Experimental Studies of the Relationship of Processing to the Crack Growth of Carbon-Black-Loaded SBR—*cis*-Polybutadiene Compounds

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Synopsis

The crack growth of a highly carbon-black-loaded SBR—*cis*-polybutadiene (BR) blend is investigated as a function of the distribution of carbon black in the individual rubber phases. The blend compound consists of SBR/BR/carbon black/oil = 60/40/85/60 by weight ratio and curatives. A new "old process" is devised to control the carbon black distribution in the individual rubber phases, that is, cross mixing the SBR and BR black master batches with different amounts of carbon black in the SBR and BR patches. The results show that crack growth is very sensitive to the carbon black distribution. A better crack growth resistance compound is seen containing proportionately more carbon black in the major rubber SBR phase. A simple analogy of rubber blends to the rubber-modified thermoplastics is proposed to interpret these findings. The heat buildup of the blends is also affected by the carbon black distribution. A low heat buildup compound is observed in the system in which more carbon black is in the SBR batch, which is also a better crack growth resistance compound. It is not unexpected that the strength of rubbers decreases with increase of temperature, and so the rate of crack growth becomes faster as heat builds up.

INTRODUCTION

Multicomponent polymer systems are increasingly used in industrial applications and in consumer products. It has been known that the processing characteristics of polymer blends are not necessarily a unique function of their blend composition, but can vary with the morphology of the system.[1-4] When adding carbon black, fillers, and curatives to a rubber blend, several important morphological features develop, e.g., the dispersion of carbon black, the size of one dispersed rubber phase, and the distribution of carbon black in each of the rubber phases.[5-11] These heterogeneity features due to the distribution of carbon black in each of the rubber phases, in turn, strongly influence the ultimate physical properties of finished rubber blend.[6,12-17] This is especially true in blends of two or more rubber used for tires, conveyor belts, or other rubber goods. Hence, it is always industrially important to unveil the relationship of the physical properties of multicomponent systems as a function of their processing characteristics.

It has been known that rubber products which are flexed in service frequently fail from the appearance and growth of cracks.[18,19] So it is industrially important to improve the crack growth resistance of rubber products. Theories for some model experimental results on crack growth of rubbers have been advanced by various academic and industrial research laboratories[20-27] and also by the BF Goodrich Co., notably J. R. Beatty.[19,28,29] In reality, however, mixing of carbon black in a rubber blend compound could result in a nonuniform distribution of

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carbon black and, consequently, also affect the cut growth.[13] Despite its industrial importance, the effect of heterogeneity in rubber blends resulting from nonuniform distribution of carbon black in the individual rubber phases is seldom systematically studied.

Recently, we have investigated the reinforcement of uncured and cured rubbers[30,31] and the morphology of carbon-black-loaded SBR—*cis*-polybutadiene (BR) blends.[10,11] We reported that the distribution of carbon black in SBR and BR phases is governed by the method of mixing. In the mechanical cross-mixing of black master batches carbon black always stays in the original rubber phase. That is, no significant amount of carbon black migration from one phase to the other phase occurred on Brabender-mixed master batching with a second rubber.[8,10,11]

In this paper, we made a comparative experimental study of how the location of carbon black in an SBR—BR blend influences the crack growth resistance. The mixing process to control the carbon black distribution in SBR and BR phases, essentially, is the extension of our previous mixing studies.[10,11] The results show how crack growth resistance can be improved by the nonhomogeneous distribution of carbon black. We will then discuss two possible important mechanisms to improve crack growth resistance, stress relief, and low heat buildup. This is a continuation of our earlier research on the relationships of processing—morphology—properties of SBR–*cis*-polybutadiene blends.[10,11,30,31] Throughout these studies, we have uncovered new principles, refined earlier fundamental concepts, and, of course, revealed further opportunities for research and practical problem solving.

EXPERIMENTAL

Recipe

The basic recipe consists of SBR:BR:black = 60:40:85 and curatives. Table I lists the ingredients and recipe weights.

Mixing

A model B Banbury along with a 10-in. mill was used to fabricate the compounds. Carbon black was incorporated into the SBR and BR in different ways. The purpose of this is to enhance the modulus difference between SBR and BR

TABLE I
Recipe of SBR—BR Blends in This Study

Ingredients	phr
Oil-extended BR {BR 100; oil 37.5}	55.0
Oil-extended SBR {SBR 100; oil 37.5}	82.5
Petroleum oil	22.2
Furnace black	85

plus

Sulfur, stearic acid, zinc oxide, accelerators,
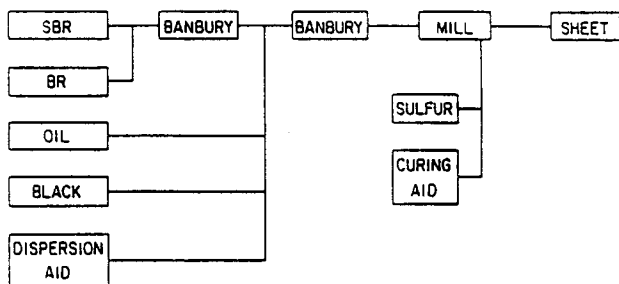antioxidants and antiozonants

Fig. 1. Block diagram of free black mixing; CPD 350.

master batches. Note that we have reported that a three (or multicomponent) system may be reduced to a two-component system by considering the black preloaded master batch as a continuum.[11] The detailed methods are described as follows.

Free Black Mixing (CPD 350)

Carbon black was added to an SBR—BR preblend in the Banbury. Curing agents were added on the 10-in. mill. Figure 1 shows the detailed procedure.

SBR–BR Black Master Batch Approach

Both SBR and BR are individually premixed with an appropriate amount of the ingredients, including carbon black and curing agents. We call these master batches SBRMB and BRMB. An appropriate quantity of SBRMB and BRMB was then finally cross-mixed on the 10-in. mill to generate a compound having the same ingredients and recipe weights as those listed in Table I. Figure 2 shows the detailed mixing procedure. Table II lists the master batch pairs studied. Note the ratio of the amounts of carbon black in the SBRMB and BRMB pairs ranges from 40/60 to 90/10. This would provide a wide variety of modulus ratios of SBRMB/BRMB.
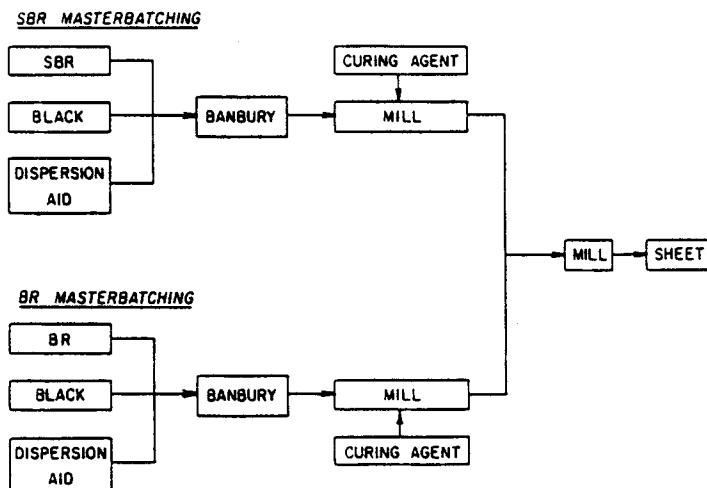

Fig. 2. Block diagram of controlled carbon black distribution mixing process.

TABLE II
Recipes of SBR and BR Master Batches

Ingredient	BRMB	SBRMB
Oil-extended BR {BR 100; oil 37.5}	55.0	—
Oil-extended SBR {SBR 100; oil 37.5}	—	82.5
Petroleum oil	6.2	16.2
Furnace black		85[a]

plus

Sulfur, stearic acid, zinc oxide, accelerators,
antioxidants, and antiozonants

[a] Detailed values are listed in Table III.

The recipe weights of carbon black in the individual masterbatches are also converted to volume fraction and are listed in Table III.

The rotor speed of the B-Banbury mixer was 77 rpm and the initial chamber temperature was 93°C. The running water control valve was open during mixing to remove the heat generated by the shear mixing. The dump temperature was controlled, not exceeding 149°C.

Curing

The compound rubber cure time was evaluated in the Monsanto Rheometer 100.[32] Optimum cure + 10 min at 149°C was the cure time selected in all cases. The rheometer test conditions were: temperature, 149°C; oscillation disk frequency, 1.66 Hz; and oscillation amplitude, half cycles of $1 \pm 0.002°$. The optimum cure was defined as time to 90% of maximum torque in the Monsanto Rheometer. This instrument has also been used to study the kinetics of vulcanization,[33] the reinforcing characteristics of carbon black in rubber,[34] and also dispersive mixing.[30]

Crack Growth Test

Crack growth was tested in a rotating ring crack growth tester which was devised by Beatty and Juve.[19] This apparatus is compact, vibration-free, and utilizes a ring-type specimen. The test conditions are as follows: chamber

TABLE III
Amounts of Carbon Black (phr and Volume Fraction ϕ_2) in SBR and BR Master Batch Pairs
Cross-Mixed to Form Blend Compounds[a]

SBR/BR blend compound	BRMB			SBRMB		
CPD	CPD	Black (phr)	ϕ_2 (%)	CPD	Black (phr)	ϕ_2 (%)
356	351	34.0	21.3	352	51	20.6
362	357	42.5	25.4	358	42.5	17.7
368	363	51.0	29.0	364	34.0	14.7
373	369	21.2	14.5	370	63.8	24.4
378	374	8.5	6.3	375	76.5	27.9

[a] Refer to Table II for whole ingredients.

temperature—70°C; load—1.36 kg (or 3 lb); scale division at start— 2.5 mm; rotation speed—320 cycles/min.

As pointed out by Beatty and Juve,[19] in the running of tires, groove cracking is a continuous problem. Cracking takes place in two steps: initiation and growth. Initiation is inevitable in service from ozone cracking, cuts, and nicks. This indicates that the study should concern itself with cut growth.

Heat Buildup Test

The operation procedures as outlined in the ASTM D623[35] were employed for the test. The flexometer was operated at 9.8×10^5 Pa load and 17.5% constant deflection starting at 48°C. The temperature rise after 25 min of deflection was measured. The relationship of the heat buildup to the dynamic mechanical properties of carbon-black-loaded rubber vulcanizates has been recently discussed.[31]

Tensile Test

The stress–strain data were obtained from an Instron Tensile Tester. The cross-head speed of the test was 25.4 cm/min.

RESULTS AND DISCUSSION

Modulus of SBR and BR Master Batches

The stress–strain data of the SBRMB and BRMB are plotted in Figures 3 and 4.

The tensile moduli of these master batches are plotted in Figure 5. It is not unexpected that the moduli of the individual master batches can be varied by adjusting the amount of carbon black. The order of the moduli ratio of the master batch pairs which were cross-mixed to form the blend compounds is as follows:

$$\frac{E_{CPD\ 375}}{E_{CPD\ 374}} > \frac{E_{CPD\ 370}}{E_{CPD\ 369}} > \frac{E_{CPD\ 352}}{E_{CPD\ 351}} > \frac{E_{CPD\ 358}}{E_{CPD\ 357}} > \frac{E_{CPD\ 364}}{E_{CPD\ 363}} \tag{1}$$

In later sections we will discuss how this moduli ratio of the master batch pairs affects crack growth.

Modulus of the Blend Compounds

Table IV lists the moduli of the cross-mixed blend compounds having different amounts of carbon black in the master batches. It is noted that there are slight differences in the moduli. If the differences in moduli as measured by the Instron stress–strain tests are significant, these may be due to the differences of morphology. However, we do not have definite proof at this moment.
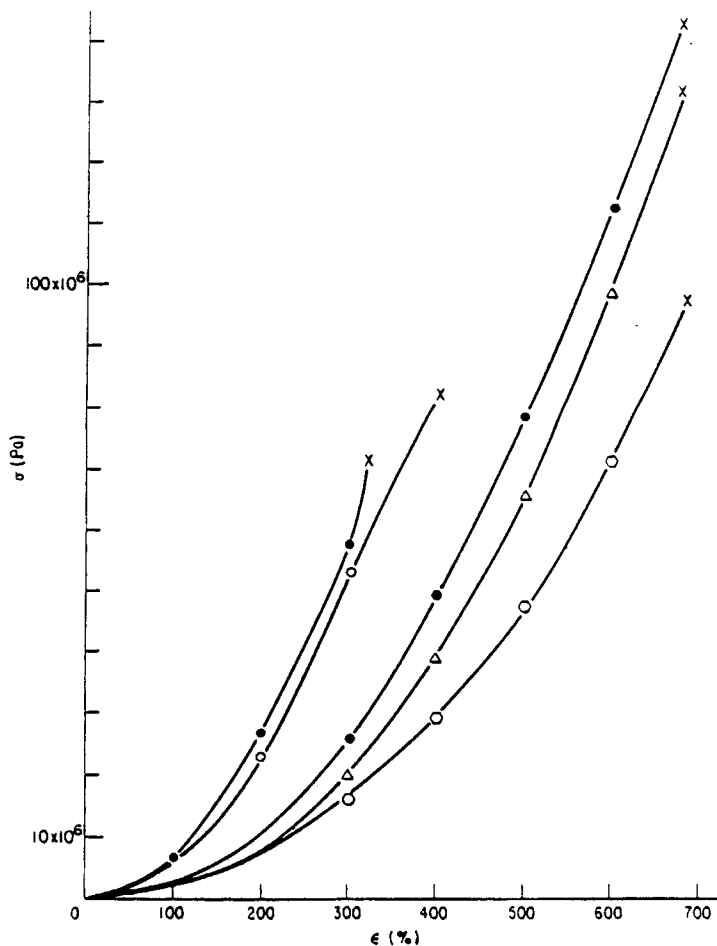
Fig. 3. Stress–strain of SBR master batches, loaded with different amounts of carbon black: (×) breaking point; (●) cpd 352; (△) cpd 358; (○) cpd 364; (○) cpd 370; (●) cpd 375.

TABLE IV
Tensile Modulus and 300% Modulus of the SBR/BR Blend Compounds Prepared by Different Mixing Methods

CPD	Tensile modulus E (Pa $\times$ 10^6)	M_{300} (Pa $\times$ 10^6)
350	6.29	7.82
356	6.25	7.17
362	6.69	7.40
368	6.08	6.43
373	5.88	9.78
378	5.18	9.92

Crack Growth of Blend Compounds

Figure 6 summarizes the results of the crack growth of the blends compounds as tested by the ring flex tester. Several points are important and worth mentioning here:

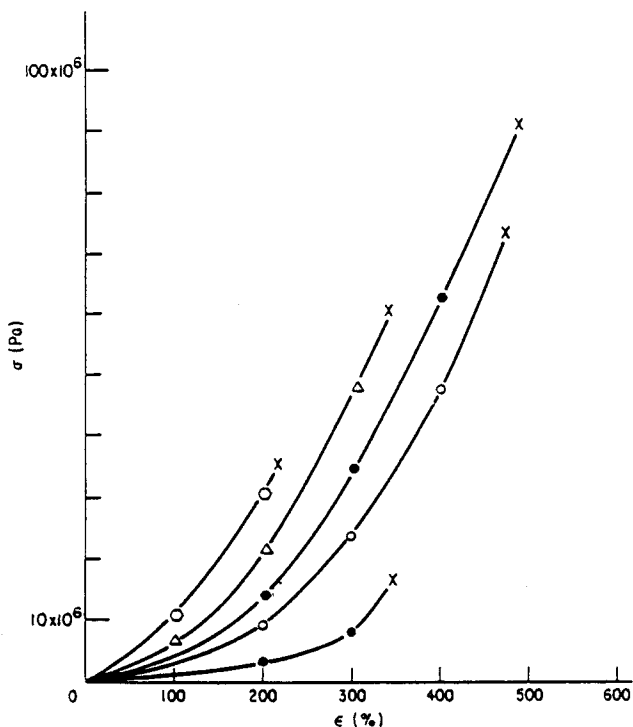1. The presence of a second rubber component in the first rubber matrix

Fig. 4. Stress–strain of BR master batches, loaded with different amounts of carbon black: (×) breaking point; (●) cpd 351; (△) cpd 357; (○) cpd 363; (○) cpd 369; (●) cpd 374.

usually improves the cut growth resistance of the first rubber compound.[29] More strictly speaking, based on our results as indicated in Figure 6, the cut growth resistance of a carbon-black-loaded rubber blend is strongly dominated by the distribution of carbon black in the individual rubber phases. This finding is experimentally in agreement with Sircar et al.[13]

2. The compounds which were prepared by the controlled-carbon black distribution process (Fig. 2) give a variety of crack growth resistance curves. The better crack growth resistance compound is the one with more carbon black initially in the SBRMB.

3. Free black mixing process usually is considered an easy and convenient mixing process. However, as far as the crack growth resistance is concerned, this mixing process is not the best process.

4. The term "cross-mixing" is not a new process, since it has been known that physical properties of rubber compounds are dependent on the method of mixing. We demonstrate here that controlled carbon black distribution in SBR/BR blends can be accomplished by this old cross-mixing process.

In the following sections, we will discuss how the heterogeneous distribution of carbon black introduces some possible mechanisms affecting the crack growth of rubber blends. We will first propose the analogy of rubber blends to rubber-modified thermoplastics, then discuss the possible favorable factors improving the crack growth resistance—stress relief and low heat buildup.
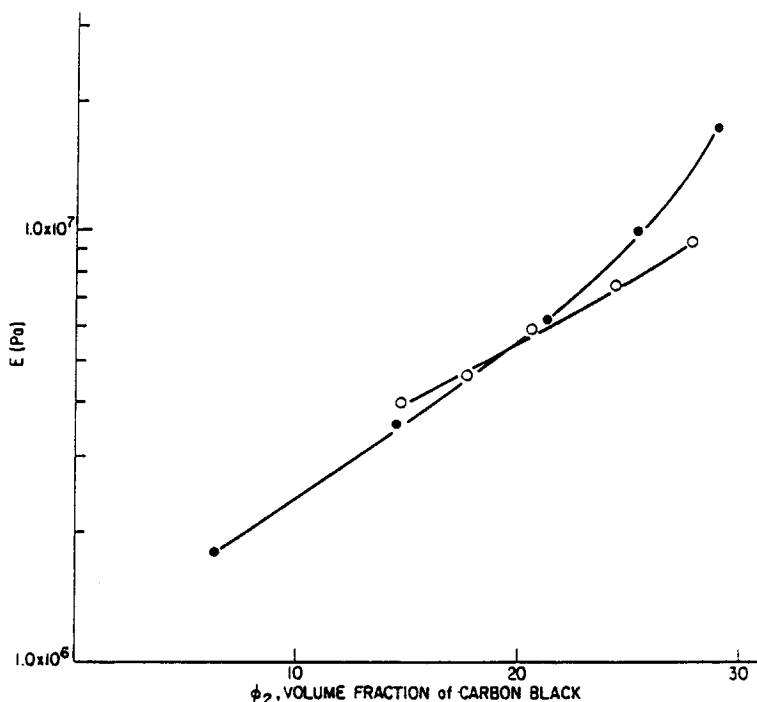
Fig. 5. Tensile (elastic) modulus of SBR (O) and BR (●) as a function of carbon black load-ings.

Effect of Modulus on Crack Growth Resistance of Rubber Blends

The crack growth resistance of rubber compounds has long been known to be affected by the modulus levels of the compounds. Auer, Doak, and Schaffner, for example, determined the cut-growth resistance of SBR as a function of modulus over a wide range of the amounts of accelerator and sulfur and proposed the following relation[36]:

$$\log(t/L) = a - bM \tag{2}$$

where t/L is the cut growth resistance (kcycles/in.), $M = 300\%$ modulus, and a and b are constants. Equation (2) states that the higher the modulus of the compound, the poorer its cut growth resistance is.

By carefully comparing the results as shown in Figure 6 and Table IV, we observe that there is no definite correlation of the cut growth resistance of SBR—BR blends with 300% modulus as indicated by eq. (2). Thus, for the cut growth of rubber blends, in which the ingredients and recipe are identical, the 300% modulus is not a primary factor affecting the cut-growth resistance.

Effect of Modulus Ratio of SBRMB/BRMB Pairs on Crack Growth

Figure 7 shows the cut-growth resistance as a function of the modulus ratio of the corresponding SBR and BR master batch pairs. This illustrates the significant effect of the carbon black distribution in SBR and BR phases on $T_{5\times}$, the time required for crack growth to 5 × the original crack length. It is admitted that the modulus as measured by the Instron tensile test is subject to some in-
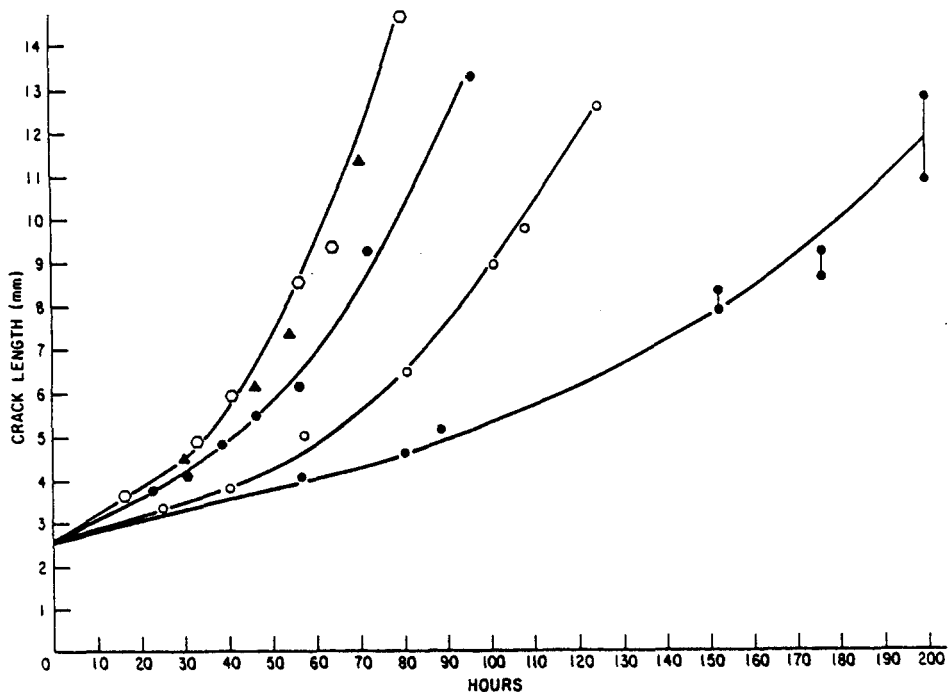
Fig. 6. Crack growth of the SBR/BR blend compounds as a function of method of mixing: Test temp = 70°C; load = 1.36 kg; scale division at start = 2.5; cure = 25 min at 149°C; (▲) cpd 350; (●) cpd 356; (O) cpd 368; (○) cpd 373; (●) cpd 378.

herent errors, but the order of magnitude should not be affected. One can easily notice that $T_{5\times}$ is shifted from 90 h to 200 h as E_{SBRMB}/E_{BRMB} changes from 1 to 5.

The curves in Figure 6 can be generalized to the following form:
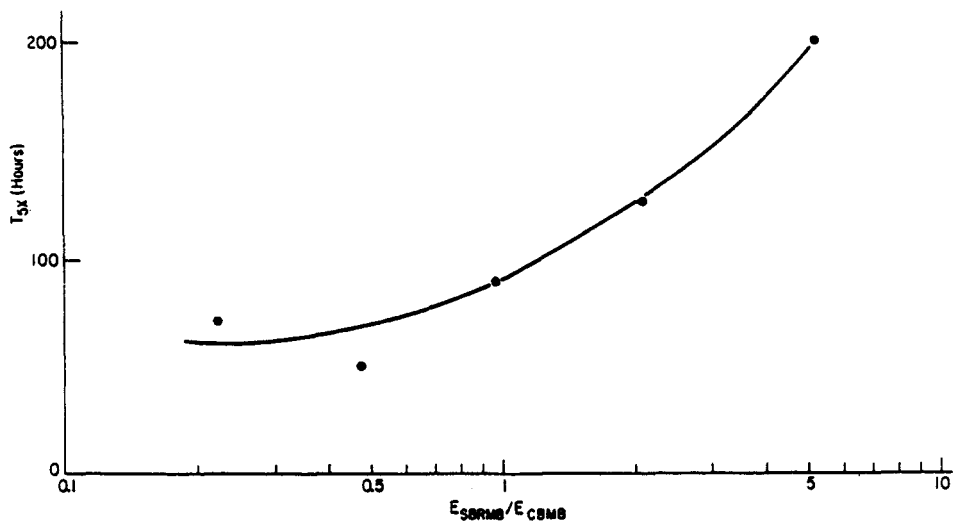
$$\frac{dL}{dt} = AL^n \tag{3}$$

Fig. 7. $T_{5\times}$, time to 5 × the initial crack length, of various SBR/BR blend compounds as a function of the modulus ratio of the master batch pairs.

where A and n are constants.

A semilogarithmic plot of the cut length vs. the time (or number of cycles) is shown in Figure 8, where the value of n is equal to 1. Equation (3) in general can fit the data, except in the region where the crack is small.

From Figure 8, we note the order of the constant A is as follows:

$$A_{378} < A_{373} < A_{356} < A_{368} \tag{4}$$

From eq. (3), a small A implies better cut growth resistance. Our results as indicated in eqs. (1) and (4) showed that a smaller value of A was obtained for the compound in which the modulus ratio E_{SBR}/E_{BR} was larger.

The form of eq. (3) was probably first proposed by Greensmith of the NRPRA group,[24] for the system consisting of one rubber phase. It seems that no single values of A can be obtained in the blends presumably due to the presence of heterogeneity as reflected by the nonuniform distribution of carbon black in the rubber blend of SBR/BR. As we will discuss in the next section, the presence of heterogeneity which gives a stress concentration and also serves as an energy dissipator, may be more significant in affecting the cut growth of rubber blends.

Analogy of Rubber Blends to Rubber-Modified Thermoplastics

One of the interesting features, as indicated in Figures 7 and 8 and eqs. (1) and (4), is the importance of the relative modulus of the individual SBRMB and BRMB. It seems that the cut-growth resistance of the rubber blends is significantly improved if one rubber phase is of lower modulus. This leads us to speculate, as far as the cut growth is concerned, on the analogy of rubber blends to the rubber modified thermoplastics. It has been well known for at least 30
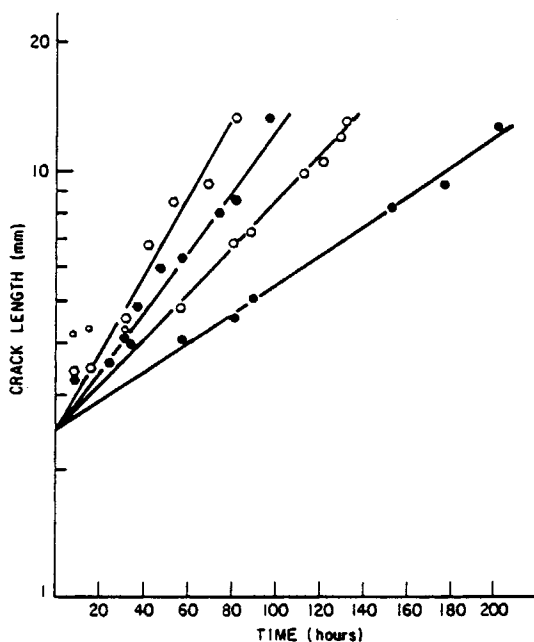

Fig. 8. Semilog relation of crack length vs. time of cycling: (●) 378; (○) 373; (○) 368; (●) 356.

years that brittle polymers can be converted into high impact materials by the addition of a low modulus rubber phase. The low modulus rubber phase can dissipate large amounts of energy. A general review on this subject is available.[37-40]

If carbon-black-loaded SBR—BR blends, to some extent, can be considered analogous to the rubber-modified thermoplastics, then the following criteria should be followed during mixing of rubber blends:

1. One phase is higher modulus, and the other phase is lower modulus. In the practical and useful rubber blends products, the higher modulus phase should be the major rubber phase.

2. There should be good adhesion between the two phases (high and low modulus phases).

This "crude" analogy then implies that, besides the relative distribution of carbon black in different rubber phases, the relative distribution of crosslinking agents and cure compatibility[41] are also very important.

It is obvious that more work should be done to examine the validity of this crude analogy. Indeed, studies on the blends of natural rubber/BR and SBR/NBR have experimentally confirmed this concept.[42]

Effect of Stress Concentrators on Crack Growth

The presence of stress concentrators, resulting from heterogeneity, is another vital factor in determining the crack growth of the materials. It is well known, for example, that the stress at the tip of a crack is concentrated according to the equation.[43]

$$\sigma_m \doteq \sigma_0[1 + 2(a/R)^2] \tag{5}$$

where σ_0 is the applied stress and σ_m is the maximum stress at the crack tip which has a radius of curvature R, and a is the length of the crack. It seems that if the mixed rubber blends follow the criteria discussed in the previous section, the crack may be retarded. The reason is that the radius of the second dispersed rubber phase is greater than the radius of curvature of the crack tip, and thus the intensity of the stress concentration is decreased.[44] More recently, Wang, Mandell, and McGarry studied the fracture of adhesive joints.[45] They reported that the stress concentration developed in the adhesive crack tip is an inverse function of the modulus ratio of the joint to that of adhesive. This result may be further employed to explain the effect of stress concentrator on crack growth. As the crack tip passes the low-modulus dispersed phase, the stress concentration at the crack tip is significantly relief. Hence the presence of the lower-modulus dispersed phase should retard the crack propagation and increase the fatigue life of the rubber blends.

Effect of Heat Buildup on Crack Growth

One of the other important factors in determining the crack growth of rubber compounds is related to their mechanical damping and the resulting heat buildup in the compounds. Figure 9 shows T_{5x} as a function of heat buildup, ΔT, which was measured by the Goodrich Flexometer. It is very obvious that the compound with low heat buildup is always better in cut growth resistance. It is not unex-
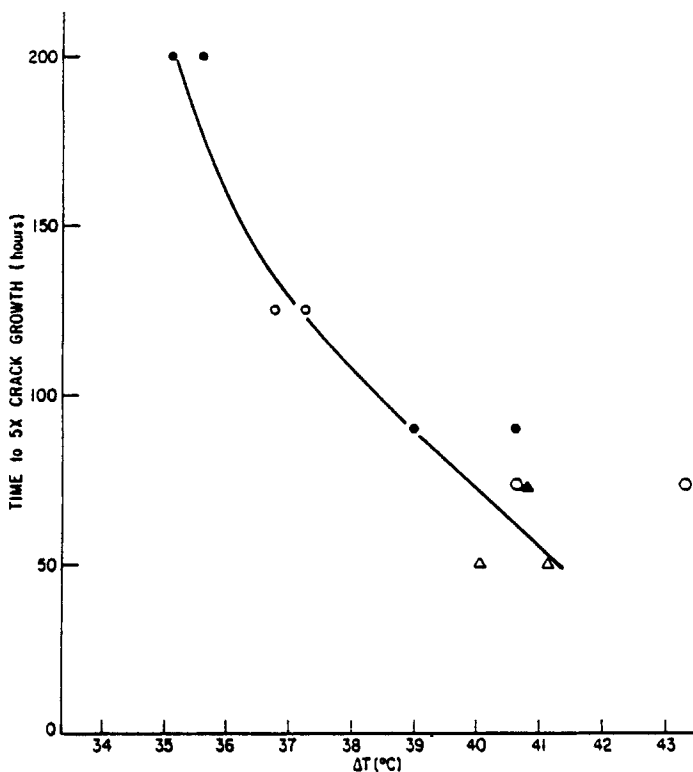
Fig. 9. T_{5X}, time to 5 × crack growth, as a function of heat buildup, ΔT: (▲) cpd 350; (●) cpd 356; (△) cpd 362; (○) cpd 368; (○) cpd 373; (●) cpd 378.

pected that the strength of polymers decreases with the increase of temperature. Thus, the crack growth becomes easier as the heat builds up.[46]

CONCLUSIONS

In carbon black loaded SBR/BR compounds, a crossmixing scheme has been devised to control the carbon black distribution in SBR and BR phases. Crack growth is observed sensitive to the heterogeneous distribution of carbon black. A better crack growth resistant SBR/BR compound is seen for the blends containing proportionately more carbon black in SBR phase than in BR phase.

Heat buildup in SBR/BR blends is also affected by heterogeneous carbon black distributions. Low heat buildup is seen in the SBR/BR compound in which more carbon black is in SBR phase than in BR phase.

The results lead us to conclude that in mixing SBR/BR compound, the following two factors are favorable to improve the crack growth resistance: (a) the presence of stress relief sites, resulting from the heterogeneous distribution of carbon black in SBR and BR rubber phases; and (b) low heat buildup.

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