

Experimental Study of the Relationship of Processing to the Morphology in Blends of SBR and *cis*-Polybutadiene with Carbon Black*

BIING-LIN LEE and CHLOE SINGLETON, *B.F. Goodrich Company, Research and Development Center, Brecksville, Ohio 44141*

Synopsis

The morphology of carbon-black-loaded styrene-butadiene rubber (SBR)/*cis*-1,4-polybutadiene (BR) blends is characterized as a function of mixing energy input. The blends consist of an 80:20 weight ratio of SBR and BR with the incorporation of 20 phr carbon black via three different schemes. These schemes are: (1) free mixing of the three components, (2) mixing of BR-black masterbatch with SBR, and (3) mixing of SBR-black masterbatch with BR. Differential scanning calorimetry (DSC) and electron microscopy (EM) results indicate that the domain morphology is strongly affected by the manner in which the carbon black is introduced into these blends. Some of the features of the blends are as follows: (1) BR, which is the minor rubber component, is always the dispersed phase, and its domain size decreases with increasing energy input during mixing. (2) In the black-rubber masterbatch mixing, the black always stays in the original rubber phase throughout the mixing process. No significant migration of carbon black from one rubber phase to the other is observed. (3) In the free mixing process, the carbon black agglomerates initially line up along the SBR-BR interfaces, and later disperse throughout the SBR matrix with increased mixing. However, the DSC results suggest that the amount of carbon-black-free BR is decreasing with increased mixing. This would occur if there is created a carbon-black-loaded SBR-BR diffuse interphase. A model is developed to interpret these findings.

INTRODUCTION

The key to efficient processing of multicomponent systems, which will yield optimum physical properties, is the morphologic characterization of polymer blends and composites. For the case of rubber blends, the ultimate physical properties of the finished products are strongly influenced by the heterogeneity of these systems and the degrees of dispersion of the additives in these blends.

Since the pioneering study of Walters and Keyte,¹ electron microscopy (EM) has been used extensively to observe the heterogenous structures in a number of gum rubber blend systems. In 1973, Kruse² published a comprehensive literature review on gum rubber microscopy. However, the introduction of carbon black rendered interpretation of the morphology of these blends extremely difficult by existing electron microscopy techniques. Alternate techniques for observing blend morphology as well as the dispersion of black had to be devised. In the last few years Hess, Scott, and Callan³⁻⁵ developed a differential swelling method to study the carbon black distribution in natural rubber blends with polybutadiene or styrene-butadiene rubber. More recently, Hess and Chirico⁶

* Based on a paper presented at the American Institute of Chemical Engineers Meeting in Miami Beach, Florida, November 12-16, 1978.

devised a method of differential pyrolysis of thin blended rubber sections. Holes in these sections indicate where the domains of the preferentially pyrolyzed rubber were located in the blend. Both these techniques involve a physical alteration of one rubber component preferential to the other. Determination of domain sizes requires use of scaling factors. Direct domain size measurements are not a feature of these methods. In 1973, Ivan et al.⁷ reported using a replication technique of freeze-fractured surfaces to study the dispersion of carbon black in blended rubber samples. However, differentiation of the rubber phases is not unambiguous by this technique.

During the course of these studies, one blend system in which the rubber phases remained difficult to distinguish from one another via standard electron microscopy techniques was that of styrene-butadiene rubber (SBR) blended with polybutadiene (BR). In the early 1970s Smith and co-workers^{8,9} utilized an ebonite specimen preparation technique in which, under the electron microscope, the SBR appears more opaque than the BR and is easily distinguished from it. Also, with a minimum of care exercised, little distortion of the rubber phases occurs during the course of EM specimen preparation. This technique has been successfully extended to carbon black-loaded SBR/BR blends and is described in this paper.

In addition to EM, differential scanning calorimetry (DSC) can be used to provide insight into the state of mix of carbon black loaded SBR/BR blends. Considerable information on the application of DSC is available.¹⁰ However, past efforts were concerned with the characterization of gum polymer blends and block copolymers¹¹⁻¹³ with less emphasis on the characterization of black-loaded rubber blends.^{13,14} Recently, Sircar and Lamond¹³ correlated DSC, dynamic modulus, conductivity, and EM results to characterize black-loaded blend systems. However, the development of the morphology as a function of energy consumption during mixing was not studied.

In this paper the morphology of carbon black-loaded SBR/BR blends is characterized as a function of mixing energy input. Minor component domain sizes and carbon black dispersions are seen to be strongly affected by the manner in which the three components are blended. DSC and EM are sensitive tools by which to detect these morphologic changes. DSC results show that the heat of fusion associated with the BR melting endotherm varies as a function of the mixing energy input and the mixing scheme utilized. The interaction and dispersion of carbon black within the blended rubber phases are described based on complementary DSC and EM results.

EXPERIMENTAL

Sample Preparation

The carbon black-loaded SBR/BR rubber blends were compounded in a Brabender PL-750 #644 internal mixer. The rotor speed was 40 rpm, and the initial chamber temperature was 93°C. The basic recipe for these blends was

Component	Amount	Mooney viscosity (ML-4 at 100°C)
SBR	80 parts	50-60
BR	20 parts	50-60
Carbon Black N303	20 phr	

Basically, as a model recipe, 20 parts of carbon black are introduced into 100 parts of rubber in three different ways in order to see how the carbon black interacts with each rubber species in the blend. The rubbers used in this study were not oil extended.

Three sets of samples were prepared for this study. Each set represents a different mixing scheme for incorporating the carbon black in the rubber blends. These schemes are:

A. **Free Mixing.** All three ingredients (80 parts SBR, 20 parts BR, and 20 phr carbon black) were put into the mixing chamber at the same time.

B. **BR-Carbon Black Masterbatch Approach.** All the carbon black of the recipe was first mixed with the BR rubber in the Brabender, mixed for 10 min, and then passed through the mill a few times. The black-loaded BR was then returned to the Brabender mixer and mixed with the 80 parts SBR.

C. **SBR-Carbon Black Masterbatch Approach.** All the carbon black of the recipe was first mixed with the SBR rubber in the Brabender mixer for 10 min and then passed through the mill a few times. The black-loaded SBR was then returned to the Brabender mixer and mixed with 20 parts BR.

Five blend samples representing various stages of mixing were prepared for each set. The mixing time for the sample in each set varied consecutively from 30 sec up to 9 min. Thus, the formation and development of BR domain structures and carbon black agglomerates and subsequent dispersion could be studied via electron microscopy of these samples. The torque τ and energy of mixing (power integrator number W_t) were recorded for each sample. General information about the application of the power integrator is available.¹⁵

Thermal Analysis

Specimens from each sample were analyzed using a Perkin-Elmer DSC-2 differential scanning calorimeter. It was noted that the size of the BR crystalline melting endotherm could be related with the mixing time of the blends.

The results of this thermal analysis study along with the electron microscopy results yield much insight into understanding the morphology of the black loading of SBR/BR blends.

The experimental conditions for the DSC analysis were: instrument, Perkin-Elmer DSC-2; sample size, ~20 mg; reference standard, empty aluminum pan; heating rate, 20°C/min starting at -130°C following a quench from room temperature; atmosphere, helium; sensitivity, 8.4 mJ/sec (2 mcal/sec).

The melting energy of the BR phases in these blends per unit sample weight was calculated using the following equation¹⁶

$$\Delta H = \frac{A_S ZK}{A_R W} \quad (1)$$

where A_S = area of the crystalline melting peak (planimeter units), A_R = area

of a unit rectangle on the chart paper (planimeter units), Z = heat associated with the unit rectangle A_R (mJ), W = sample weight (mg), and $K = 1.04$ = instrument calibration constant.

Electron Microscopy

The specimens were prepared for examination in a Phillips EM 100B electron microscope using the ebonite technique devised by Smith and co-workers.^{8,9} This technique was used for this study because, to date, it is the only EM specimen preparation technique known which contrasts SBR and BR with little dimensional distortion to either phase.

This technique consists of immersing a small ($2 \times 2 \times 5$ mm) piece cut from the interior of a blend in a molten sulfur mixture at 120°C , for approximately 8 hr. This mixture is composed of sulfur, a sulfenamide-type accelerator, and zinc stearate in a 90:5:5 weight ratio. After this curing operation, the blend specimen is sufficiently hardened so that it may be sectioned with an ultramicrotome. These sections are approximately 50–100 nm thick.

Recently, x-ray microanalysis¹⁷ has shown that near the surface of the specimen deposits rich in zinc preferentially reside in the SBR phases. Since zinc atoms contain more electrons than any other atoms in the ebonite recipe, the SBR phases appear "darker" in the electron microscope than do the BR phases, which contain no zinc elements or compounds.

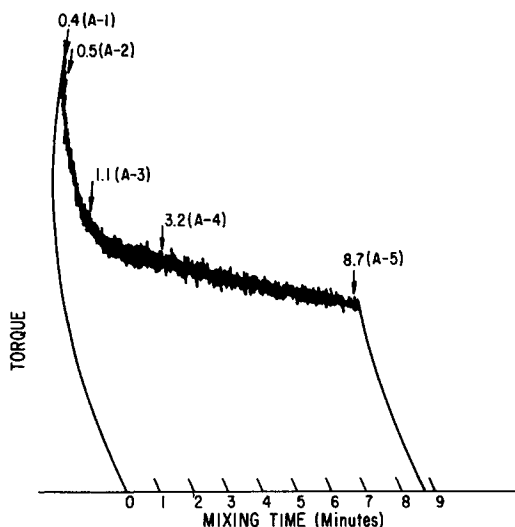


Fig. 1. Brabender mixer torque vs. mixing time for the free mixing of 80 parts SBR, 20 parts BR, and 20 phr carbon black. The mixing time in minutes and the sample number in parentheses are given for each sample in this series.

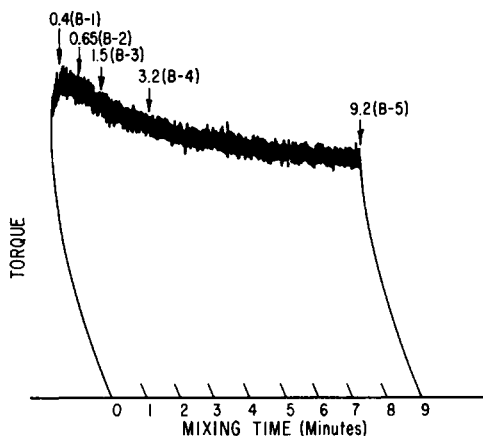


Fig. 2. Brabender mixer torque vs. mixing time for 80 parts SBR and 20 parts black-loaded BR. Previous to this operation the 20 phr carbon black was mechanically mixed with the BR. The mixing time, in minutes, and the sample number, in parentheses, are given for each sample in this series.

RESULTS AND DISCUSSION

Brabender Mixing Torque

The Brabender torque curves (mixing torque vs. mixing time) for each of the three mixing schemes (A, B, and C) of the black-loaded SBR/BR rubber blends are shown in Figures 1 through 3, respectively. It is quite obvious that these torque curves are very different depending on the mixing scheme used. These torque curves yield characteristic information about the state of mix. For the free black mixing process (A) (see Fig. 1), the torque initially reaches a high value and then drops off and levels out as the mixing continues. The torque curve for the Br-black masterbatch method (B) is shown in Figure 2. This curve initially attains only a moderate value and maintains this value throughout the mixing process. The torque curve for the SBR-black masterbatch method (C) (shown in Fig. 3) is very similar to the curve for method A. A discussion of the morphologic interpretation of the shapes of these curves appears in the following sections.

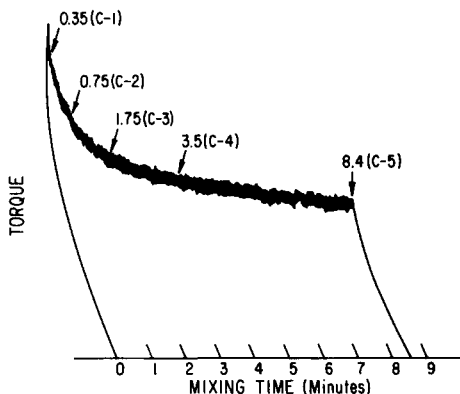


Fig. 3. Brabender mixer torque vs. mixing time for 20 parts BR and 80 parts black-loaded SBR. Previous to the operation the 20 phr carbon was mechanically mixed with the SBR. The mixing time in minutes and the sample number in parentheses are given for each sample in this series.

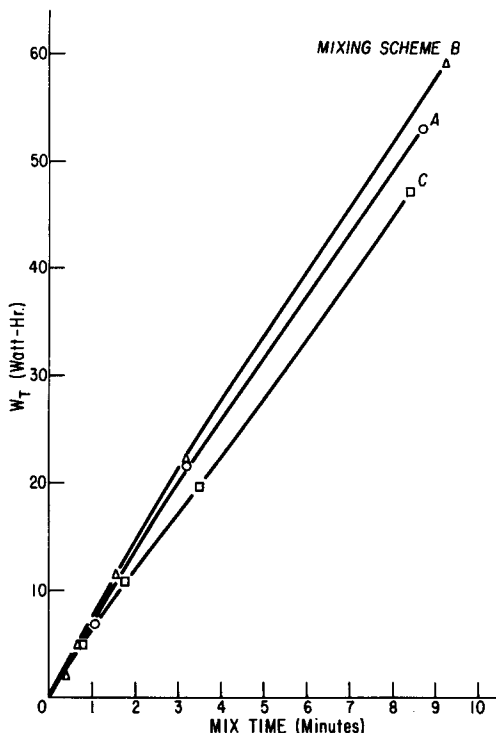


Fig. 4. Energy input vs. blending time: A = free black approach; B = mechanically mixed BR-carbon black masterbatch approach; C = mechanically mixed SBR-carbon black masterbatch approach.

Energy Input Versus Method of Mixing

The power integrator number¹⁵ W_t for the different mixing schemes is plotted as a function of mixing time in Figure 4. W_t as defined here is the energy put into the blends. It corresponds to the torque shown in Figures 1 to 3. This quantity does not include the energy needed to form the masterbatches for methods B and C. It is shown that method B requires more energy for mixing in a given time interval while methods A and C require less. These facts imply that the rheological properties of identical composition blends could be significantly affected by the manner in which the blends were mixed and, hence, the resultant morphologies.

Thermal Analysis

DSC traces of the carbon black-loaded SBR/BR blends prepared by each of the three mixing schemes are shown in Figures 5 through 7. The size of the melting endotherms for crystalline BR is strongly affected by the state of mix. This phenomenon is most pronounced for methods A and C.

The melting energy of the crystalline BR phase of these black-loaded SBR/BR blends can be related semiquantitatively to the mixing time as shown in Figure 8. However, one must keep in mind that two competing mechanisms may affect the size of the BR melting endotherm and, hence, the amount of BR that is available for crystallization. These mechanisms are: (a) the immobilization

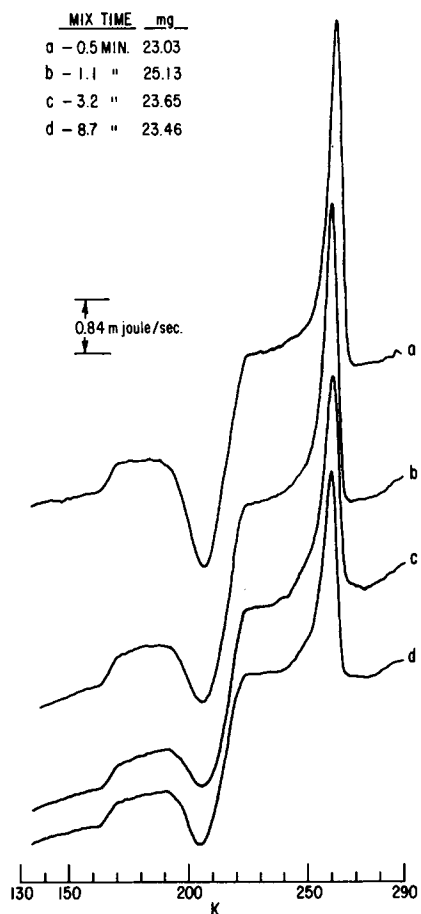


Fig. 5. DSC scans of 80 parts SBR, 20 parts BR, and 20 phr carbon black blends as a function of mixing time. These blends were prepared by a free black mixing process.

of the rubber molecules which are at the surfaces of the carbon black particles and (b) the intermixing of SBR and BR molecules in the interfacial regions. In Figure 8, we note that the curves for mixing schemes B and C level out around 4 min of mixing time, whereas the curve for mixing scheme A does not. In both the black masterbatches, many rubber molecules initially are immobilized at the carbon black particle surfaces. Thus, during the subsequent blending processes with the other rubber, not as many molecules in the masterbatched rubber are available for intermixing in the interfacial regions. However, in method A, the molecules at the surfaces of the carbon black particles are immobilized during the blending process and not prior to it. Also, during blending by method A, the rubber molecules of both rubber species are free to move around and can intermix in the interfacial zones. Since, as will be shown in the next section by electron microscopy, the carbon black particles show a preference for SBR phase, more BR molecules are available to intermix with the SBR molecules to form broader interfacial zones. Therefore, the BR crystalline content and, hence, the size of the melting endotherm should significantly decrease with increased mixing time. These observations are based on the results of Figure 8.

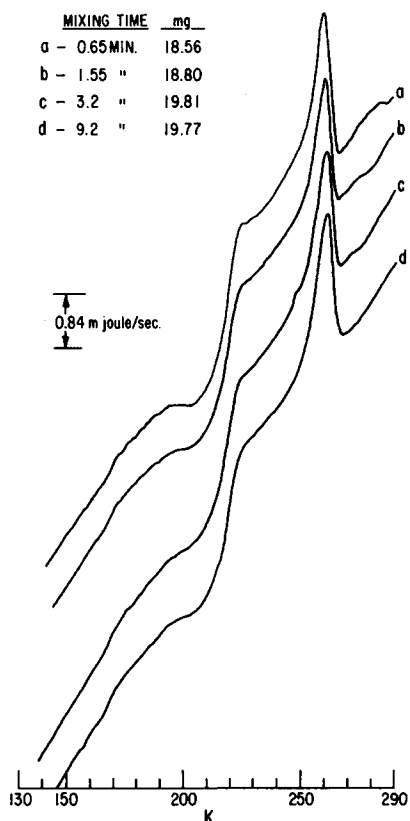


Fig. 6. DSC scans of 80 parts SBR, 20 parts BR, and 20 phr carbon black blends as a function of mixing time. These blends were prepared by a mechanically mixed BR-black masterbatch approach.

Each mixing scheme has an effect on the absolute value of ΔH , the heat of fusion. The order is

$$\Delta H_C > \Delta H_A > \Delta H_B \quad (2)$$

where the subscripts A, B, and C refer to the methods of mixing described in the experimental section. As is expected, ΔH_B is the smallest in value. In method B, more BR molecules are in contact with the carbon black particles and are immobilized. Thus, the amount of BR molecules that are able to crystallize is decreased. ΔH_C has the highest value. In method C, the SBR molecules are immobilized at the carbon black surfaces and are inhibited, to some extent, to intermix with the BR molecules in the interfacial zones. Therefore, most of the BR molecules remain adjacent to one another and mobile. Thus, ΔH_C has a high value. ΔH_A has an intermediate value since during the method A blending time the SBR and BR molecules are both intermixing in the interfacial regions and coming in contact and being immobilized at the carbon black particle surfaces. Since these processes are occurring simultaneously during the course of blending, one would expect a continuously decreasing value of ΔH_C as the mixing time increases.

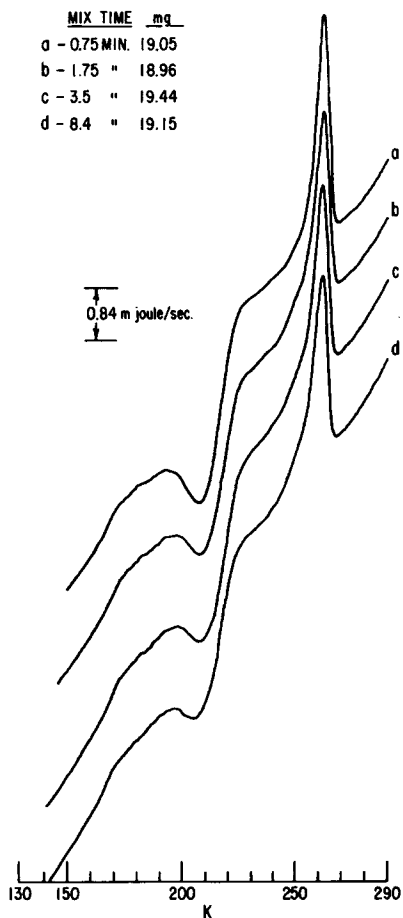


Fig. 7. DSC scans of 80 parts SBR, 20 parts BR, and 20 phr carbon black blends as a function of mixing time. These blends were prepared by a mechanically mixed SBR-black masterbatch approach.

Electron Micrographs

The structural characteristics of carbon black-loaded SBR/BR blends have also been examined by electron microscopy for the three different mixing schemes of black incorporation. The formation, breakdown in size, and dispersion of the BR domains and carbon black agglomerates in these blends are shown in Figures 9 through 11 as a function of the state of mix. For each mixing scheme, representative micrographs of the first, third, and fifth samples of each set are shown in these figures. Refer to Figures 1-3 to see at what stage of mixing the samples were taken (i.e., A-1 is the first sample removed from the free black mixing scheme).

For method A, the carbon black particles and agglomerates of particles initially align along the interfacial regions sandwiched between the SBR and BR phases. (In Fig. 9(a), the SBR portion of the blend contains a myriad of droplets, rich in zinc, which are an artifact of the ebonite technique. Even though these droplets are present, they can be easily distinguished from carbon particles. The carbon particles have a more well-defined structure or shape than the droplets.)

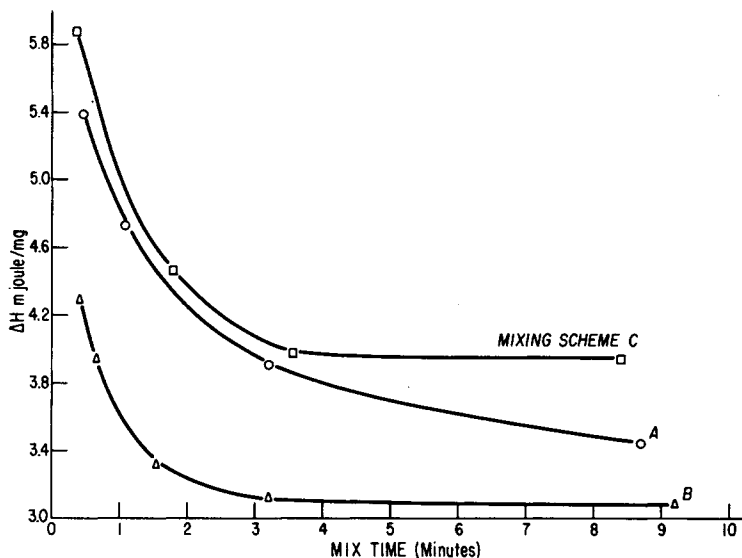


Fig. 8. Melting energy of BR per unit sample weight vs. blending time for 80 parts SBR, 20 parts BR, and 20 phr carbon black model compounds: A = free black mixing; B = mechanically mixed BR-black masterbatch approach; C = mechanically mixed SBR-black masterbatch approach.

As mixing proceeds, the BR domains begin to break down in size and disperse throughout the SBR matrix. At the same time, the carbon black agglomerates also break down and disperse preferentially throughout the SBR matrix, see Figure 9(b). Since the BR and SBR rubbers in this blend have similar Mooney viscosities, it is interesting to note that the carbon black mixes with the SBR more readily. At the end of this experimental run, see Figure 9, the BR domains have broken down to the $0.1\text{--}0.5\ \mu\text{m}$ size level. The carbon black agglomerates have also broken down to smaller sizes. Both of these components have dispersed through the SBR matrix.

For the BR-black masterbatch scheme (method B), 20 phr (recipe measure) of carbon black is first mixed with 20 parts BR in a Brabender mixer for 9 min. The resulting material is very coarse in texture and still has free black particles on the surface probably due to the high loading of black. This BR-black masterbatch was then mixed with 80 parts SBR in the Brabender (refer to Fig. 10). Initially, the black-loaded BR enters the SBR matrix in the form of very large domains, on the order of $50\text{--}100\ \mu\text{m}$ in size. As the mixing process continues, these black-loaded domains break down somewhat in size and disperse throughout the SBR matrix. After 9 min of mixing, these black-loaded BR domains are still quite large ($1\text{--}10\ \mu\text{m}$). In Figure 10(c), one can see some carbon black particles in the SBR matrix. It is believed that these particles are the free black that had resided on the BR-black masterbatch surface prior to mixing with the SBR.

For the SBR-black masterbatch scheme (method C), 20 phr carbon black is first incorporated into 80 parts SBR prior to blending with 20 parts BR. This SBR-black masterbatch was essentially smooth in texture. As shown in Figure 11, the carbon black particles are already well dispersed throughout the SBR matrix prior to blending with BR rubber. As mixing time continues, the BR domains break down in size and disperse throughout the black-loaded SBR

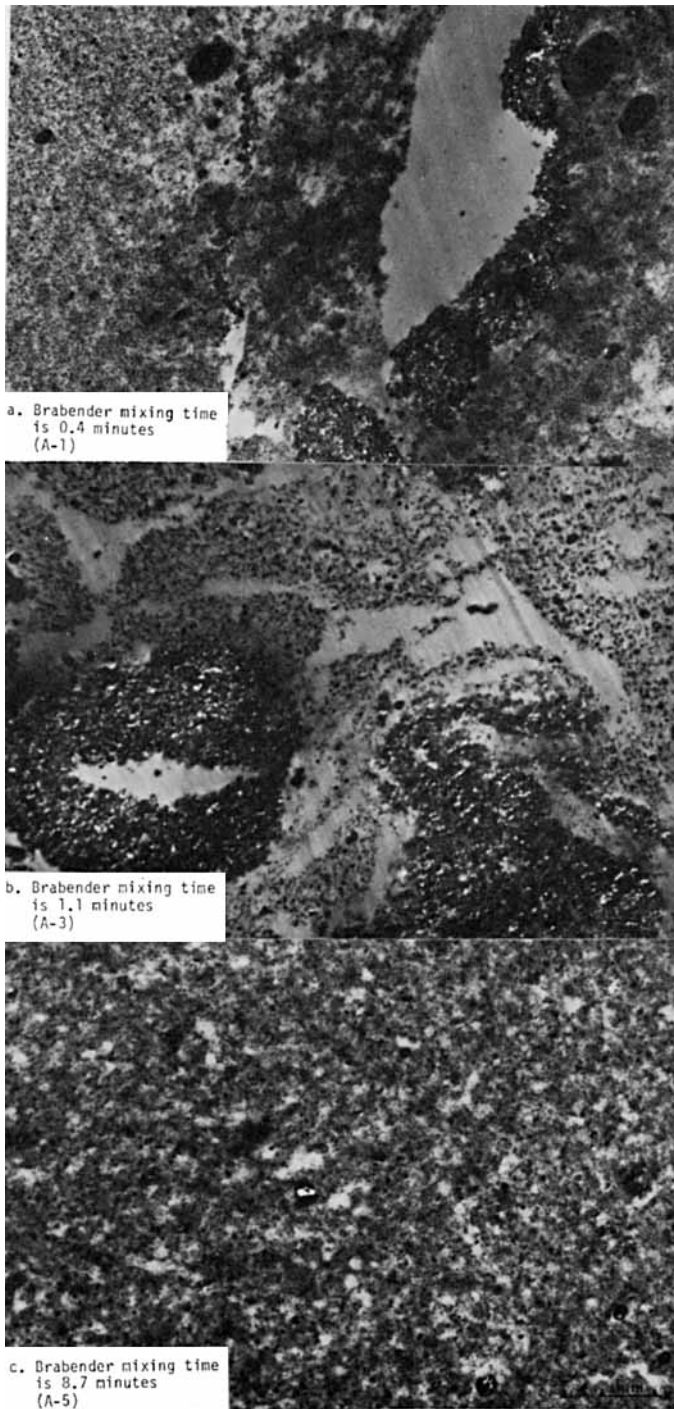


Fig. 9. 80/20 Weight ratio SBR/BR blend with 20 phr carbon black N303 introduced by free mixing scheme (method A). Brabender mixing time: (a) 0.4 min (A-1); (b) 1.1 min (A-3); (c) 8.7 min (A-5).

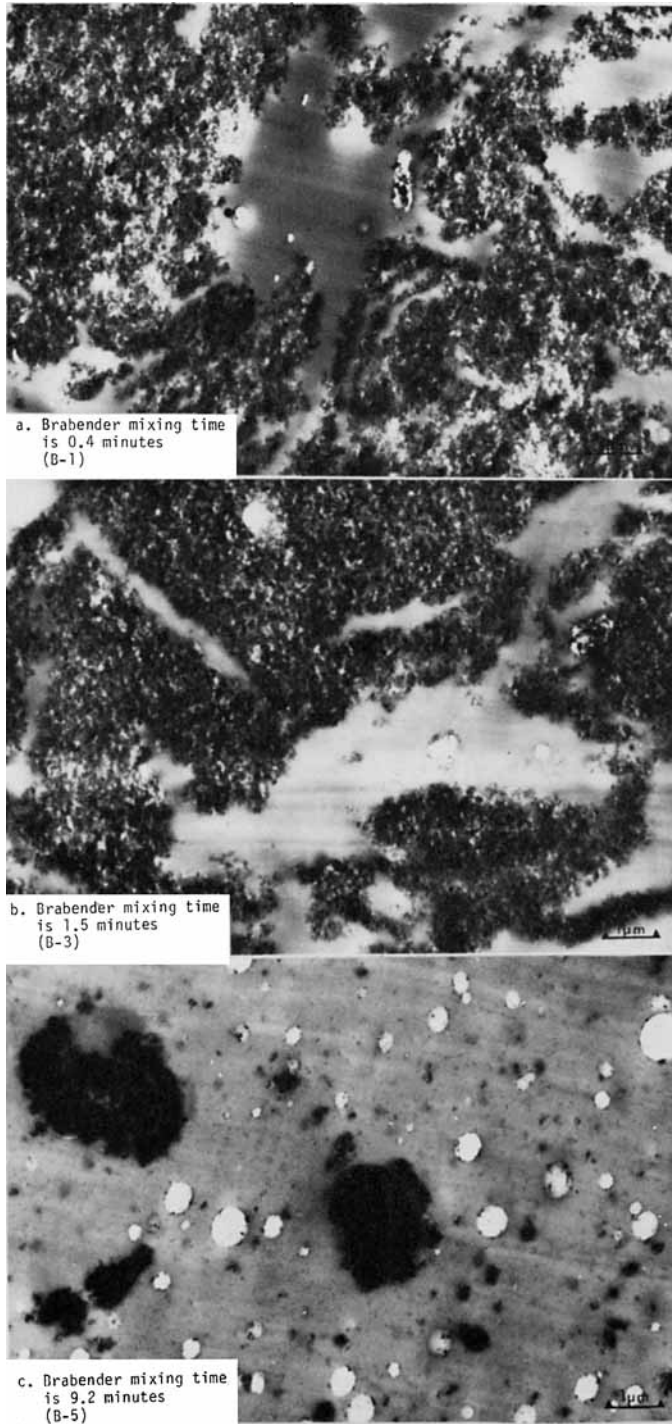


Fig. 10. 80/20 Weight ratio SBR/BR blend with 20 phr carbon black N303 introduced by BR-black masterbatching approach (method B). Brabender mixing time: (a) 0.4 min (B-1); (b) 1.5 min (B-3); (c) 9.2 min (B-5).

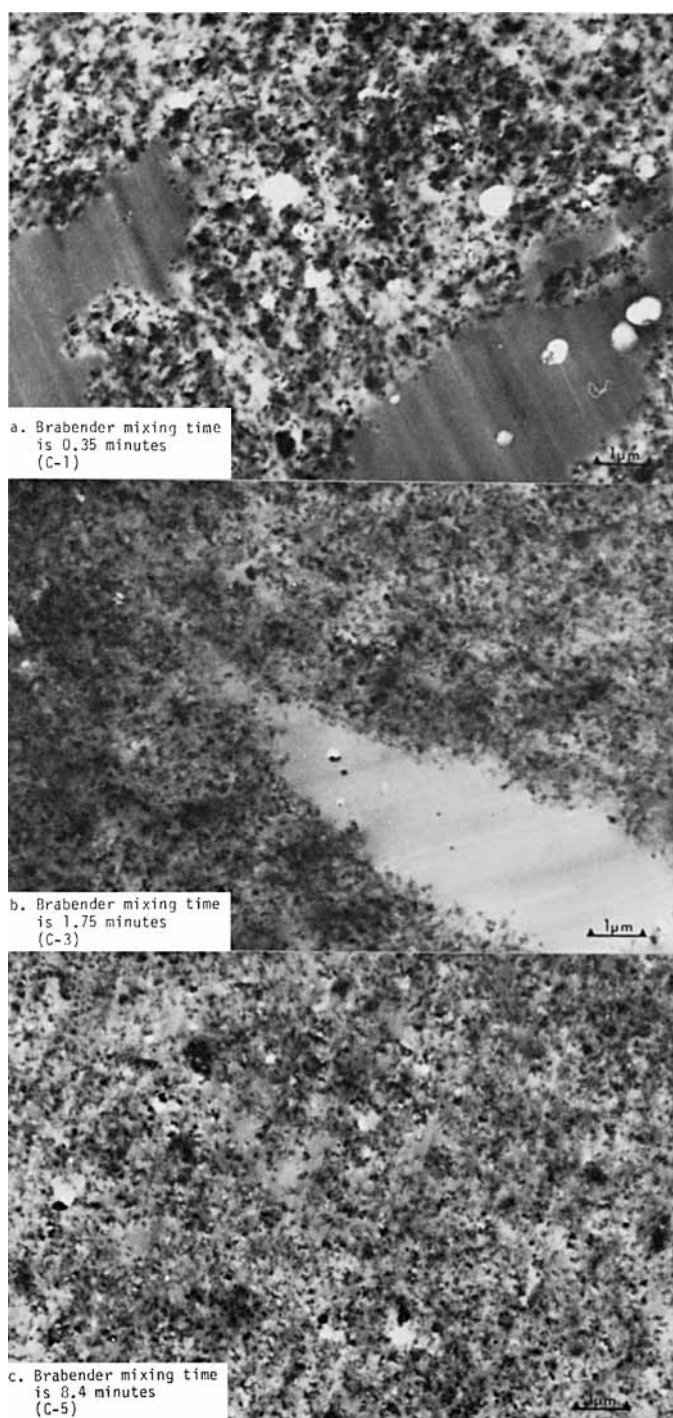


Fig. 11. 80/20 Weight ratio SBR/BR blend with 20 phr carbon black N303 introduced by SBR-black masterbatching approach (method C). Brabender mixing time: (A) 0.35 min (C-1); (b) 1.75 min (C-3); (c) 8.4 min (C-5).

matrix until a dispersion very similar to that shown in Figure 9(c) (method A) is achieved. Again no migration of the carbon black particles from the SBR phase to the BR phase was detected.

Two of the important points observed in this electron microscopy study are: (a) for BR and SBR rubbers of similar Mooney viscosities, carbon black prefers to incorporate with the SBR rubber; and (b) when carbon black is masterbatched into either one of the two rubbers, it continues to remain incorporated in that particular rubber upon blending with the second rubber. The latter finding is in agreement with the results of Sircar and Lamond^{13,14} and Hess and Chirico.⁶

At this point, electron microscopy and differential scanning calorimetry results provide experimental evidence for a blend which consists of (1) decreasing BR domain sizes with increased mixing energy input, (2) formation of diffuse interfacial zones between rubber components, and (3) immobilization of the rubber molecules at carbon black particle surfaces.

CONCLUSIONS

In carbon black-loaded SBR/BR blend systems, in which the Mooney viscosities of the rubber components are approximately equal, the dispersion and distribution of the black are governed by the blending conditions.

When the black is first introduced into the blend, the carbon black agglomerates initially line up along the SBR-BR interfaces. Increased mixing causes the BR domains to decrease in size and the black to disperse throughout the SBR matrix. However, if the black is first masterbatched with either rubber phase prior to blending with the other rubber, it will remain in the original rubber phase throughout the mixing process. No significant migration of carbon black from one rubber phase to the other was observed. The sizes of the BR domains formed at various stages of mixing also vary according to how the black is incorporated into the blend. At any given state of mixing, these domains are, in general, smaller for the free black mixing and the SBR-black masterbatch method and larger for the BR-black masterbatch scheme. These phenomena were detected by electron microscopy and thermal analysis. The variation in size of the melting endotherms of crystalline BR correlates well with the BR domain sizes and dispersion seen via electron microscopy. These experimental results are also supporting evidence for the immobilization of BR molecules which come in contact with carbon black particles and also imply the formation of diffuse interfacial zones between the rubber components.

The authors would like to thank Dr. L. E. Hewitt and Ms. J. L. Savoca for their helpful suggestions and assistance concerning the thermal analysis experiments. The many valuable discussions with Drs. M. H. Lehr and C. E. Wilkes during the course of study are gratefully acknowledged. Recognition is also extended to Dr. F. S. Meyers for his practical suggestions concerning the preparation of the blends. The authors would like to express their appreciation to B. F. Goodrich Company for permission to publish this work.

References

1. M. H. Walters and D. N. Keyto, *Trans. Inst. Rubber Ind.*, **38**(2), T40 (1962); *Rubber Chem. Technol.*, **38**, 62 (1965).
2. J. Kruse, *Rubber Chem. Technol.*, **46**, 653 (1973).
3. W. M. Hess, C. E. Scott, and J. E. Callan, *Rubber Chem. Technol.*, **40**, 371 (1967).

4. C. E. Scott, J. E. Callan, and W. M. Hess, *J. Rubber Res. Inst. Malaya*, **22**, 272 (1969).
5. J. E. Callan, W. M. Hess, and C. E. Scott, *Rubber Chem. Technol.*, **44**, 814 (1971).
6. W. M. Hess and V. E. Chirico, Paper #36 presented at 110th Rubber Division Meeting, October 5-8, 1976, San Francisco.
7. G. Ivan, M. Ganea, and I. Lanquiri, *Proc. C.N.R.S.*, **231**, 332 (1973).
8. V. L. Folt and R. W. Smith, *Rubber Chem. Technol.*, **46**, 1193 (1973).
9. R. W. Smith and J. C. Andries, *Rubber Chem. Technol.*, **47**, 64 (1974).
10. *A Bibliography of the Application of DSC*, Perkin-Elmer Corporation, Norwalk, Connecticut, 1976.
11. V. R. Landi, *Rubber Chem. Technol.*, **45**, 222 (1972).
12. R. W. Seymour and S. L. Cooper, *J. Polym. Sci. B*, **9**, 689 (1971).
13. A. K. Sircar and T. G. Lamond, *Rubber Chem. Technol.*, **46**, 178 (1973).
14. A. K. Sircar and T. G. Lamond, *Rubber Chem. Technol.*, **48**, 301, 631, 640, 653 (1975).
15. W. W. Newell, J. P. Porter, and H. L. Jacobs, "The Power Integrator—A New Instrument for Controlled Mixing," paper presented at 107th Rubber Division Meeting, May 6-9, 1975, Cleveland.
16. *DSC-2 Operation Manual*, Perkin-Elmer Corporation, Norwalk, Connecticut, February, 1976.
17. C. J. Singleton, unpublished data, 1976.
18. P. A. Marsh, A. Voet, L. D. Price, and T. J. Mullens, *Rubber Chem. Technol.*, **41**, 344 (1968).
19. P. A. Marsh, T. J. Mullens, and L. D. Price, *Rubber Chem. Technol.*, **43**, 400 (1970).

Received June 14, 1979