

# Effect of Types of Carbon Black and Cure Conditions on Dynamic Mechanical Properties of Elastomers

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## Synopsis

The dynamic mechanical properties of natural rubber and bromobutyl rubber (used in automotive suspension parts) were investigated to determine the effect of particle size of carbon black filler and state of cure of the rubber matrix. The results indicate that state of cure has little effect on storage modulus (hardness and stiffness). However, elastomers with a desirable storage modulus, with low sensitivity to temperature change, can be developed using a filler with a small particle size.

## INTRODUCTION

Elastomers are a very important class of engineering materials for automotive suspension systems. This is because elastomers possess unique properties, such as their ability to undergo large elastic deformation and to absorb energy. However, the dynamic mechanical properties of elastomers are, in general, very sensitive to temperature changes. An improperly formulated elastomer composition used for an automotive suspension system may result in a harsh ride at low temperatures. In the past, several investigations on the dynamic mechanical properties of elastomers have been reported,<sup>1-7</sup> including studies on the effects of particle size of the filler and the cure conditions of elastomers on the dynamic mechanical properties. However, most of these studies were conducted above room temperature<sup>7</sup> or using just one type of carbon black. In order to further extend the above knowledge, it would help to obtain experimental results from elastomers filled with different particle sizes measured over wide temperature ranges. These results would then be adequate for automotive engineers to use in designing elastomer suspension parts with the required performance at all services temperatures.

Among the many different elastomers used in automotive suspension systems, natural rubber and bromobutyl rubber (or butyl rubber) possess quite different dynamic mechanical characteristics. A typical example is the difference in storage moduli of the two elastomers as a function of test temperature, shown in Fig. 1. In the case of natural rubber, the storage modulus decreases with the increase of temperature up to about  $-10^{\circ}\text{C}$ . Below this temperature, the elastomer is in an enthalpy-dominant deformation regime.<sup>8</sup> In this regime, the internal friction among the polymer chains during the deformation of the elastomer network structure is the controlling mechanism.<sup>8</sup> Consequently, a high damping characteristic of the elastomer is expected. Above  $-10^{\circ}\text{C}$ , the storage modulus increases with the increase of

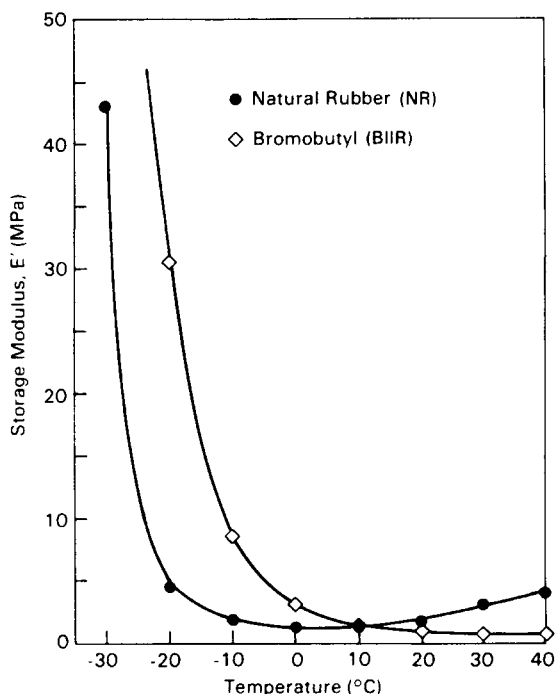


Fig. 1. Storage moduli as a function of temperature for a natural rubber and a bromobutyl rubber.

temperature. This defines the entropy-dominant deformation regime<sup>8,9</sup> in which the configurational change of polymer chains during the deformation of an elastomer network structure is the controlling mechanism. In other words, the elastomer network approaches a perfect network deformation and the elastomer exhibits a low damping characteristic.<sup>9</sup> In the case of bromobutyl rubber, the storage modulus decreases monotonically with increasing temperature throughout the temperature range from  $-30$  to  $40^{\circ}\text{C}$ . This implies that, in the above temperature range, the bromobutyl rubber undergoes enthalpy-dominant deformation.

Payne<sup>2</sup> reported that the state of cure and the particle size of a given filler may also affect the deformation mechanisms of filled elastomers. Since the natural rubber and the bromobutyl rubber have shown significant differences in their deformation mechanisms as a function of temperature, the purpose of this work is, therefore, to determine the effects of particle size of the filler and the state of cure on the dynamic mechanical properties of these two elastomers. The results can then be used as guidelines to develop elastomer compositions for suspension parts with the required performance.

## EXPERIMENTAL

### Materials

The elastomers used in this work were natural rubber (SML-5L, NR) and bromobutyl rubber (Polysar Bromobutyl X2, BIIR). Three carbon black fill-

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ers were used with each elastomer. They were (1) N110, a superabrasion furnace black with a particle size of 20 nm; (2) N550, a fast extrusion furnace black with a particle size of 46 nm; and (3) N990, a medium thermal black with a particle size of 300 nm. All compositions were cured with sulfur. The elastomer compositions investigated are shown in Table I. The volume fraction of carbon black used in each of the formulations of the two elastomers was 10%.

### SAMPLE PREPARATION

The elastomer compositions were mixed in a 1-kg Banbury mixer and sheeted out on a 152.4 × 304.8 mm two-roll mill following conventional mixing procedures. Test slabs (101.6 × 101.6 × 3.17 mm) were molded using a 300 × 450 mm hydraulic press at the molding conditions shown in Table I. These molding conditions were determined using a rheometer (Monsanto R-100). Test specimens for measuring the dynamic mechanical properties were prepared by die cutting. The dimensions of the test specimens were 12.7 × 6.35 × 3.17 mm.

### TEST PROCEDURE

The dynamic mechanical properties of the compositions were determined using the du Pont 1090 thermal analyzer and the 982 dynamic mechanical analyzer (DMA). The conditions of the test were (1) temperature range, from -100 to 40°C; (2) heating rate, 5°C/min; (3) frequency range, 2.56–50 Hz;

TABLE I  
Composition of Natural and Bromobutyl Rubber

Ingredients (phr) <sup>a</sup>	N-1	N-2	N-3	B-1	B-2	B-3
SMR-5L, natural rubber	100	100	100	0	0	0
Bromobutyl X2	0	0	0	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5
Symmetrical dibetanaphthyl- <i>p</i> -phenylenediamine	2	2	2	2	2	2
Tetramethyl thiuram disulfide	0.2	0.2	0.2	0.2	0.2	0.2
<i>N-t</i> -butyl-2-benzothiazole sulfenamide	1	1	1	1	1	1
Sulfur	3	3	3	3	3	3
Diphenyl guanidine	0.2	0.2	0.2	0.2	0.2	0.2
Dioctyl sebacate	18.8	18.8	18.8	18.8	18.8	18.8
Aromatic oil	6.3	6.3	6.3	6.3	6.3	6.3
N110 carbon black	18 <sup>b</sup>	0	0	18	0	0
N550 carbon black	0	18	0	0	18	0
N990 carbon black	0	0	18	0	0	18
100% Cure time						
Minutes at 135°C	40	40	40	—	—	—
Minutes at 163°C	—	—	—	32	30	23

<sup>a</sup> phr = parts per hundred parts of rubber.

<sup>b</sup> 18 phr = 10% volume fraction.

and (4) vibrational amplitude, 0.2%, which is within the amplitude range governed by the interaggregate interaction suggested by Panne.<sup>5</sup> To study the degree of dispersion of the elastomer compositions, the cryogenically fractured surface of each composition was examined using a scanning electron microscope (Inter. Sci. Inst. DS130) at a magnification of 4000X. The test specimens were obtained by fracturing the elastomer DMA samples after they had been immersed in liquid nitrogen for at least 15 min. The glass transition temperature  $T_g$  of each composition was determined using the differential scanning calorimeter at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Effect of Particle Size of Carbon Black on Storage Modulus $E'$

The effects of particle size of the carbon black on the storage moduli of natural rubber and bromobutyl rubber compositions were determined using DMA. The data are shown in Tables II and III, and the plotted results are shown in Fig. 2. For the case of natural rubber, the storage moduli at various temperatures decrease for the sample containing the 46-nm carbon black (N550) compared with the sample containing the 20-nm carbon black (N110). A further decline in modulus is observed when a larger size (300 nm) carbon black is used. However, in the latter case the decrease is less dramatic. In the case of bromobutyl the modulus values at each test temperature are higher for the sample containing the 46-nm carbon compared with the sample containing the 20-nm carbon black. The maximum storage moduli at 46 nm may be attributed to the void formation in the bromobutyl rubber matrix. More experimental work will be carried out to investigate this phenomenon.

### EFFECT OF STATE OF CURE ON STORAGE MODULUS

The storage modulus for each elastomer composition was determined at various temperatures and different states of cure, namely, 75, 80, 90, and 100% of complete cure. The results are also shown in Tables II and III. Plotted results are shown in Figs. 3 and 4 for natural rubber and bromobutyl rubber, respectively. For all the carbon black-filled natural rubber compositions, the changes in storage modulus with respect to the state of cure studied are insignificant at test temperatures ranging between room temperature and  $-10^\circ\text{C}$ . At  $-20^\circ\text{C}$ , all the black-filled compositions generally exhibit an increase in storage modulus as the state of cure increases to 100%. The increases of storage moduli with respect to state of cure at  $-20^\circ\text{C}$  for N110 black-filled natural rubber composition is more pronounced than those for the N550- and N990-filled compositions.

The effect of state of cure on the storage moduli of bromobutyl compositions is relatively moderate. Within the temperature range from 20 to  $-20^\circ\text{C}$ , the changes in storage moduli with respect to the state of cure are generally insignificant. The only exception is the N550 black-filled bromobutyl composition. The significant change in storage moduli for N550-filled bromobutyl composition at  $-20^\circ\text{C}$  as a function of the state of cure may be due

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**TABLE II**  
Storage Moduli Versus Test Temperatures for the Natural Rubber Compositions at Various States of Cure

Types of black	Temperature (°C)	Storage moduli (MPa) at various states of cure (%)			
		75	80	90	100
N110	20	1.46	1.46	1.45	1.32
N110	10	1.44	1.42	1.43	1.40
N110	0	1.41	1.40	1.40	1.50
N110	-10	1.70	1.60	1.90	2.30
N110	-20	3.90	3.40	4.60	7.10
N550	20	1.48	1.72	1.38	0.96
N550	10	1.44	1.46	1.35	0.93
N550	0	1.40	1.41	1.32	0.91
N550	-10	1.70	1.70	1.60	1.30
N550	-20	3.80	4.30	3.50	4.90
N990	20	1.12	1.12	1.12	1.03
N990	10	1.06	1.04	1.04	0.97
N990	0	0.98	0.94	0.94	0.86
N990	-10	0.90	0.90	1.00	1.00
N990	-20	1.90	2.20	3.30	3.10

**TABLE III**  
Storage Moduli Versus Test Temperatures for the Bromobutyl Compositions at Various States of Cure

Types of black	Temperature (°C)	Storage moduli (MPa) at various states of cure (%)			
		75	80	90	100
N110	20	0.9	0.8	0.9	0.8
N110	10	1.6	1.4	1.5	1.4
N110	0	3.4	3.0	3.3	3.0
N110	-10	9.3	8.4	9.3	8.1
N110	-20	32.7	31.1	33.5	29.4
N550	20	1.0	0.6	0.8	1.0
N550	10	1.9	1.2	1.5	1.8
N550	0	4.0	2.7	3.2	4.0
N550	-10	11.3	8.1	8.6	12.0
N550	-20	38.3	30.7	29.1	50.0
N990	20	0.2	0.2	0.1	0.1
N990	10	0.2	0.3	0.2	0.6
N990	0	1.8	2.9	1.4	2.7
N990	-10	8.6	8.8	7.3	10.0
N990	-20	23.9	27.3	24.4	26.4

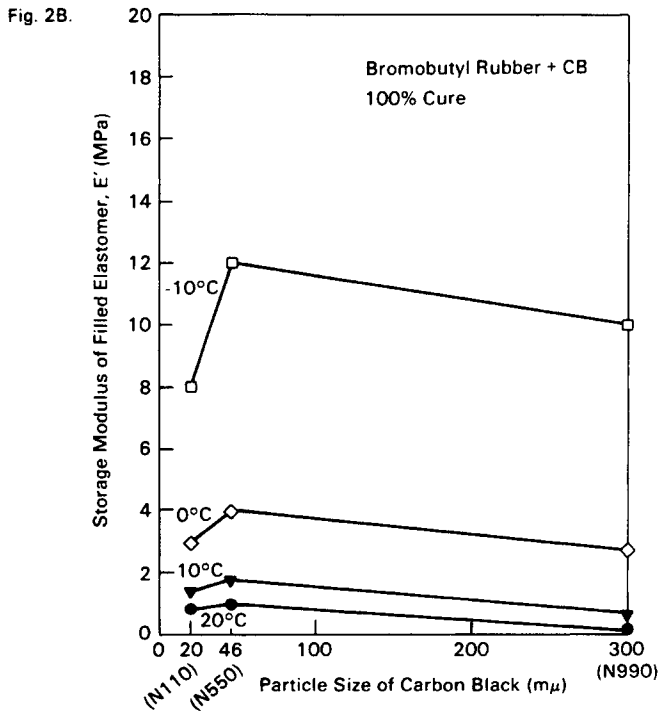
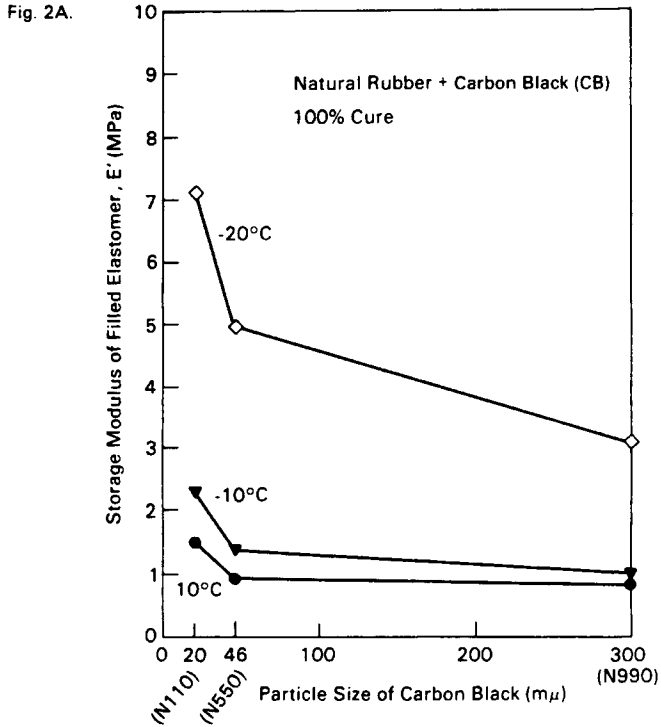


Fig. 2. (a) Effects of the original particle size of carbon black on the storage modulus property of natural rubber at various test temperatures. (b) Effects of the original particle size of carbon black on the storage modulus property of bromobutyl rubber at various test temperatures.

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Fig. 3A.

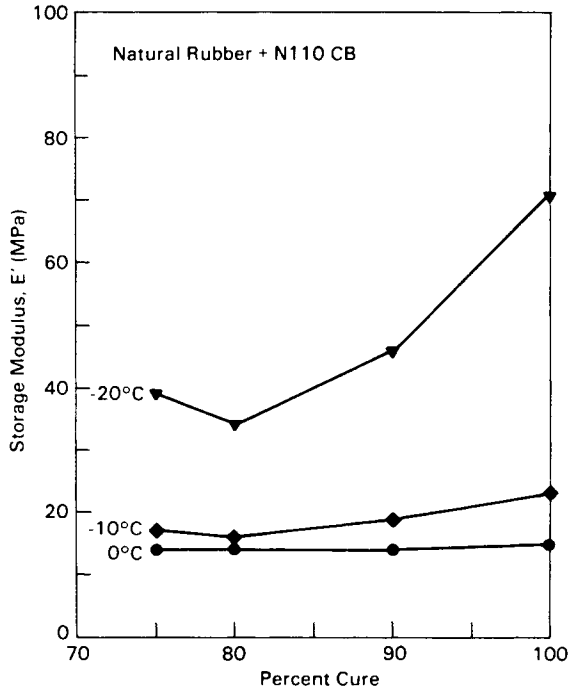


Fig. 3B.

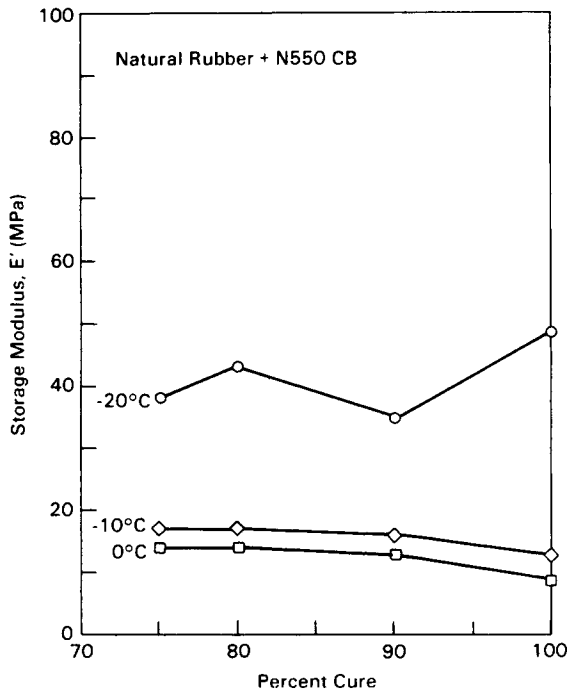


Fig. 3. (a) Effects of the state of cure on the storage modulus property of N100 carbon black-filled natural rubber at various test temperatures. (b) Effects of the state of cure on the storage modulus property of N550 carbon black-filled natural rubber at various test temperatures. (c) Effects of the state of cure on the storage modulus property of N990 carbon black-filled natural rubber at various test temperatures.

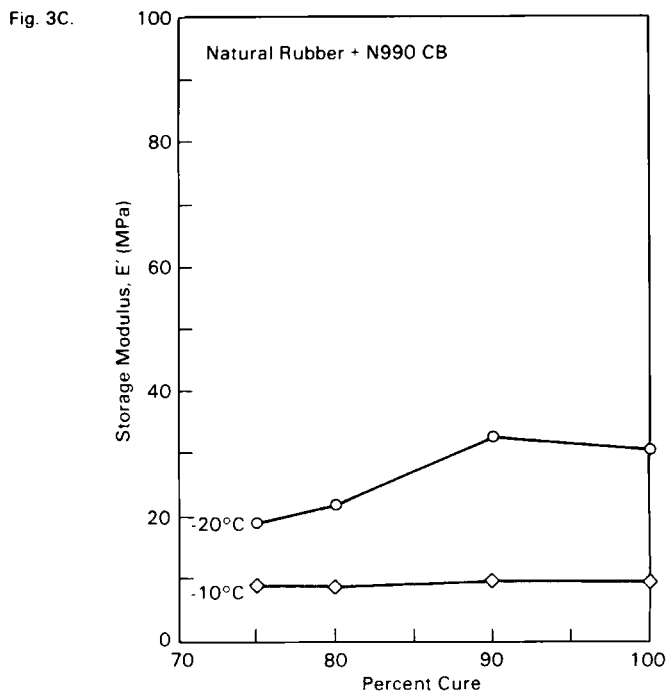


Fig. 3. (continued from the previous page.)

to the heterogeneous dispersion of the cure agent in the rubber matrix. More work will be conducted to investigate this phenomenon.

In summary, the above results generally shown that the state of cure has insignificant effects on the storage modulus for both the natural rubber and bromobutyl compositions within the temperature range from 20 to  $-20^{\circ}\text{C}$ .

### GLASS TRANSITION TEMPERATURES FOR THE ELASTOMER COMPOSITIONS

The glass transition temperature for each elastomer composition was determined by the differential scanning calorimeter. The results show that the type of carbon black and the state of cure have no effect on the glass transition temperatures for both natural rubber and bromobutyl rubber compositions. The glass transition temperatures for the natural rubber and the bromobutyl rubber compositions are  $-68$  and  $-73^{\circ}\text{C}$ , respectively. Similar results were previously reported by Fletcher and Gent.<sup>4</sup>

### RELATIVE STORAGE MODULUS-TEMPERATURE RELATIONSHIP FOR ELASTOMER COMPOSITIONS

The storage modulus-temperature relationship for elastomer compositions is very important for engineers to design elastomer suspension parts with the required low-temperature dynamic mechanical performance. An elastomer whose dynamic mechanical properties are less sensitive to temper-



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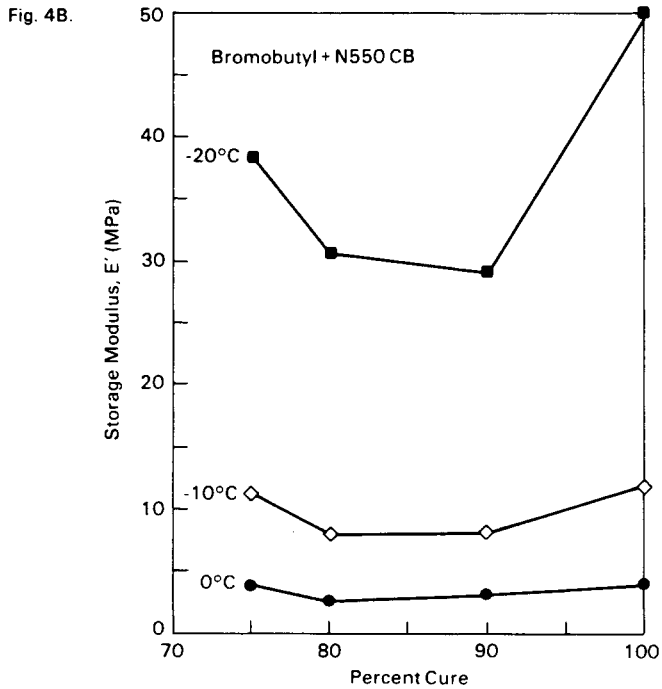
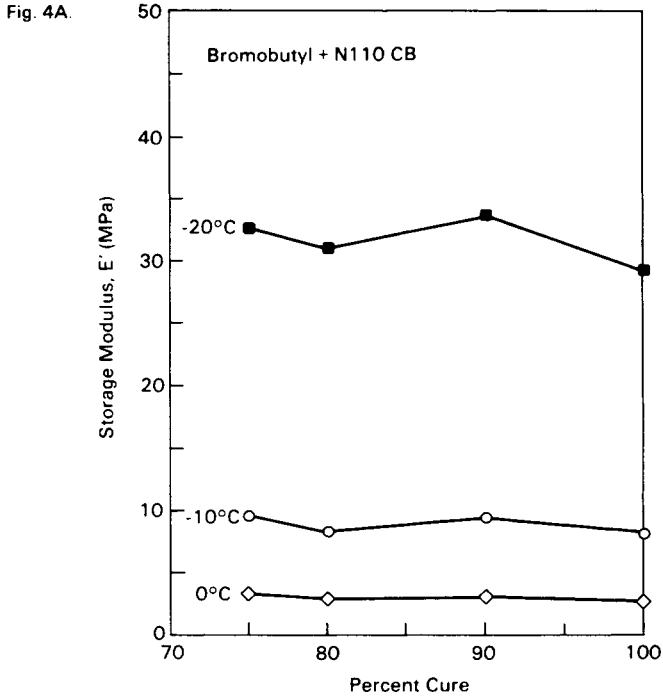


Fig. 4. (a) Effects of the state of cure on the storage modulus property of N110 carbon black-filled bromobutyl rubber at various temperatures. (b) Effects of the state of cure on the storage modulus property of N550 carbon black-filled bromobutyl rubber at various temperatures. (c) Effects of the state of cure on the storage modulus property of N990 carbon black-filled bromobutyl rubber at various temperatures.

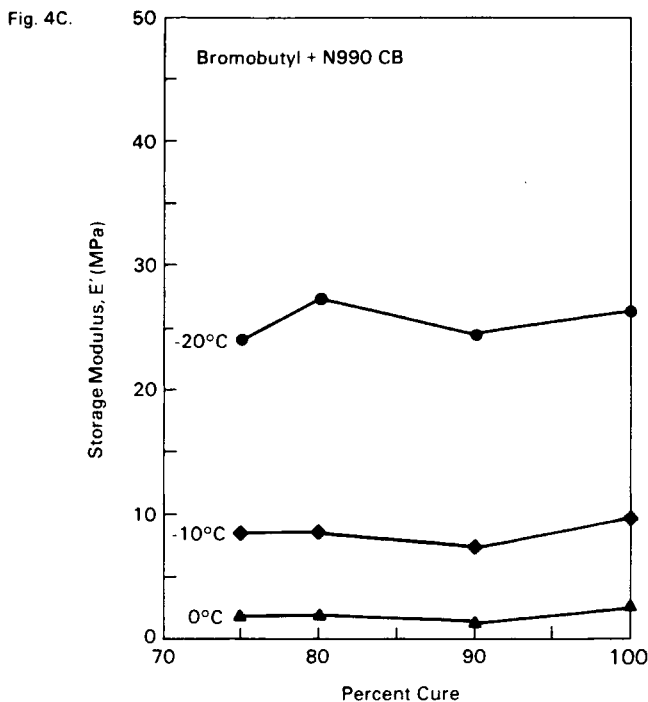


Fig. 4. (continued from the previous page.)

ature change is required for maintaining ride comfort at low temperatures.<sup>10,11</sup> The relative storage modulus is a useful parameter to evaluate the low-temperature sensitivity of the modulus properties of elastomers.<sup>10,11</sup> It is defined as the storage modulus at any low temperature,  $E'(T)$ , divided by the storage modulus at room temperature  $E'(20^\circ\text{C})$ . The relative storage moduli (storage modulus ratio) for all the completely cured elastomer compositions (i.e., 100% cure) were determined and are shown in Table IV. Plotted results for these elastomer compositions are shown in Fig. 5.

The storage modulus-temperature relationships for the natural rubber and the bromobutyl rubber compositions are quite different. For all the bromobutyl rubber systems investigated, the relative storage moduli decrease with the increase of temperature throughout the whole testing range. For the natural rubber systems, the relative storage moduli decrease with the increase of temperature up to  $-10^\circ\text{C}$ . Above  $-10^\circ\text{C}$  the relative storage moduli are not very sensitive to further temperature increases. The temperature  $-10^\circ\text{C}$  is very close to the temperature at which a minimum in storage modulus is observed for the natural rubber, as shown in Fig. 1.

As discussed earlier, the natural rubber composition shows two different deformation mechanisms below room temperature. They are the enthalpy-dominant regime (below  $-10^\circ\text{C}$ ) and the entropy-dominant regime (above  $-10^\circ\text{C}$ ). On the other hand, the bromobutyl rubber shows only the enthalpy-dominant deformation below room temperature. These two different deformation mechanisms may be employed to explain the different storage mod-

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TABLE IV  
Relative Storage Moduli  $E''/E'$  (20°C) Versus Test Temperatures for the Natural Rubber and Bromobutyl Rubber Compositions

Temperature (°C)	$E''/E'$ (20°C)		
	N100	N550	N990
<b>Natural rubber</b> (100% cure)			
20	1.00	1.00	1.00
10	1.06	0.97	0.94
0	1.14	0.95	0.84
-10	1.74	1.35	0.97
-20	5.37	5.10	3.01
-30	10.53	14.60	26.50
<b>Bromobutyl rubber</b> (100% cure)			
20	1.00	1.00	1.00
10	1.75	1.80	6.00
0	3.75	4.00	27.00
-10	10.13	12.00	100.00
-20	36.75	50.00	264.00
-30	155.00	283.00	371.00

ulus-temperature relationships shown in Fig. 5 for the natural rubber and the bromobutyl rubber.

Based on the above results, three key points can be highlighted. They are as follows. (1) Within the enthalpy-dominant deformation regime, the relative storage moduli for elastomers increase with decreasing test temperatures. (2) Within the enthalpy-dominant deformation regime, high values for the sensitivity of the storage modulus to temperature changes are obtained for all black-filled elastomer compositions. (3) Within the entropy-dominant deformation regime (natural rubber above  $-10^{\circ}\text{C}$ ), values for the relative storage modulus and for the sensitivity of the storage modulus to temperature are low for the carbon black-filled elastomers investigated.

## CORRELATION BETWEEN THE RELATIVE STORAGE MODULUS AND CRYOGENIC FRACTURE MORPHOLOGY

The scanning electron micrographs for the cryogenically fractured surfaces of the completely cured elastomer compositions are shown in Figs. 6 and 7. The aggregate sizes for N110- and N550-filled natural rubber compositions are about  $0.8\ \mu\text{m}$ ; the aggregate size for the N990-filled natural rubber is about  $1.0\ \mu\text{m}$ . The N990-filled natural rubber also contains more microvoids, which can be attributed to the poor polymer-filler adhesion and the void formation during mixing. The aggregate size for the N550-filled bromobutyl rubber, which is of the order of  $1.5\ \mu\text{m}$  is slightly larger than that for the N110-filled bromobutyl rubber. The aggregate size for the N990-filled bromobutyl, on the other hand, is greater than  $2\ \mu\text{m}$ .

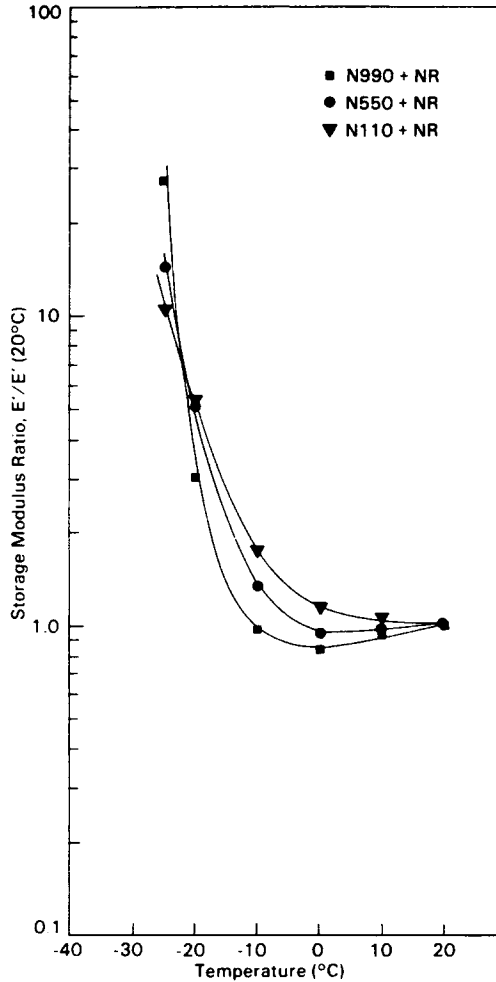


Fig. 5. Storage modulus ratio-temperature relationships for carbon black-filled natural rubber compositions.

Based on the above findings, we conclude that, for both elastomers within their enthalpy-dominant deformation regime, increasing the aggregate size will result in an increasing value for the sensitivity of the relative storage modulus to temperature changes. For example, the sensitivities of the relative storage modulus to temperature for the N990-filled natural rubber and bromobutyl rubber are much higher than those for the N110- and N550-filled systems. In other words, in order to obtain an elastomer with a low value of sensitivity of relative storage modulus to temperature change, decreasing the aggregate size is required. This conclusion has been reported in an earlier study for a neoprene system<sup>11</sup> in which the aggregate size can be reduced by improved mixing. For elastomers containing entropy-dominant deformation regime (natural rubber above  $-10^{\circ}\text{C}$ ), the sensitivity of the relative storage modulus to temperature changes is less affected by the aggregate size or, correspondingly, the initial particle size, of the filler.

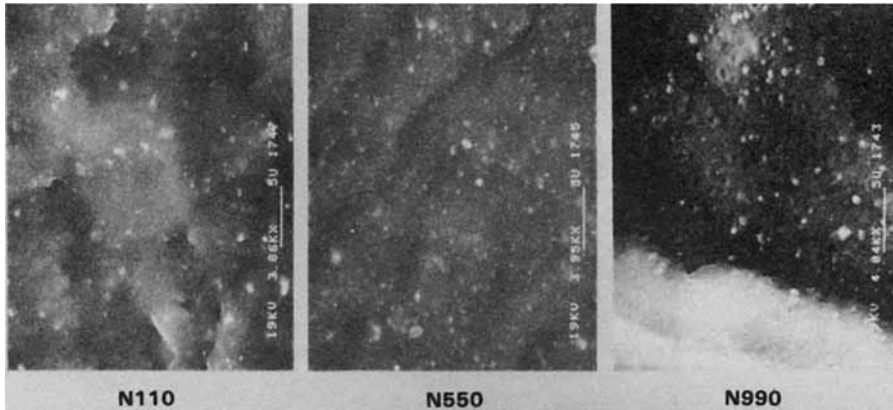


Fig. 6. Cryogenically fractured surfaces of natural rubber composition filled with different types of carbon black: (a) N110 (left), (b) N550 (center), and (c) N990 (right).

### SUMMARY AND CONCLUSIONS

Among the various automotive elastomer suspension parts, natural rubber and butyl rubber (including bromobutyl rubber) are the two most widely used elastomers. In this work, the effects of particle size of carbon black fillers and state of cure of the rubber matrix on the dynamic mechanical properties of reinforced elastomers have been investigated using a du Pont 1090/982 dynamic mechanical analyzer. Experimental results indicate that the state of cure has little effect on the glass transition temperatures and the storage moduli of the elastomers investigated. The results also imply that an elastomer having a desirable storage modulus with low sensitivity to temperature changes can be developed by using a filler with a small particle size. The above findings can now be used as guidelines to develop elastomer compositions for automotive parts with the required performance.

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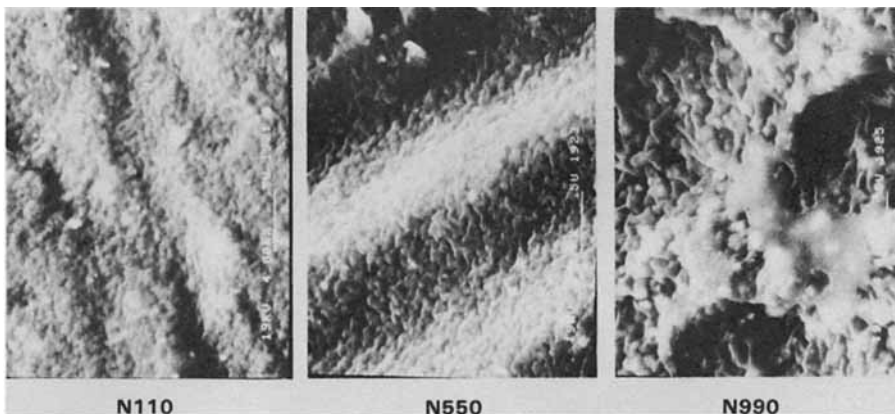


Fig. 7. Cryogenically fractured surfaces of bromobutyl rubber composition filled with different types of carbon black: (a) N110 (left), (b) N550 (center), and (c) N990 (right).

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