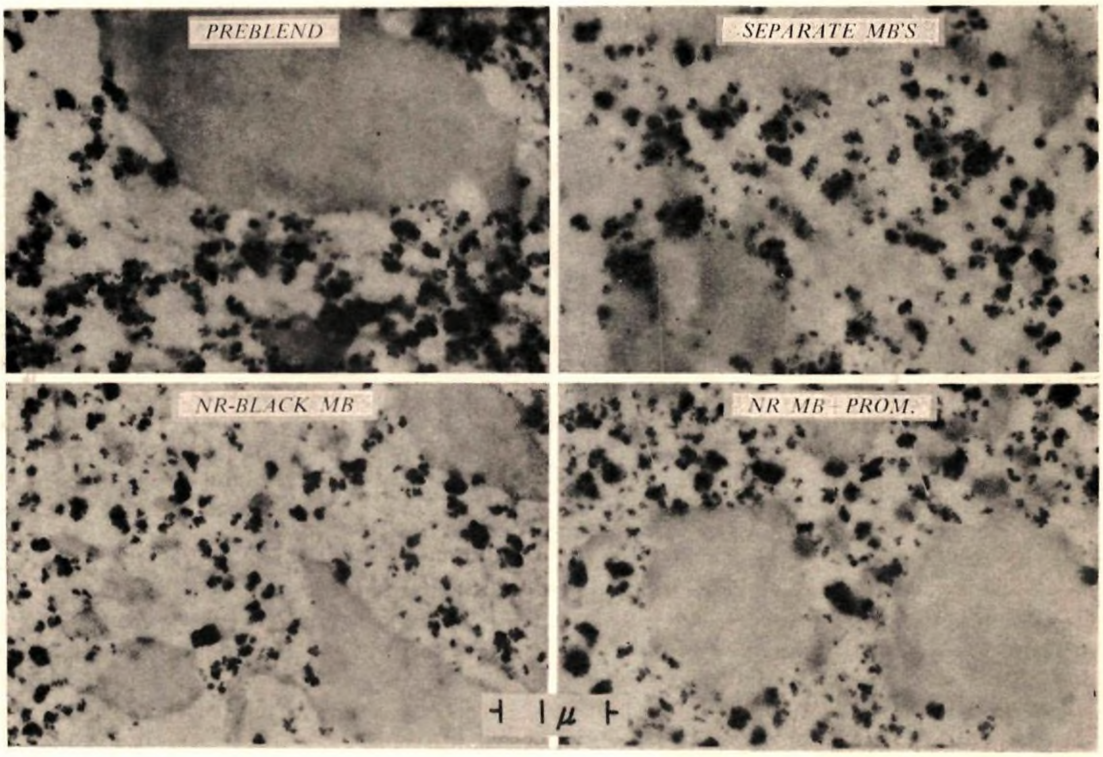

Figure 14. Carbon black distribution in preblends of NR/SBR illustrated microscopically [NR (ML–50)——SBR (ML–90); 50/50 blend + 40 p.h.r. ISAF].

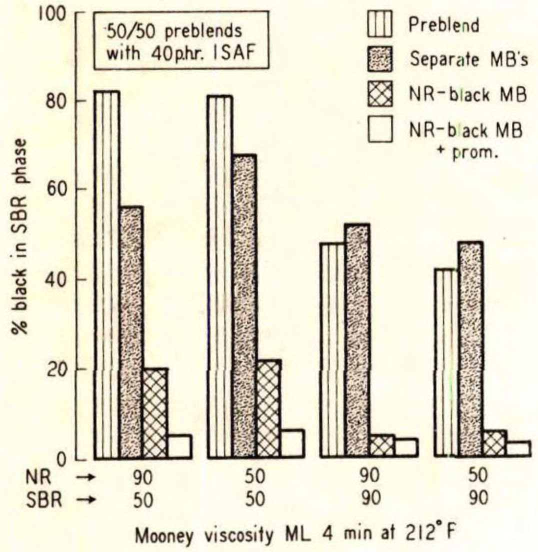

Figure 15. Black distribution in NR/SBR blends as a function of viscosity and mixing procedure.

This compound also showed the coarsest zone size. A somewhat lower black preference was also indicated for SBR 1712 in comparison to SBR 1500. This result may have been influenced somewhat by the relatively poor inter-zone contrast which was obtained with the SBR 1712 stocks. The dilution effect caused by the oil in the SBR 1712 compound may have caused a further worsening of contrast. However, based on the same mixing studies illustrated in *Figures 11* to *14*, the overall results with SBR 1712 appear to be quite similar to those with SBR 1500.

The general findings on 50/50 preblends (40 p.h.r. ISAF) of NR with SBR and BR are summarised graphically in *Figure 17.* The overall indication is that SBR and BR are quite similar in their affinity for carbon black in blends with natural rubber. At lower loadings (*e.g.*, 20 p.h.r.), however, the BR black affinity appears to be stronger. This may be due to the excellent black-wetting characteristics which have been attributed to polybutadiene (HESS AND FORD 1963).

Comparison of NR and Cis-*1,4 Polyisoprene in Blends with SBR and BR*

The relative compatibility of natural rubber and synthetic polyisoprene with SBR and BR in 50/50 blends is illustrated in *Figure 18.* It can be seen that the two polymers are quite similar in their blending characteristics. The only difference among these blends is that zone size is somewhat larger for the polybutadiene compounds than for those containing SBR 1500. Studies were also carried out on blends of natural rubber and synthetic polyisoprene, with and without a curative imbalance between the two polymers. These studies failed to reveal any inter-zone contrast between these two elastomers either by phase contrast optical microscopy or by electron microscopy. On this basis, the two polymers are completely compatible.

Carbon black distribution studies on the above blends (*Figure 19*) also failed to reveal any significant differences. Again, the tendency for coarser zone size in the BR compounds was indicated.

Fillers of Varied Surface Chemistry

Previous studies indicated that the tendency for the filler to locate in the BR phase in 50/50 NR, BR preblends could be altered if oxidised carbon black or silica were employed. It was hypothesised at that time that this might be a polar effect attributable to the protein content in the natural rubber. These experiments were repeated in the present paper using *cis*–1,4 polyisoprene in place of natural rubber so that the protein effect, if any, could be eliminated. IR/BR preblends containing 40 p.h.r. loadings of ISAF, chemically oxidised ISAF (nitric acid treatment) and precipitated silica are illustrated in *Figure 20.* The results are essentially identical to those previously attained with natural rubber. There is a tendency for both the oxidised black and the silica to locate preferentially in the isoprene phase. Similar results were also attained in the studies on NR/SBR blends containing the same pigments. These, along with the IR/BR and NR/BR results, are summarised in *Figure 21.* The silica preference for NR or IR was the strongest and was essentially the same for all

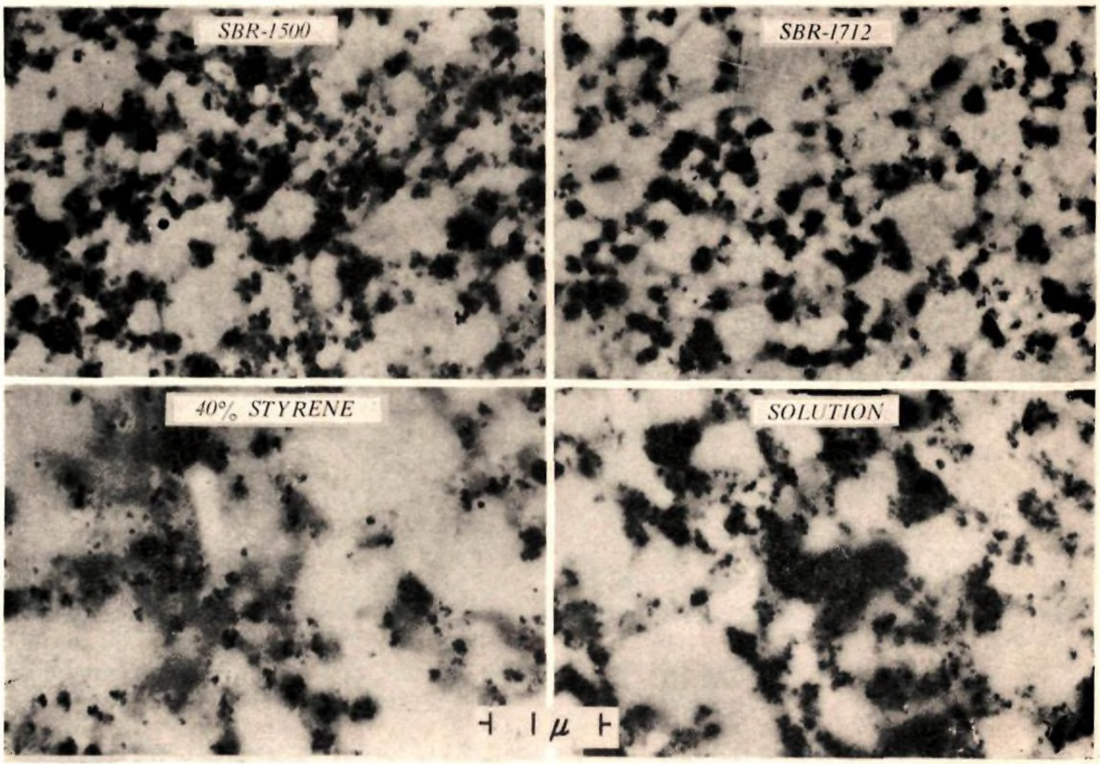

Figure 16. Carbon black distribution in blends of NR with different SBR's (50/50 preblend + 40 p.h.r. ISAF).

Figure 17. Carbon black distribution in blends of NR with SBR and BR.

three blends. At a 20 p.h.r. filler loading, the NR or IR preference for the chemically oxidised ISAF carbon black was equally pronounced. This was minimised, however, at the 40-part loading. In each instance the standard ISAF exhibited a real preference for the SBR or BR phase.

It is now doubtful that these results are explainable on the basis of a polar interaction. Rather, they may be attributable to the lack of affinity of these pigments for polybutadiene or SBR. It is possible that the tendency for a standard carbon to locate in the SBR or BR phase in blends with natural rubber is related primarily to preferential wetting rather than differences in viscosity. When the wetting effects are reduced or eliminated, as with the oxidised black or silica, the distribution mechanism may then revert back to one based on a viscosity differential. However, as pointed

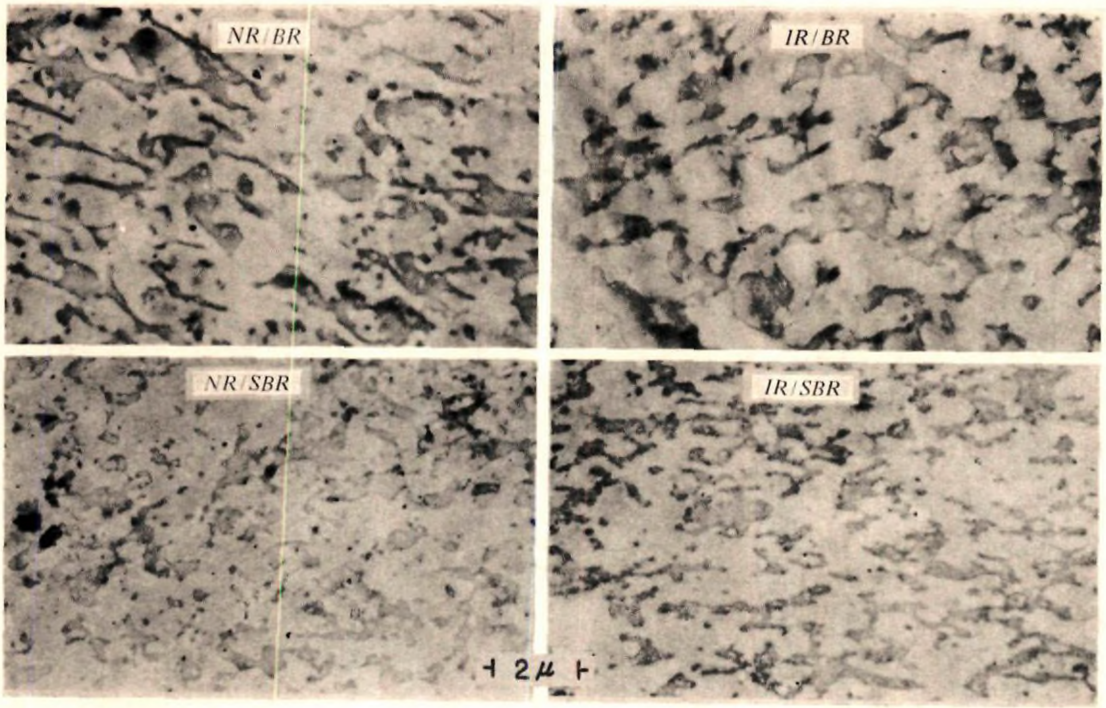

Figure 18. Comparison of NR and synthetic polyisoprene in blends with SBR and BR (50/50 pure gum blends).

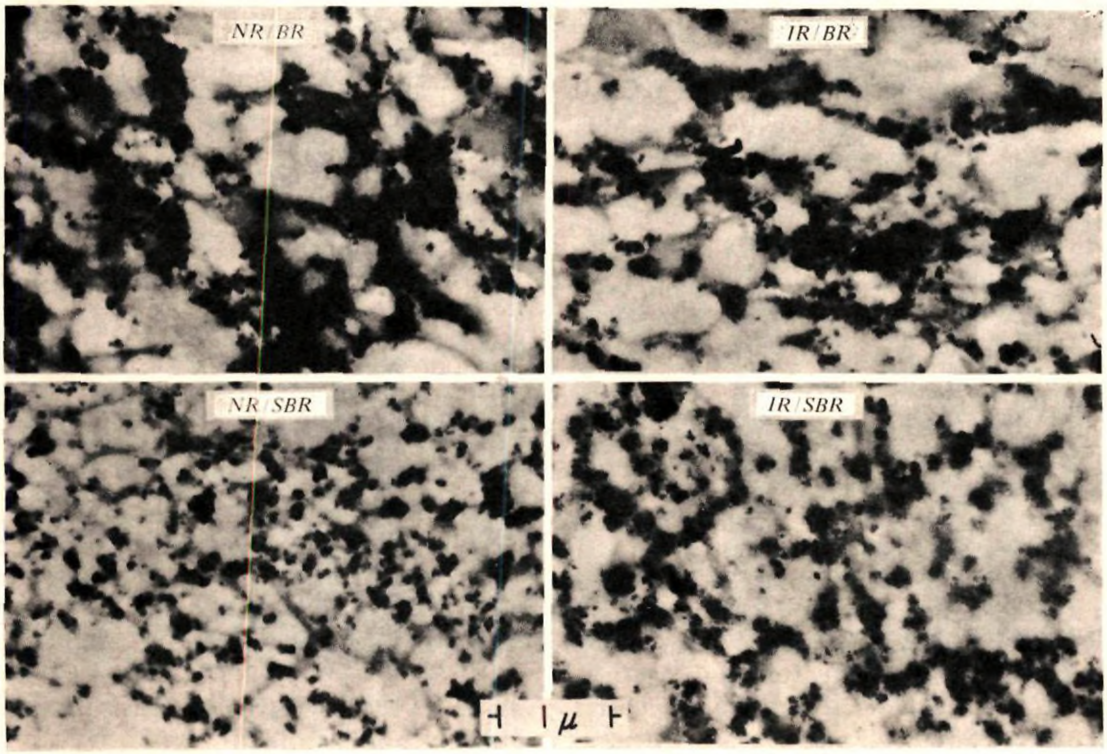

Figure 19. Comparison of NR and synthetic polyisoprene in blends with SBR and BR (50/50 preblends + 40 p.h.r. ISAF).

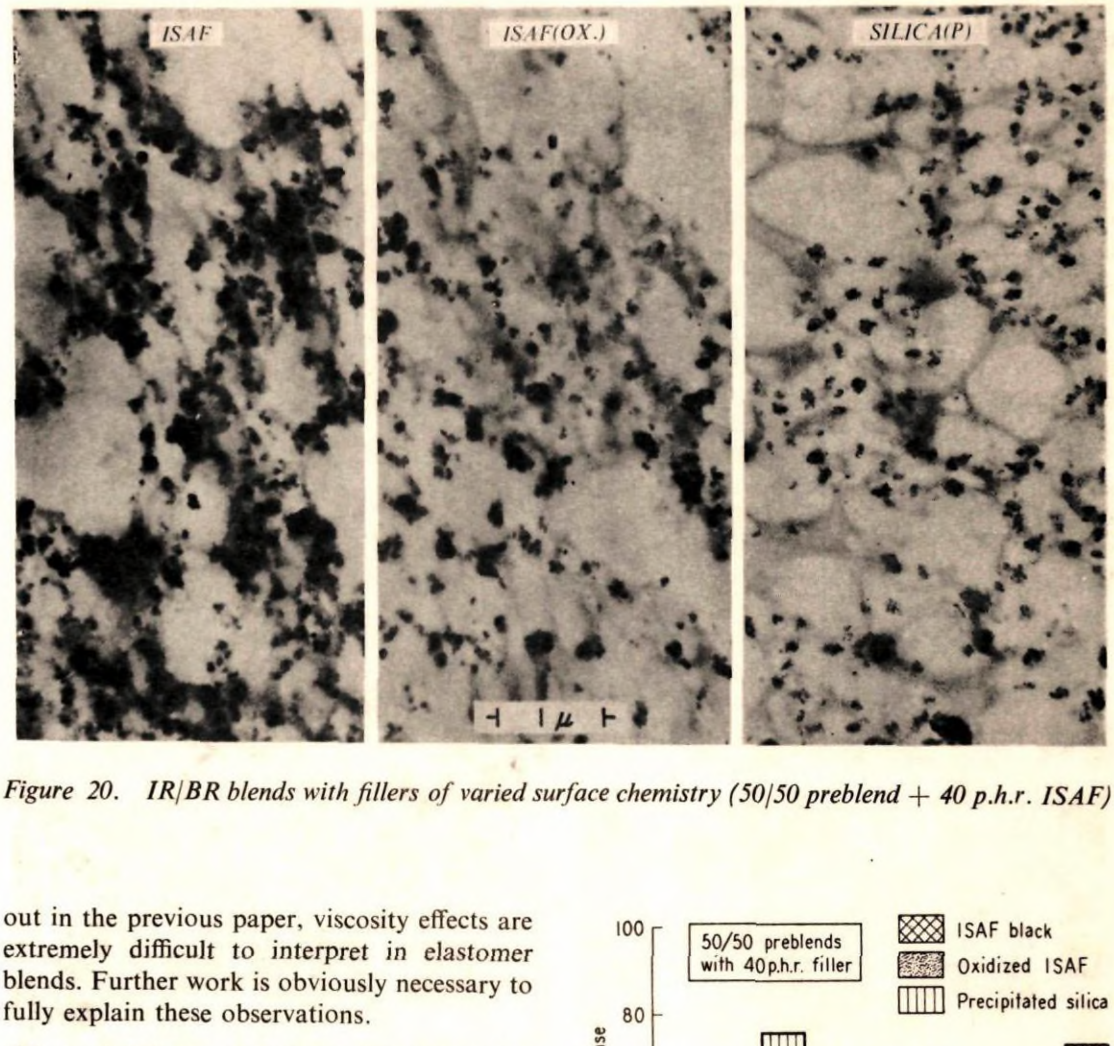

Figure 20. IR/BR blends with fillers of varied surface chemistry (50/50 preblend + 40 p.h.r. ISAF).

out in the previous paper, viscosity effects are extremely difficult to interpret in elastomer blends. Further work is obviously necessary to fully explain these observations.

Effect of Solution and Latex Masterbatching on Black Distribution

The previous work of WALTERS AND KEYTE (1962) and CALLAN *et al.* (1965) has indicated that solution blending of polymers tends to increase the zone size of the two phases. All of these previous studies were carried out on pure gum systems. In the present work, solution and latex masterbatches containing 40 p.h.r. of ISAF were evaluated both with no mechanical work and after various increments of milling. The solution studies also investigate the effect of SBR viscosity on blend homo-

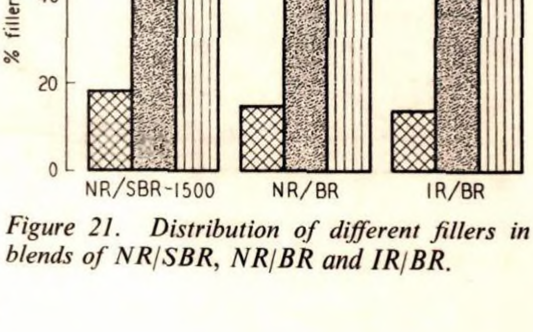

Figure 21. Distribution of different fillers in blends of NR/SBR, NR/BR and IR/BR.

geneity. All curing agents were added during the masterbatching process.

Contrary to the results on the dry mix preblends, the polymer viscosity differences did not cause any significant variations in solution masterbatching. As shown in *Figure 22*, the solution masterbatches were initially characterised by much coarser zone size, and the tendency for the black to locate preferentially in the SBR phase was eliminated. The heterogeneous nature of the blends resulted in part from the incomplete solubility of NR in hexane. This made measurements on black distribution quite difficult, but the general appearance of the solution masterbatches indicated a relatively equal distribution of black between the two polymer phases. A typical solution masterbatch before and after five minutes of milling is illustrated in *Figure 23*. A streaky pattern of coarse polymer zones, with the carbon black located in both phases, is indicated in the unmilled sample. However, after only a minimum of mixing, the solution compounds reverted back to the general appearance of a dry mix preblend; *i.e.*, the carbon black located preferentially in the SBR phase.

The results on an NR/SBR latex masterbatch (*Figure 24*) were essentially the same although this stock required considerably more mixing to produce a uniform carbon black dispersion. The unmilled sample indicated little or no black preference for either polymer, but milling again produced the characteristic SBR black preference.

Filler Transfer Studies

The above studies, along with those carried out previously, indicate the ability of a pigment to transfer from one polymer to another under the conditions of high shear mixing.

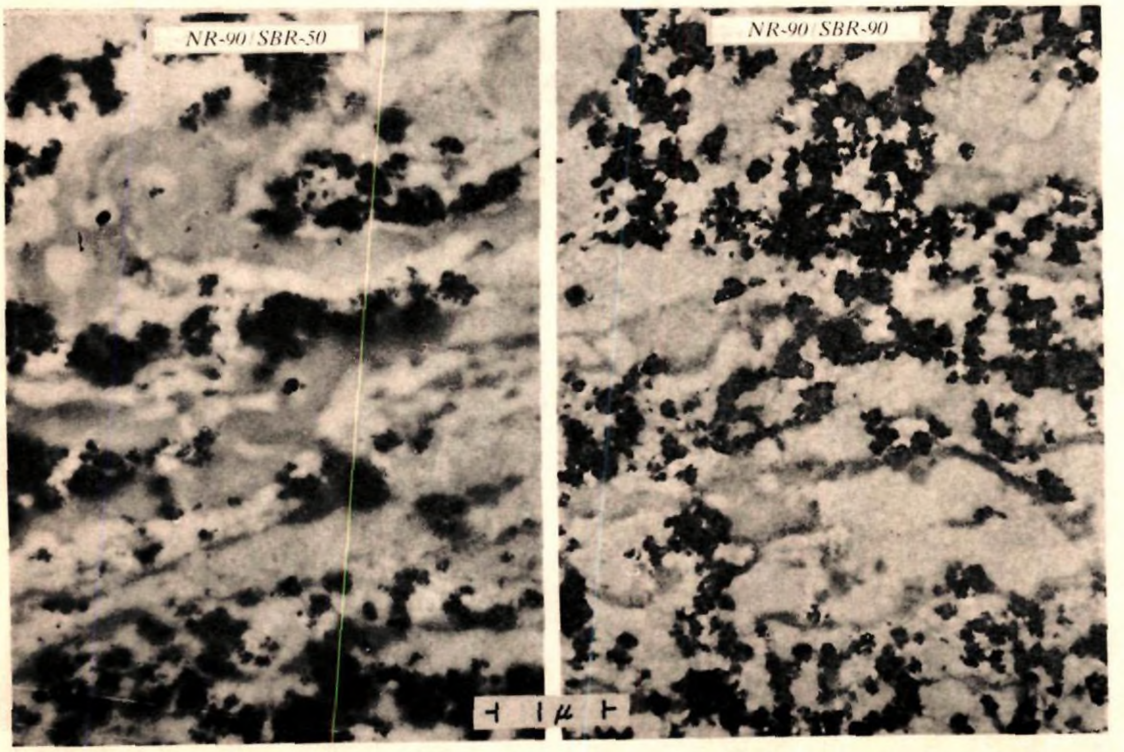

Figure 22. Hydrosolution masterbatches (HSMB) of 50/50 NR/SBR blends of varied Mooney viscosity (no additional mixing).

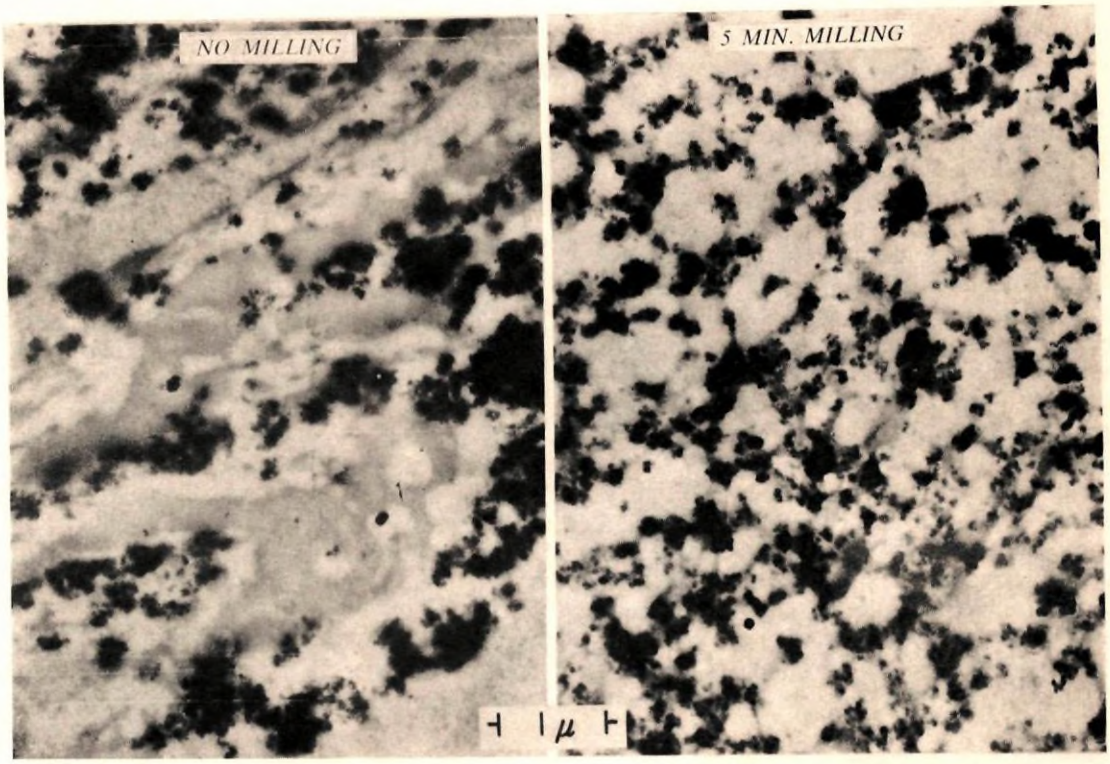

Figure 23. Carbon black distribution in NR/SBR hydrosolution masterbatches (50/50 blend + 40 p.h.r. ISAF).

Figure 24. Carbon black distribution in NR/SBR–1712 latex masterbatch (50/50 blend + 40 p.h.r. ISAF).

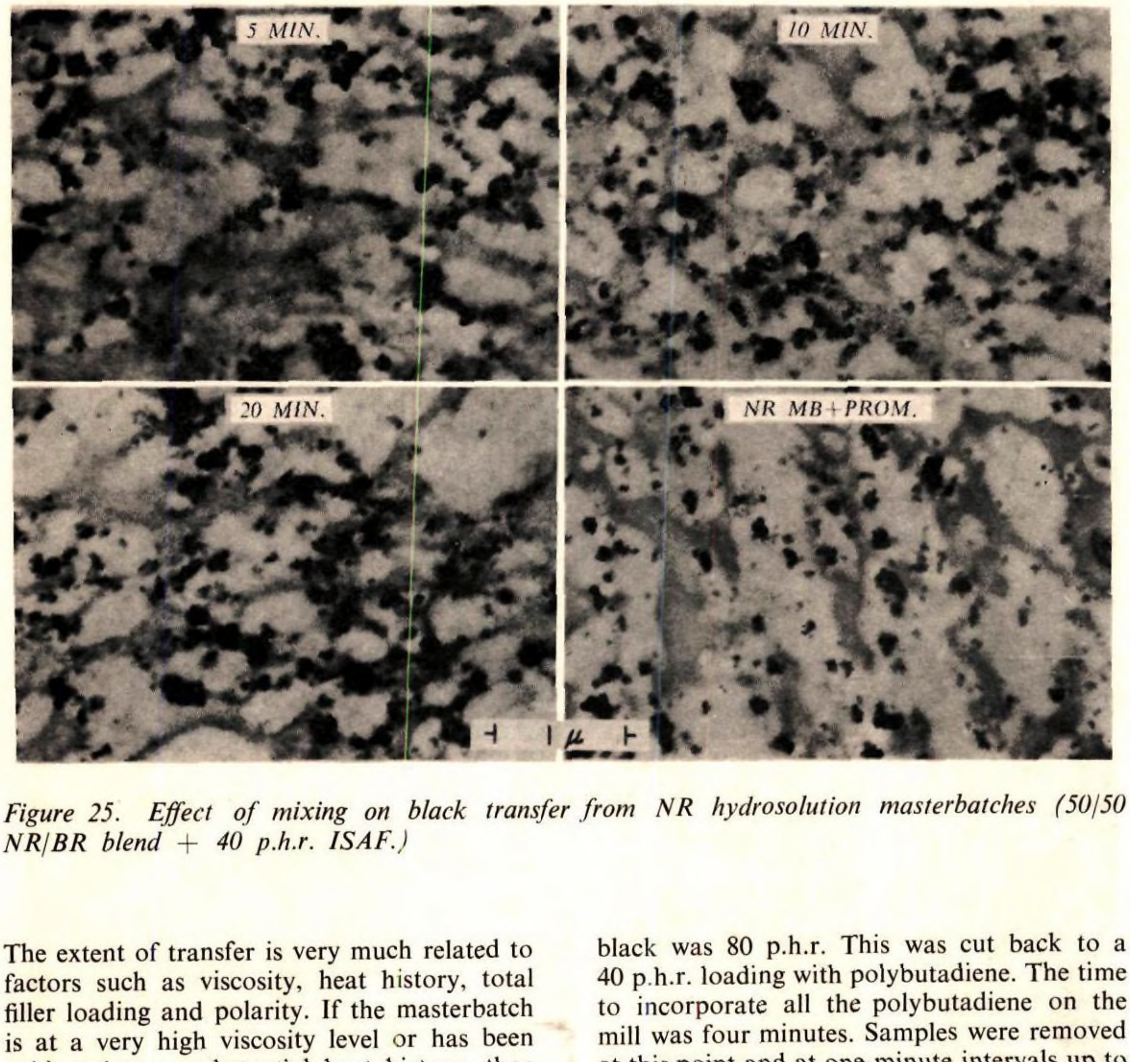

Figure 25. Effect of mixing on black transfer from NR hydrosolution masterbatches (50/50 NR/BR blend + 40 p.h.r. ISAF.)

The extent of transfer is very much related to factors such as viscosity, heat history, total filler loading and polarity. If the masterbatch is at a very high viscosity level or has been subjected to a substantial heat history, then filler transfer is minimal. Transfer is favoured by filler loadings, provided that the viscosity does not become too high. This, of course, relates very much to mixing efficiency. And finally, the relative affinity of the two polymers for the pigment is an extremely important factor. Thus, carbon black transfer from a natural rubber masterbatch to polybutadiene has been observed extensively, but the reverse effect has not been indicated.

Additional transfer studies on an NR carbon black solution masterbatch are detailed in *Figure 25*. The initial loading of ISAF carbon black was 80 p.h.r. This was cut back to a 40 p.h.r. loading with polybutadiene. The time to incorporate all the polybutadiene on the mill was four minutes. Samples were removed at this point and at one-minute intervals up to a total of twenty minutes of mixing. In *Figure 25*, the distribution of black is illustrated at five minutes, ten minutes, and twenty minutes along with a sample of a heat promoted NR black masterbatch which was cut back with polybutadiene. At the early stages of mixing, zone size was large and most of the black aggregates were confined to the NR phase or at the interface of the BR zones. At mixing times in the range of seven to ten minutes, some encapsulation of the black aggregates by the BR zones was evident, indicating that transfer had taken place. In the range of 15 to 20

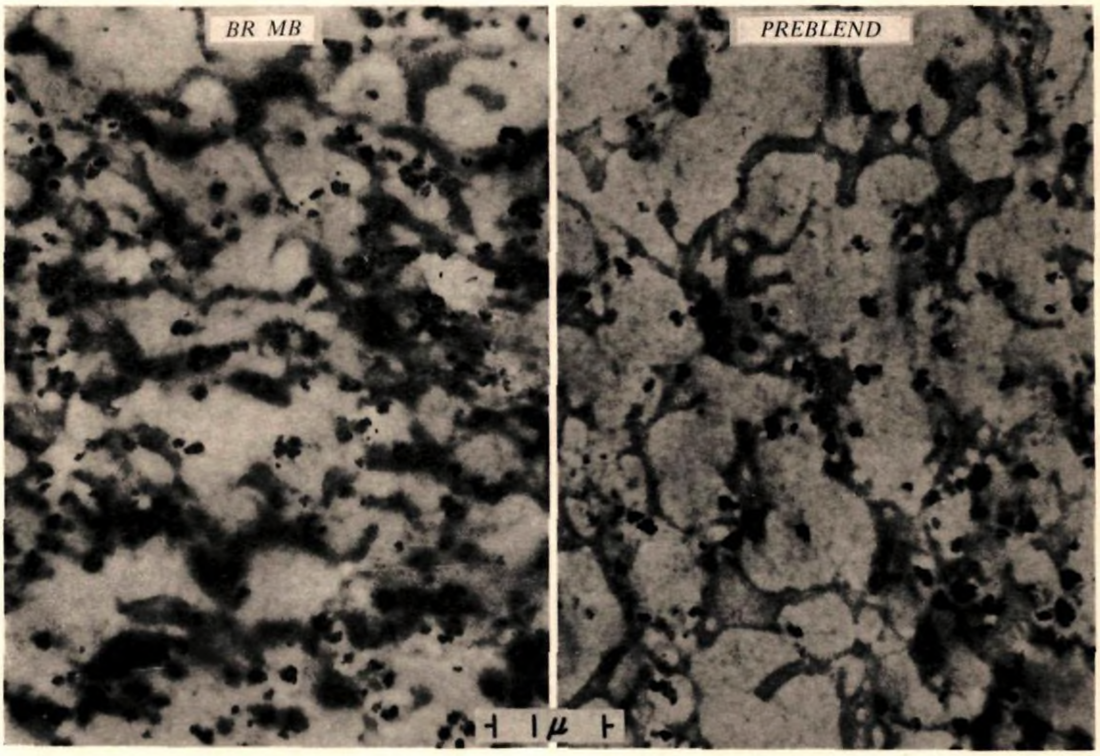

Figure 26. Transfer studies on silica in 50/50 IR/BR blends (20 p.h.r. loading).

minutes of mixing, transfer was quite extensive as illustrated on the electron micrograph of the twenty-minute sample. For the sake of comparison, the promoted NR black masterbatch shows little or no transfer. This was mixed under the same conditions for a period of 15 minutes.

Silica Transfer

In view of the dissimilarity of the distribution of silica in IR/BR or NR/BR preblends, as compared to carbon black, transfer studies were also carried out with this pigment. The results with a precipitated silica in 50/50 IR/BR blends are illustrated in *Figure 26.* Compared here are the distributions of silica in a preblend and in a polybutadiene masterbatch which was subsequently cut black with polyisoprene. The silica BR masterbatch was let down from a 40 p.h.r. to a 20 p.h.r. loading. The appearance of the two stocks is quite similar, indicating that fairly extensive transfer to the IR phase has taken place. It should be noted, however, that the result is not quite as pronounced as it appears since it has been partly influenced by dispersion. Some of the silica is located in the BR phase in agglomerates, which are not shown on this micrograph. As would be expected from these results, studies in NR silica masterbatches which were cut back with polybutadiene showed little or no transfer of pigment to the BR phase. Further studies of this type employing other pigments and polymer systems are now in progress, and will be reported in a subsequent paper.

CONCLUSIONS

(1) In 50/50 preblends with natural rubber, the commonly used commercial types of SBR show a strong affinity for carbon black when it is added to the blend at relatively high loadings (*e.g.*, 40 p.h.r.). This finding is similar to the previously reported results on NR/BR blends containing carbon black. Zone size is somewhat smaller for the SBR blends in comparison to BR, either unpigmented or containing filler.

(2) In unmilled solution or latex black masterbatches of NR and SBR, no preferential distribution of black was observed. Zone size was much larger than in conventional dry mixed blends. With further mixing the HSMB and latex masterbatch blends indicated an SBR black preference similar to the dry mix compounds.

(3) Comparison of synthetic polyisoprene and natural rubber in blends with SBR and BR revealed no significant differences either in regard to zone size or filler distribution.

(4) Studies on 50/50 preblends of IR/BR and NR/BR containing precipitated silica gave results different from the findings on carbon black. Here, there was a strong tendency for the silica particles to locate preferentially in the isoprene phase. Similar results were also obtained with NR/SBR blends. Distributional studies using a chemically oxidised ISAF carbon black produced intermediate results in these three blend systems, with a slight tendency to favour the isoprene phase.

(5) Further studies on filler transfer again indicated that carbon black will migrate from an NR masterbatch to polybutadiene under high shear mixing conditions. High transfer was favoured by a relatively high black loading and low heat history for the NR black masterbatch. With an NR silica masterbatch, little or no transfer to polybutadiene was observed. In the reverse experiment, considerable transfer of silica took place from a BR masterbatch which was cut back with natural rubber.

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APPENDIX

I. *Carbon Loaded Formulation* (Figures 4 *and* 5)

Polymer (varied)	100
ISAF	40
Aromatic process oil	10
ZnO	4
Stearic acid	2
Flexamine G	1.5
Santoflex 77	1.0
Santocure NS	0.4
Sulphur	2.0

II. *Mixing Procedure for Carbon Loaded Recipe* (Figures 4 *and* 5)

(Banbury second speed, cold water on)

	Time (min)
Breakdown polymer and/or HSMB	0
Add all carbon (if present), ZnO, stearic acid and anti-oxidants	2
Sweep down	3
Add oil at 350°F	4–6
Scrape down	6
Dump at 310–320°F	8–9
Finish compound on 8″ × 18″ mill at 190°F.	4

III. *Peroxide Cured Formulation for Phase and EM Studies*

Polymer (varied)	100
Carbon	varied
PBNA	1
Dicup 40C	4

IV. *Mixing Procedures for Peroxide Cured Formulation*

(*a*) *Polymer preblend*
Cold (70°F) 18″ mill.
Polymers blended thoroughly for twelve minutes—carbon added if present. PBNA and Dicup 40C added after carbon is incorporated.
Total Time: Pure gum 14 minutes.
Carbon loaded 20 minutes.

(*b*) *Carbon Initially Present In One Polymer*
Stage I: Cold (70°F) 18″ mill. Carbon added to polymer.
Total time 10 minutes.
Stage II: Cold (70°F) 18″ mill. Masterbatch and raw polymer blended for eight minutes. PBNA and Dicup 40C added.
Total time 10 minutes.

(*c*) *Separate Masterbatches*
Stage I: Same as *Stage I* of *(b)* above.
Stage II: Cold (70°F) 18″ mill. Masterbatches from *Stage I* blended for eight minutes. PBNA and Dicup added.
Total time 10 minutes.