

# Effect of Mode of Filler Addition on the Dynamic Mechanical Properties of Epoxidized Natural Rubber-*cis*-1,4-polybutadiene Rubber Blend

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## SYNOPSIS

The effect of different modes of filler addition on dynamic mechanical properties of 50/50 blends of epoxidized natural rubber (ENR) and *cis*-1,4-polybutadiene rubber (BR) has been studied. The present study is confined to the systems that have fillers alone to reduce complexities due to the presence of other compounding ingredients and vulcanization. The effects of both carbon black and silica filler have been investigated. The mode of filler addition was found to have a profound influence on the loss tangent ( $\tan \delta$ ) peak height, its spread, and the storage modulus,  $E'$  value. The tendency of the filler to adhere predominantly to one of the phases depends on the mode of filler addition and the processing history rather than the individual component polarity or viscosity. © 1993 John Wiley & Sons, Inc.

## 1. INTRODUCTION

Blends of two or more elastomers are widely used for many applications. In general, polymer blends are incompatible on a molecular level and each polymer forms definite discrete zones of either dispersed or continuous phase in the other. Addition of carbon black reduces this zone size. For pure gum blends, measurement of dynamic properties as a function of temperature gives an indication of zone size.<sup>1</sup> De Decker and Sabatine<sup>2</sup> studied the effect of carbon black and compatibility on the loss tangent ( $\tan \delta$ ) peaks of rubber blends using a rotary hysteresis meter. The distribution of carbon black between the polymer phases depends on the relative viscosity of the polymers, their difference affinity for carbon black, and the formation of bound rubber.

Different mixing techniques and their effect on various physical properties and the migration phenomenon of fillers to different phases have been dis-

cussed by numerous researchers.<sup>3-6</sup> Sircar and co-workers<sup>5,6</sup> mixed N347 black (50 phr) into 50/50 blends of various elastomers in four different ways. In general, the lowest  $G'$  (difference between the nature of the shear modulus at the lowest applied strain amplitude and that at dynamic strains above 10%) and highest rebound was obtained by mixing all the black into one of the elastomers first. The amplitude dependence of dynamic properties of the blends was studied by Sircar and Lamond<sup>7</sup> using a conventional mixing technique in which elastomers were preblended before adding carbon black. It was concluded from these works that the secondary networks arising from carbon black particle aggregation retain their characteristics even in the composite matrices of elastomer blends.<sup>8</sup>

However, a systematic study has not yet been carried out to determine the effect of mode of filler addition on the low-temperature relaxation spectra of the blends. Though studies were carried out in the case of carbon black-filled systems, nonblack fillers are left unanalyzed. In the present study, we studied the effect of different modes of adding carbon black and silica to a 50/50 epoxidized natural rubber

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(ENR): *cis*-1,4-polybutadiene rubber (BR) blend, which is a typical immiscible blend.<sup>9</sup> The present study is confined to systems having fillers alone to reduce complexities due to the presence of other compounding ingredients and vulcanization.

## 2. EXPERIMENTAL

Details of materials used are given in Table I. Epoxidized natural rubber (50 mol % epoxidized) was supplied by the Malaysian Rubber Producers' Research Association (MRPRA), Brickendonbury, U.K., and BR was supplied by the Indian Petrochemical Corp. Ltd. (IPCL), Baroda, India.

For studying the effect of the mixing sequence, four different methods were followed: (1) Filler was added to the ENR phase and then diluted with BR; (2) filler was added to the BR phase and then diluted with ENR; (3) masterbatches of ENR and BR were prepared separately and blended; and (4) filler was added to a preblend of BR and ENR. These four mixes are designated as BL1, BL2, BL3, and BL4, respectively.

Mixing and blending were done on a laboratory-size, two-roll mixing mill (32.5 × 15 cm). The friction ratio between the mill rolls was 1 : 1.2. The speed of the front roll was 24 rpm, and that of the back roll, 20 rpm. Care was taken to keep the mill roll temperature low (60–70°C) by circulating cold water.

In the case of unvulcanized samples, test pieces were cut out from the milled-out sheets for the dynamic mechanical analysis. Sample length was 3–5 cm and the cross-sectional area was 0.5 × 0.3 cm. Since the samples were uncured, test pieces were cut from sheeted compounds. Test samples were conditioned at room temperature for a minimum period of 48 h prior to testing in all the cases.

Dynamic mechanical studies were carried out on a dynamic viscoelastometer, Rheovibron Model DDV-III-EP (Orientec Corporation, Japan) for a temperature range of –120 to +250°C. The test frequency was 3.5 Hz and the heating rate used for dynamic testing was 2°C/min. Errors in measurements are expected only in the high-temperature range where the modulus of the compounds drop drastically. These results are not taken for comparative studies.

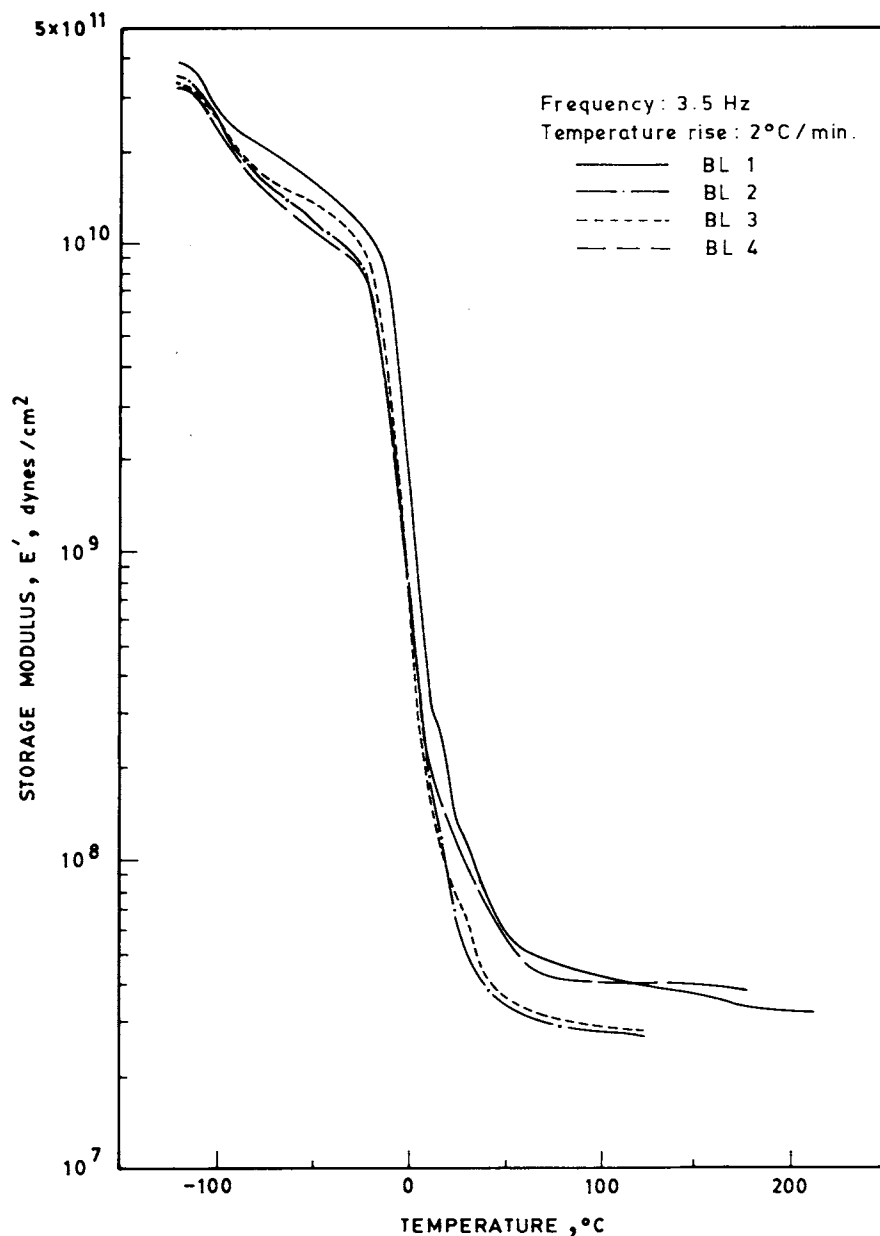
## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Mode of Filler Addition on the Elastic Modulus, $E'$ , and Loss Tangent, $\tan \delta$

The effect of the mode of carbon black addition on the elastic modulus,  $E'$ , values is shown in Figure 1. When black is added to the ENR phase and then diluted with BR and when a preblend of ENR and BR are prepared and filler added, the mixes behaved almost similarly, whereas in the case of BL2 and BL3, the spread of the  $E'$  curve is less than that in the case of BL1 and BL4. This increase in spread of the modulus curve can be correlated to the fact that in the case of BL1 and BL4 black concentration in the ENR phase is more. This is more predominant after the glass transition temperature of the ENR phase. This shift in modulus values to the higher-temperature zone may be attributed to the higher agglomerating tendency of the filler particles in BL1 and BL4.<sup>10</sup> This may be because the processing of BL1 and BL4 is much easier and is of shorter duration than that of BL2 and BL3. In the case of BL2, where black is incorporated in the BR matrix and then diluted with ENR, due to the longer mixing time required for obtaining a homogeneous mix, a considerable filler agglomerate structure breakdown may be taking place during the mixing itself. When

**Table I** Materials Used and Specifications

Materials	Specifications
Epoxidized natural rubber (ENR)	50 mol % epoxidized; specific gravity 1.03; glass transition temperature $-20 + 2^\circ\text{C}$ ; Mooney viscosity $\text{ML}_{(1+4)} 100^\circ\text{C} 96$
<i>cis</i> -1,4-Polybutadiene rubber (BR)	96% <i>cis</i> -1,4 content; specific gravity 0.93; Mooney viscosity $\text{ML}_{(1+4)} 100^\circ\text{C} 46$ ; glass transition temperature $-106 + 2^\circ\text{C}$
Carbon black	ISAF (N-220), DBP absorption – 114 mL/100 g; density 0.83; surface area 119 m <sup>2</sup> /g; pH 7.6
Silica	Ultrasil VN3

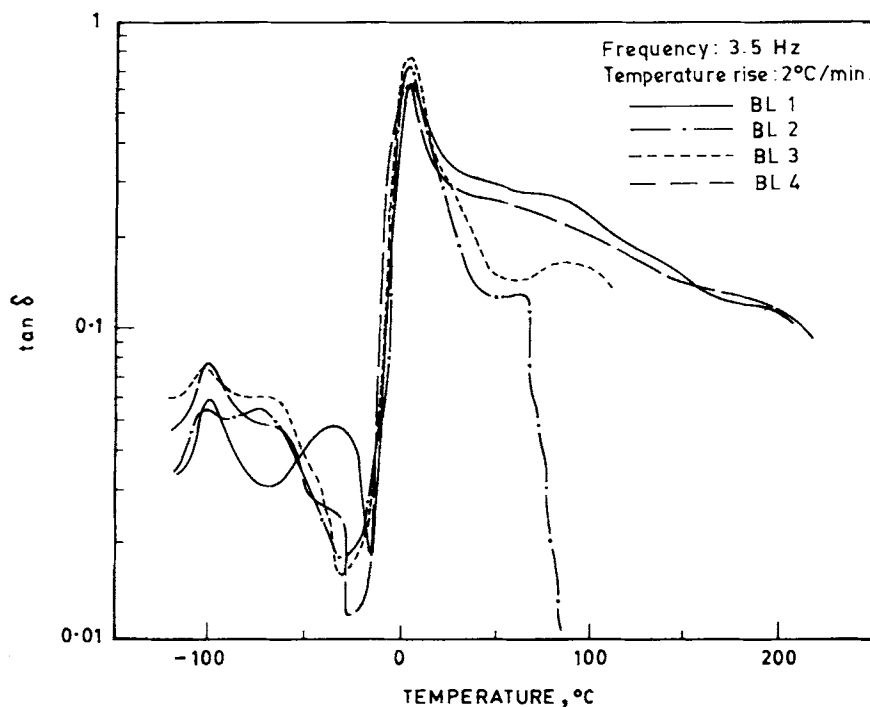


**Figure 1** Storage modulus,  $E'$  vs. temperature plots of ENR/BR 50/50 blends. Effect of mode of black addition.

the two individual masterbatches are prepared separately and then blended, as in the case of BL3, chances of filler agglomerate breakdown is more and, hence, a lower dynamic modulus value may be expected.

Figure 2 depicts the effect of the mode of carbon black addition on the loss tangent,  $\tan \delta$ , values. It may be noted here that the polymer-filler interaction parameters are playing a more significant role on parameters like the glass transition temperature,  $T_g$ , the  $\tan \delta$  peak height, and its spread. In the case of

single-component systems, the addition of an interacting filler (reinforcing type) will result in a reduction in the  $\tan \delta$  peak height and an increase in its spread.<sup>11</sup> However, Lee and Neilson<sup>10</sup> reported that it is not always essential to have a shift in the  $T_g$  values to a higher temperature region with enhanced filler-polymer adhesion or adsorption alone. A number of cases have been reported in which some agents that can destroy filler-polymer interaction also result in an increase in the  $T_g$  (or maximum in damping peaks) rather than the silane coupling



**Figure 2** Loss tangent  $\tan \delta$  vs. temperature plots of ENR/BR 50/50 blends. Effect of mode of black addition.

agents that increase the adhesion.<sup>12,13</sup> This phenomenon was explained by the theory put forward by Lee and Neilson. They suggested that the agents that are used to destroy the polymer-filler interaction might have resulted in the formation of more agglomerates, and this, in turn, resulted in a shift in the modulus and  $T_g$  values to higher temperature. In light of this, in a blend containing filler, this theory should give the necessary explanation for the changes occurring in the damping peak height and spread and the  $T_g$  values. However, in this case, none of the blends showed any shift in their  $T_g$  values (Table II). Since the ENR-BR system is an incompatible blend,<sup>9</sup> it is easier to analyze the changes taking place in the individual phases. However,

considerable changes could be observed in the damping peak height values and their spread (Table II) when carbon black is added in the ENR phase and then diluted with BR or when carbon black is added to a preblend. The tendency to find more black in the ENR phase is obvious from the spread of the  $\tan \delta$  peak corresponding to the ENR phase in the case of these two mixes, whereas BL2 showed the least spread with a sudden drop in the  $\tan \delta$  values after the  $T_g$  corresponding to the ENR phase was reached. The mix BL3 also tends to show a drop in the  $\tan \delta$  values in a similar way. However, in this case, the trend is intermediate to that of mixes BL2 and BL4, indicating probabilities of distribution of more carbon black in the ENR phase. This may be

**Table II** Glass Transition Temperatures and  $\tan \delta_{\max}$  Values

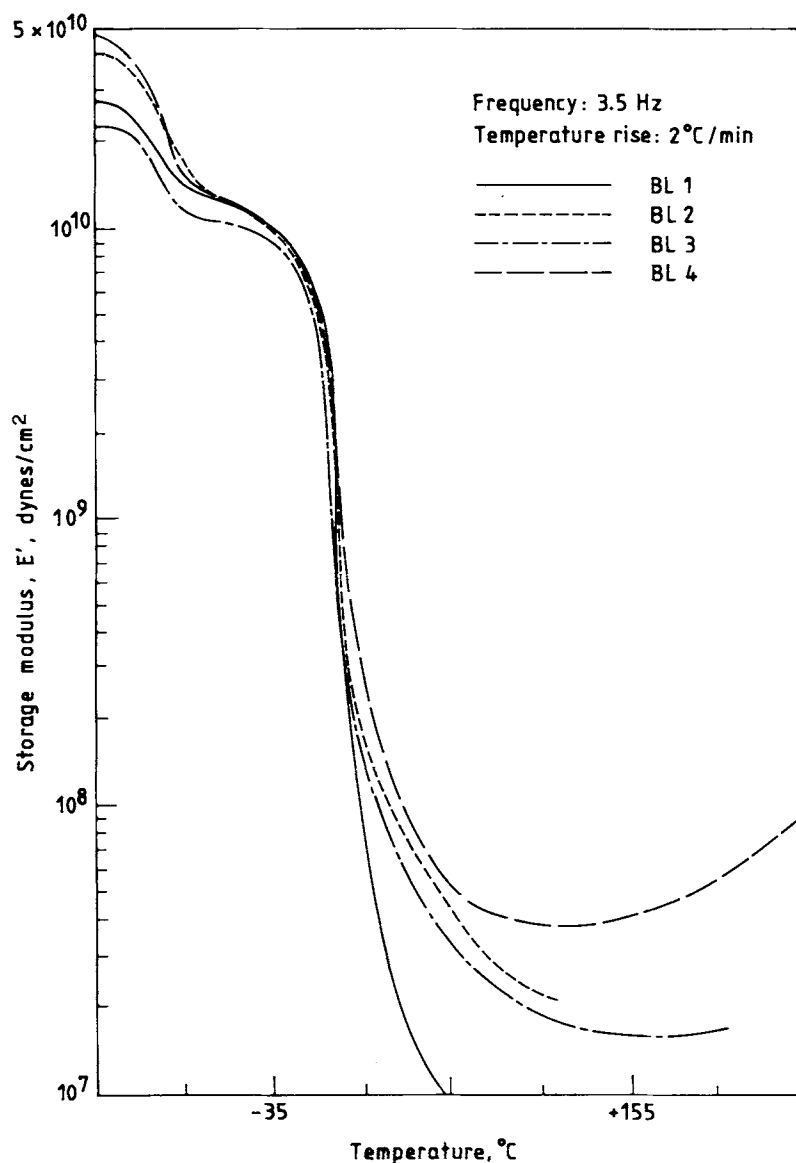
Mix Designation	Glass Transition Temperature ( $^{\circ}\text{C}$ )		$\tan \delta_{\max}$ Values	
	$T_{g(\text{BR})}$	$T_{g(\text{ENR})}$	Peak <sub>1</sub> (BR)	Peak <sub>2</sub> (ENR)
BL1	-101	+5	0.06	0.61
BL2	-101	+5	0.06	0.72
BL3	-102	+3	0.07	0.76
BL4	-101	+3	0.08	0.62

supported by the fact that in BL1 the crystallization peak corresponding to the BR phase is more prominent and larger in size. Sircar and Lamond<sup>5</sup> observed in their studies on blends of BR that the presence of a second polymer phase or carbon black can decrease the crystallinity and crystallization rate of BR. We have also observed this phenomenon in gum ENR-BR blends.<sup>9</sup>

Similarly, when carbon black is more dispersed in the BR phase, a spread in the  $\tan \delta$  peak corresponding to the BR phase can be observed (Fig. 2, curves BL2 and BL3). In these cases, the crystallinity peaks are not as prominent as in the case of

BL1 and BL4. This again gives additional evidence for the fact that black concentration is greater in the BR phase in blends BL2 and BL3.

Figure 3 shows the effect of four modes of adding silica to the blend on the  $E'$  vs. temperature plots. Results show deviation from that observed in the case of black-filled systems. When silica is added to the preblend (BL4) and in the case of the masterbatch (BL3),  $E'$  values show a higher ability to withstand the high-temperature zone, whereas in the case of BL1 where silica is added to the ENR phase,  $E'$  values suddenly drop after the glass transition temperature was reached. This is more clearly dem-

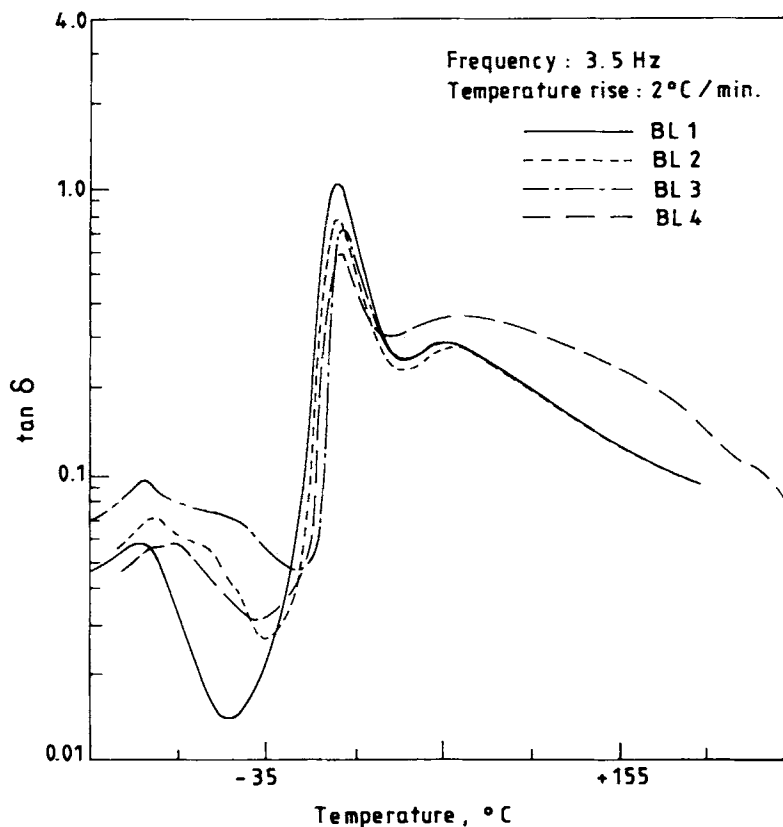


**Figure 3** Storage modulus,  $E'$  vs. temperature plots of ENR/BR 50/50 blends. Effect of mode of silica addition.

onstrated in Figure 4, where the  $\tan \delta$  vs. temperature plots of the four mixes are shown. The  $\tan \delta_{\max}$  values corresponding to the  $\alpha$ -relaxation of the ENR phase is comparatively higher in the case of BL1. When silica was added to the preblend and in the case of the masterbatch (BL4 and BL3, respectively), the  $\tan \delta_{\max}$  values corresponding to the ENR phase are lower compared to those of BL1. BL2 also showed a similar trend, since the loss tangent peak height and its spread are highly affected by the nature of the filler<sup>11</sup> and the affinity of the rubber to the filler differences observed here can be attributed to these factors. Selective adsorption of polymers on silica from mixed elastomer systems was demonstrated by Botham and Thies.<sup>14</sup> Studies on NR-based blends with silica showed the affinity of silica for the NR phase<sup>15</sup> rather than for the BR phase. In the present study, in the absence of any heat treatment, silica may be becoming dispersed in the BR phase compared to the ENR phase. The broadening of the  $\tan \delta_{\max}$  peak corresponding to the BR phase (BL3) shows the pronounced effect of silica being dispersed either in the interface or the BR phase. BL2 and BL3 also show similar

trends. In the case of BL1, dilution with BR resulted in the lowering of  $\tan \delta_{\max}$  corresponding to the BR phase.

Table III gives the Mooney viscosity values of ENR-50 and BR with the number of mill passes. It is seen that for the same number of mill passes the molecular chain breakdown is much higher in the case of ENR. From the discussion, it may be noted that the viscosity parameter is not of much consequence and filler migration is not taking place to a considerable extent in these blends during or after the mixing. It may be concluded that if carbon black is incorporated into one of the phases and then diluted with the second polymer the probability of the filler adhering to the first phase is greater and this is irrespective of the individual polymer's viscosity or polarity. However, when preblends are prepared and then black is incorporated, the viscosity factor comes into the picture and there are chances of filler migrating to the polymer phase having lower viscosity. However, in the case of individual masterbatches prepared and blended, filler migration to any of the phases is negligible, and in this case also, the viscosity and polarity factors are unaccountable.



**Figure 4** Loss tangent  $\tan \delta$  vs. temperature plots of ENR/BR 50/50 blends. Effect of mode of silica addition.

**Table III Mooney Viscosity of ENR and BR with Number of Mill Passes**

No. Mill Passes	Mooney Viscosity $ML_{(1+4)}$ at 100°C	
	ENR-50	BR
0	95	48
12	31	48
25	19	48
50	12	46
100	8	46

#### 4. CONCLUSION

From the study conducted on 50/50 ENR/BR blends of the effect of mode filler addition on the dynamic mechanical properties, it may be concluded that the mode of filler addition has profound influence on the loss tangent ( $\tan \delta$ ) peak height, its spread, and the storage modulus,  $E'$ , values of an incompatible blend. The tendency of the filler to adhere predominantly to one of the phases depends on the mode of filler addition and the processing history rather than on the individual component polarity or viscosity.

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