

# INTERAGGREGATE INTERACTION IN FILLED RUBBER\*

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## INTRODUCTION

Recent studies of miscible blends of 1,2-polybutadiene with *cis*-1,4-polyisoprene revealed that for certain compositions the glass to rubber transition occurs over a very broad temperature range. This transition breadth, moreover, is not associated with any structural heterogeneity; the blends are thermodynamically miscible<sup>1-5</sup>. The unusual nature of the material's glass transition inspired efforts to exploit this feature for practical purposes. Obviously the intended application must be sensitive to behavior in the transition zone for any advantageous performance to be realized.

A glassy material will respond to deformation primarily in an elastic fashion; thus, despite the high viscosity of a glass, minimal energy will be dissipated. The response of rubber to an applied stress involves cooperative motions of polymer chains which retard the response; nevertheless, the typically low viscosity enables deformation of a rubber to proceed with relatively small energy loss. In the glass-transition region, the competing effects of viscosity and retardation are such that the energy dissipation is maximized. Indeed, the condition whereby the dynamic loss modulus or the loss tangent is at a maximum serves as a common mechanical definition of the glass transition. As a consequence of the high energy dissipation associated with the glass transition, a material employed for the attenuation of mechanical or sonic energy will often be selected by virtue of its undergoing the glass to rubber transition at the appropriate combination of frequency and temperature. Clearly, having this transition transpire over a broad range has appeal for many damping applications, since broader band damping with less sensitivity to temperature can be realized.

Blends of 1,2-BR and NR are attractive candidates in this regard. When the BR has the higher relative concentration, and provided it is very high in 1,2-content (>90%), the glass transition, as measured by a marked increase at  $T_g$  of either the heat capacity or thermal expansion coefficient, transpires over a roughly 30° broader temperature range than is otherwise observed for such blends<sup>4,5</sup>. When the discontinuities at  $T_g$  in the relevant thermodynamic quantities (*e.g.*, heat capacity or thermal expansivity) are less abrupt, the onset of segmental motion in the polymer molecules is not simultaneous<sup>6</sup>; consequently, a broad transition exhibits a weaker intensity. A high magnitude of broadband damping can be maintained only if additional energy dissipation mechanisms are provided.

In a carbon-black-reinforced elastomer, flocculation (or agglomeration), resulting from interaction between aggregates of the carbon black, gives rise to a network structure that is responsible for high electrical conductivity<sup>7-10</sup>, yield stresses (thixotropy)<sup>11-13</sup>, and a modulus inversely dependent on strain<sup>14-16</sup>. The latter phenomena reflect the breakup of the flocculated structure, as the mechanical stress overcomes the van der Waals forces responsible for bonding of the particles<sup>17-21</sup>. This breakup of the network of aggregates is well known

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as an energy dissipative mechanism<sup>17</sup>. The development of extensive carbon-black agglomeration therefore has the potential to introduce higher levels of damping. This particular source of damping, however, is strongly dependent on the magnitude of the strains imposed on the filled rubber. Exploitation of an agglomerated filler structure for damping applications requires consideration of the relevant deformations for which damping is intended.

The purpose of this work was to explore the use of 1,2-BR/NR blends with an agglomerated filler structure as damping materials. The preliminary work described herein was directed toward characterizing the dynamic-mechanical response of these mixtures and to analyze the potential contributions of aggregate interactions on the damping behavior.

### EXPERIMENTAL

Rubber formulations are given in Table I. Mixing of the filled stocks was, in most cases, carried out in a Brabender Precenter, followed by sheeting on a two-roll mill to provide high levels of carbon-black dispersion. To obtain stocks with well distributed carbon black but varying degrees of dispersion, SBR samples were prepared from a black masterbatch (Carbomix 1848 from the Copolymer Rubber and Chemical Corporation). The masterbatch was unmilled (SBR-83-0), passed 5 times through a two-roll mill with a 0.7 mm nip (SBR-83-5), or passed 20 times through a 0.25 mm nip (SBR-83-20). The increasing degree of carbon-black dispersion is seen in comparing the electrical resistivities of these samples, measured (in ohm-cm) to be 639, 11 160 and 23 700 for SBR-83-0 through SBR-83-20 respectively. Electrical resistivities were measured at room temperature using test leads adhered to the ends of rectangular bars. The ends were coated with colloidal graphite to minimize contact resistance.

Mechanical testing was carried out with an Imass Co. Dynastat Mark II instrument. The resolution of the displacement transducer, 0.05 nm, enables imposition of very small strains.

TABLE I  
SAMPLE FORMULATIONS

	NR-0	NR-45	NR-60	NR-75	NR-90
NR (SMR-L)	100	100	100	100	100
N110 <sup>a</sup>	0	45	60	75	90
Dicumyl peroxide	3	3	3	3	3
Antioxidant <sup>b</sup>	1	1	1	1	1
Total	104.0	149.0	164.0	179.0	194.0
	BR-100	Br-75	BR-50	BR-75F	SBR-83
1,2-BR <sup>c</sup>	100	75	50	75	0
NR (SMR-L)	0	25	50	25	0
SBR <sup>d</sup>	0	0	0	0	100
N110	0	0	0	75	0
N339 <sup>d</sup>	0	0	0	0	82.5
Oil <sup>d</sup>	0	0	0	0	62.5
Dicumyl peroxide	0.5	0.5	0.5	0.5	1.0
Total	100.5	100.5	100.5	175.5	246.0

<sup>a</sup> Vulcan 9 SAF carbon black (Cabot Corporation).

<sup>b</sup> Agerite DDPD (R.T. Vanderbilt Company).

<sup>c</sup> 97% 1,2-polybutadiene (Firestone Tire and Rubber Company).

<sup>d</sup> Included in Carbomix 1848 Masterbatch (Copolymer Rubber and Chemical Corporation).

For NR samples, bonded cylindrical specimens were utilized. The shearing at the ends, which accompanies the deformation of a bonded cylinder<sup>22</sup> was negligible for the sample geometry used (height = 19 mm and diameter = 12.5 mm). A mean level of zero strain (*i.e.*, the cylinder experienced alternately tension and compression over a strain cycle) was employed for the data reported herein. Experiments were also conducted in tension (minimum amplitude equal to zero strain) and in compression (maximum strain equals zero). These results were quantitatively equivalent, both with respect to the magnitude and the strain dependence of the modulus, to the zero mean level data. For the other rubbers used herein, thin (1.6 mm) strips were tested in uniaxial extension. Although the instrumental compliance was low (0.001 mm/kg), correction for it<sup>23</sup> significantly altered the obtained results, particularly for cylindrical test specimens.

To improve the signal to noise ratio, data taken at the lowest strain amplitudes were averaged over at least 60 cycles. Viscous heating was minimized by employing a 0.1 Hertz frequency for testing of the cylindrical specimens. Individual measurements over the course of the 60 cycles confirmed the absence of any measurable thermal effects.

For simultaneous dynamic and static measurements, the Dynastat was used to obtain dynamic data at 40 Hz, during which a static displacement was superposed and the transient load data collected from the instrument using a Hewlett Packard Vectra computer.

Acoustic moduli were measured using a resonance apparatus<sup>24</sup>. An electromagnetic shaker drives the specimen (10.2 × 0.6 × 0.6 cm) with a random noise input. Accelerometers at each end measure the driven acceleration and the response of the free end. The amplitude of the strain varied from roughly 10<sup>-9</sup> through 10<sup>-6</sup>. The acceleration data were analyzed (Hewlett Packard 3582A) to yield the dynamic-mechanical spectra. Samples were maintained in an environmental chamber at 30°C during the measurements.

## RESULTS

### DYNAMIC-MECHANICAL BEHAVIOR

Calorimetry and thermal expansivity measurements rely on the discontinuity at  $T_g$  in the first derivatives of enthalpy and volume, respectively, to provide a measure of the transition. The corresponding increase in segmental mobility at  $T_g$  enables its determination by mechanical means, and the latter is, for damping purposes, the relevant glass-transition behavior. The dynamic moduli of a 97% 1,2-BR, NR, and their blends were measured at various frequencies over a temperature range encompassing the glass transition, with the empirically superpositioned results displayed in Figures 1 through 3. The pure polyisoprene rubber has a narrower transition than any of the stocks containing 1,2-BR; more significant, however, is the strikingly different behavior of BR-75 (which is 75% 1,2-BR). Unlike the other compositions, its transition from rubber to glass occurs over a range of more than fifteen decades of frequency, with a maximum barely seen in the loss modulus. This is consistent with calorimetry and expansivity measurements, in which only blends with a high concentration of BR high in 1,2-microstructure exhibit broad  $T_g$ 's<sup>4,5</sup>.

It is not clear why the transition anomaly is restricted to particular compositions. Miscible blends exhibit only a single  $T_g$ , since the chain units of the components experience the same free volume, both on average and with respect to its fluctuations. From solid-state carbon-13-NMR experiments, it is known that in blends with a high concentration of high 1,2-BR, the vinyl carbons of polyisoprene develop liquid-like motion at temperatures for which the vinyl carbons of the BR are still in the glassy state<sup>6</sup>. A greater local free volume is evidently required for the onset of mobility in the vinyl carbons of the BR. It can be rationalized that the free volume requirements for segmental mobility are different for the two components. Segmental motions in the mixtures are undoubtedly interrelated. The reason that the appearance of very broad transitions is restricted to blends comprised primarily of high 1,2-BR is currently being studied.

For a damping material present as a single layer (*i.e.*, extensional damping), the loss modulus governs the effectiveness of the damping<sup>25</sup>. Constrained layer damping, however,

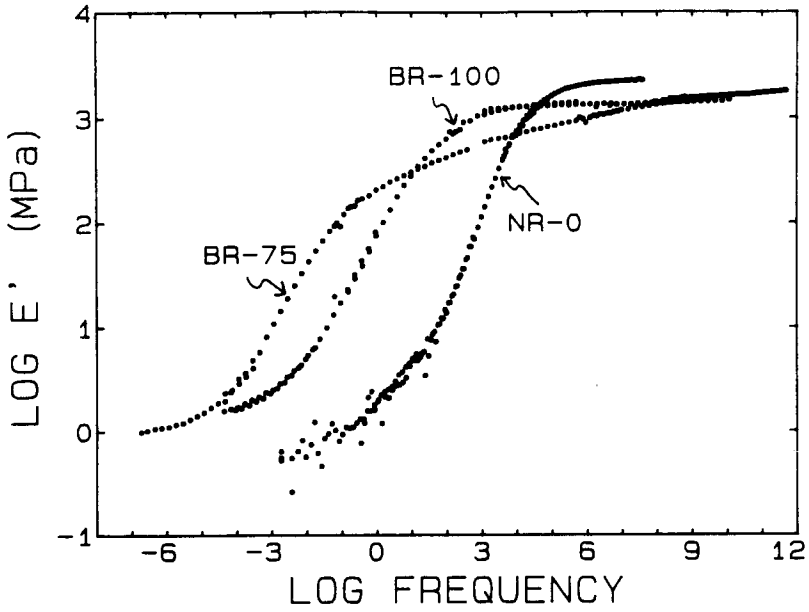


FIG. 1.—Empirically shifted mastercurves of the storage moduli for NR-0, BR-100, and BR-75 with different reference temperatures ( $-50$ ,  $+5$ , and  $-20^{\circ}\text{C}$  respectively) employed to allow depiction of the data on an expanded scale. The transition temperature of the blend is between that of the pure components  $T_g$ 's ( $-63^{\circ}\text{C}$  for the NR-0 and  $0^{\circ}\text{C}$  for the BR-100).

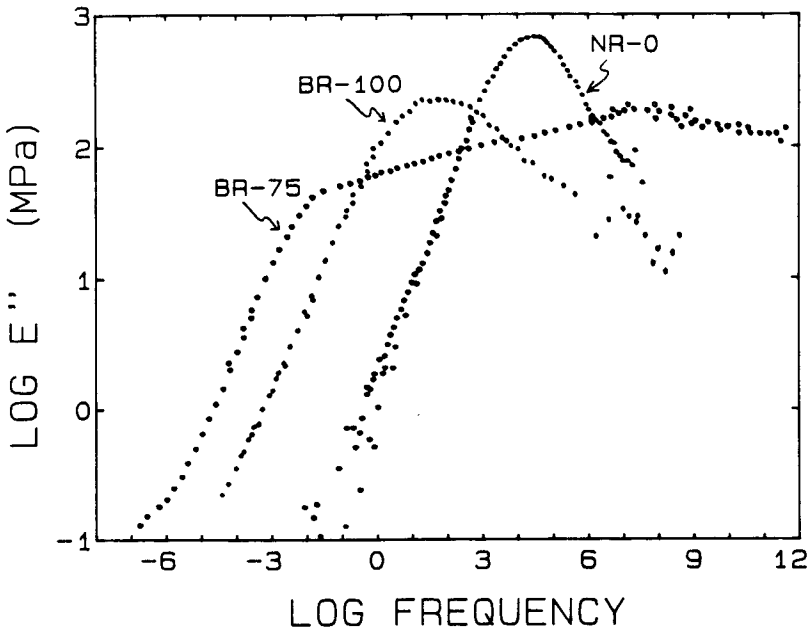


FIG. 2.—The loss moduli corresponding to the data in Figure 1. Note that different reference temperatures were chosen in order to allow the curves to be displayed on an expanded scale.

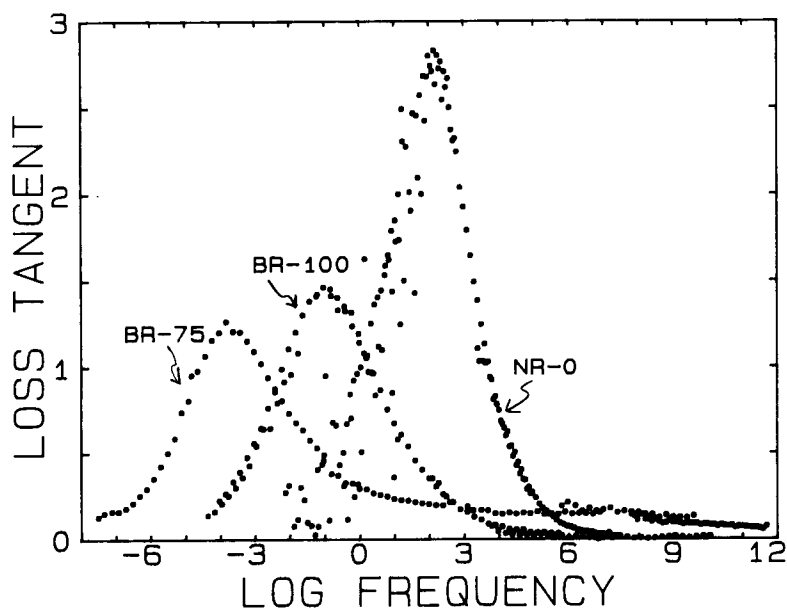


FIG. 3.—The loss tangents corresponding to the data in Figure 1.

in which the rubber is in contact with a layer of higher modulus, is controlled by the magnitude of the loss tangent<sup>25</sup>. The width of the loss tangent peak for the BR-75 is roughly equal to that of the other 1,2-BR containing samples (Figure 4). The only manifestation in the loss tangent spectrum of anomalous glass-transition behavior is the enhanced magnitude of the loss tangent in the glassy region.

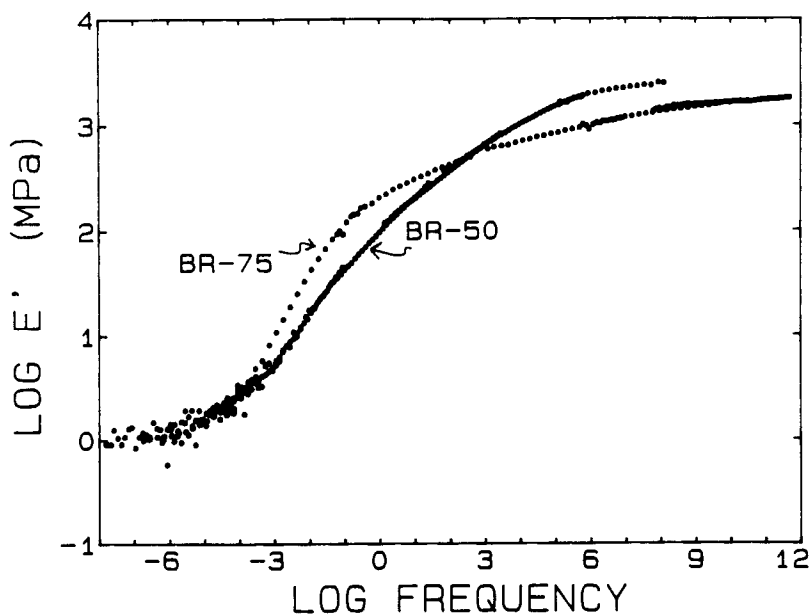


FIG. 4.—Superpositioned storage moduli for BR-75 and BR-50 at a reference temperature of  $-20^{\circ}\text{C}$  in both cases. The transition of the former is significantly broadened.

## STRAIN DEPENDENCE OF AGGREGATE INTERACTION

The peak magnitude of the loss modulus is lower for BR-75 than for the other compositions, reflecting the fact that at a given temperature and frequency, fewer dissipative mechanisms are active. For optimal damping, the intensity of the energy dissipation should be amplified. The introduction of carbon black is a potential route to providing additional hysteresis. Such excess hysteresis is well known in filled rubbers subjected to dynamic strain amplitudes of *circa*  $10^{-3}$  or larger<sup>17</sup>. Of relevance herein is the behavior of filled rubber at the much lower strains ( $10^{-6}$  to  $10^{-9}$ ) associated with acoustic deformation.

Very generally, the response of a system to small perturbations can be related to its equilibrium fluctuations<sup>26</sup>; hence, a linear response to sufficiently small perturbations is expected. The storage modulus of filled rubber is known to exhibit an invariance to deformation over a range of strain amplitudes down to roughly  $10^{-3}$ <sup>16,17,27</sup>. The available data on filled rubber at lower strain amplitudes suggests an absence of linearity, with broad maxima observed for the dependence of the dynamic modulus on strain amplitude<sup>28-32</sup>. Multiple maxima in the loss modulus *versus* strain relationship have also been reported<sup>28,30-32</sup>. The inference from these results is that the agglomeration (flocculation) of the aggregates is promoted by small deformation, which, at higher amplitude, can break up the agglomerates. An example of such deformation-induced aggregate interaction can perhaps be seen in the increase in electrical conductivity of filled rubber when elongated more than about 25%<sup>33</sup>. The reports of maxima in the dynamic moduli at low strains<sup>28-32</sup> have been disparaged as artifacts of measurements made at strain amplitudes beyond the range of the experimental apparatus<sup>16</sup>. In the absence of corroborating data, it has been suggested that experiments on more sensitive instrumentation are needed to resolve this issue<sup>17</sup>.

The dynamic-mechanical properties were measured for polyisoprene containing various levels of carbon black (Figures 5 and 6). As expected, the maxima of both the storage and loss moduli increase with carbon-black loading. At all concentrations of filler, the storage modulus is independent of strain amplitude when the latter is less than about  $10^{-4}$ . The high value associated with low strain amplitudes is maintained down through the lowest strains

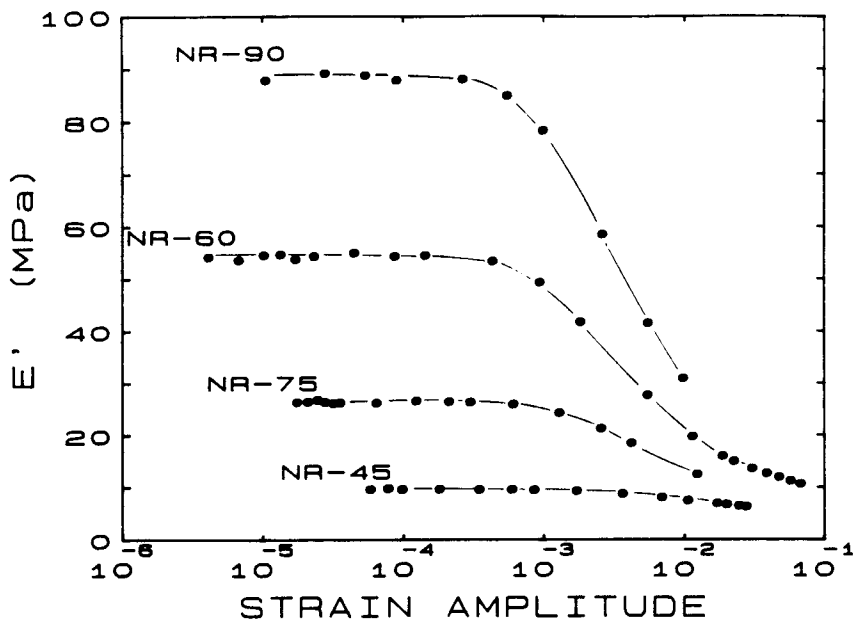


Fig. 5.—The strain dependence of the storage modulus measured (at 30°C and 0.1 Hertz) for natural rubber with various levels of N110 carbon black. It is seen that  $E'$  becomes invariant at low strain.

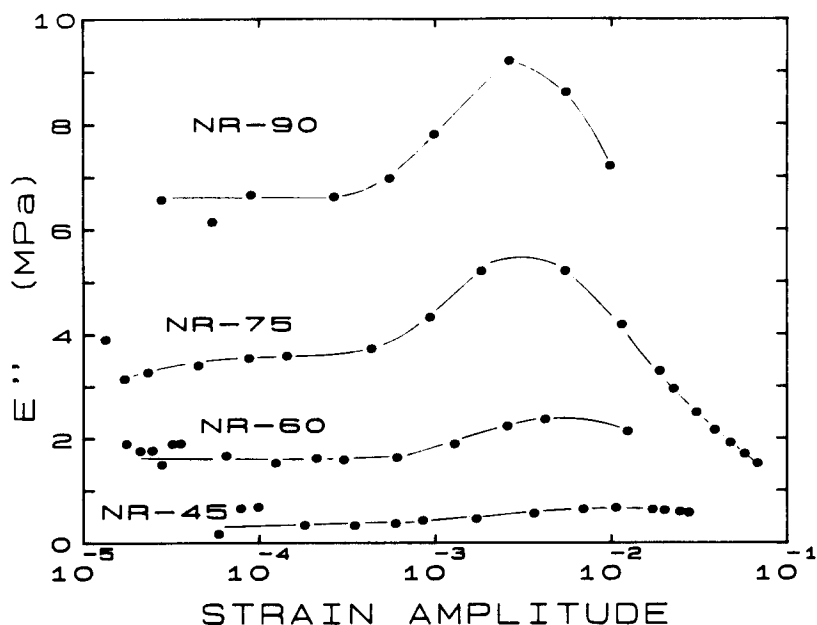


FIG. 6.—The loss modulus results corresponding to the data in Figure 5.

at which the measurements could be made (*circa*  $10^{-6}$ ). The loss modulus could be reliably measured only at strain amplitudes above about  $10^{-5}$  and was essentially constant prior to an increase at deformations approaching the level at which the storage modulus markedly decreases. This maximum is well established as reflecting the hysteresis arising from the breakup of the filler network<sup>16,17,27</sup>. The previously reported low strain maximum in the storage modulus and multiple maxima in the loss modulus are in fact nonexistent.

The mechanical results for the lowest strains in Figures 5 and 6 just approach the amplitude level typically experienced in rubber-damping applications. To corroborate an extrapolation of Figures 5 and 6 to lower strains, a direct comparison was made between dynamic properties measured mechanically and acoustically. Since the frequencies of these measurements could not be made identical, relative comparisons were made on a filled rubber (SBR-83) subjected to a progressively greater extent of mixing (designated as -0, -5, and -20 to signify the number of passes through a two-roll mill). This gave three compounds of increasing carbon-black dispersion. Except for the degree of mixing, the samples were identical. The acoustic properties are compared to the dynamic-mechanical results in Table II.

TABLE II  
ACOUSTIC AND MECHANICAL RESULTS FOR SBR-83

	Storage modulus, MPa		Loss modulus, MPa	
	Acoustic <sup>a</sup>	Mechanical <sup>b</sup>	Acoustic <sup>a</sup>	Mechanical <sup>b</sup>
SBR-83-0	35.5	26.7	6.7	3.70
SBR-83-5	32.6	22.1	6.8	3.31
SBR-83-20	30.6	15.0	5.2	2.67

<sup>a</sup> At 1 kHz, 30°C, and strains between  $10^{-9}$  and  $10^{-6}$ .

<sup>b</sup> At 40 Hz, 26°C, and a strain amplitude equal to  $10^{-4}$  (100 cycles averaged).

It is seen that while the higher frequency acoustic measurements give higher moduli, both sets of data indicate that the dynamic properties are directly influenced by the level of carbon-black dispersion. As the frequency is increased, the viscoelastic contribution increases relative to the more elastic filler effect. For this reason, the effect of carbon-black dispersion is relatively higher in the mechanical measurements. Of primary significance is that the very low strain acoustic response reflects the carbon-black network structure, consistent with Figures 5 and 6 and contradictory to earlier claims<sup>28-32</sup>.

The magnitude of the hysteresis at the lowest strains in Figure 6 exceeds that at strain amplitudes greater than  $10^{-2}$ . This indicates that a certain degree of energy dissipation is transpiring in the filler phase at strains insufficient for significant irreversible (during the time scale of a strain cycle) alteration of the filler phase. Rearrangement of the carbon-black morphology without changes in the dynamic modulus have in fact been observed in combined static and oscillatory deformation experiments<sup>34</sup>. These processes apparently leave the filler network intact, whereby the modulus is undiminished. A larger hysteresis can be obtained at low strain (demonstrated from Table II to be at least as low as  $10^{-9}$  in amplitude) by increasing the carbon-black flocculation. This appears to be a feasible method for the incorporation of additional acoustic-energy-dissipation mechanisms into rubber.

The dependence of the low strain storage and loss moduli at various temperatures approaching  $T_g$  is illustrated in Figure 7 for a blend of 1,2-BR with 25% NR and 75 phr filler (BR-75F). The contribution of the filler phase is maintained despite the approach of the rubber to glassy behavior. It was also observed that the qualitative dependence of  $E'$  on strain amplitude was comparable at the various temperatures. The breakup of the carbon-black network evidently occurs for all temperatures at essentially the same strain, implying that the conditions necessary for network disruption are essentially independent of the mechanical response of the polymeric phase. This has direct implications regarding the nature of the aggregate interactions<sup>17-21</sup>. As the temperature is lowered, the extent of inter-

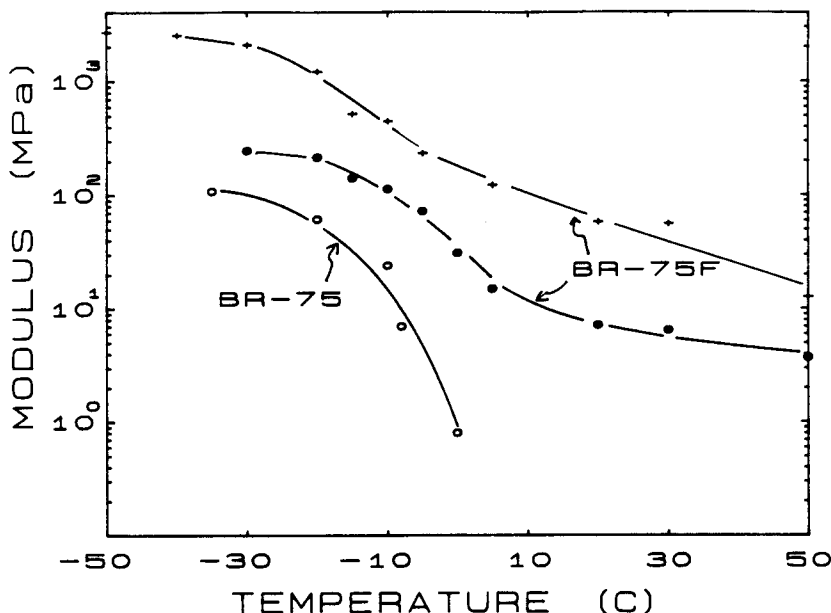


FIG. 7.—The storage (+) and loss (●) moduli for BR-75F at various temperatures. The increase in modulus as the temperature approaches that of the glass transition of the rubber phase is greater than that observed at strains ( $>10^{-3}$ ) for which the contribution of the filler to the mechanical behavior is reduced. As seen by comparison to the  $E'$  for sample BR-75 (○), as the temperature is reduced, there is continued augmentation of the hysteresis at low strain by the filler agglomeration.



aggregate contacts increases (as reflected in Figure 7 in the increasing storage and loss moduli); consequently, the effectiveness of a filled rubber for extensional damping would improve at lower temperatures. The fact that two effects are operative as the temperature is altered (*i.e.*, changes in both filler structure and polymer segmental mobility) implies that time-temperature superpositioning may not be accurate for carbon-black-reinforced rubber. Successful superpositioning of filled-rubber viscoelastic data has been reported<sup>34-36</sup>, and mastercurves for the BR-75F derived from the acoustic measurements are displayed in Figure 8. Nevertheless, the utility of such superpositioning in the prediction of damping variations with temperature and frequency must be regarded as questionable.

#### RECOVERY OF FILLER STRUCTURE

A highly flocculated carbon-black structure provides added hysteresis to a rubber; however, this feature necessarily confers, as well, a strain sensitivity to the damping performance. The breakup of the filler network at higher dynamic strain amplitudes attenuates the hysteresis. This breakup can also be effected by static strains. Decreases in the low strain storage modulus of filled rubber upon imposition of a moderately large static strain have been described<sup>34,37</sup>. The original magnitude of the storage modulus is recovered over time, in accord with a healing of the aggregate network<sup>20,28,34,37</sup>. This recovery transpires whether or not the original static strain has been removed. The loss modulus has been variously reported to decrease slightly<sup>37</sup> or to be unaffected<sup>34</sup> by superposed static strains. An invariance in the loss modulus would conflict with the data in Figure 6.

The dynamic properties of the SBR-83 series of rubbers with varying carbon-black dispersion were measured during the course of a stress-relaxation experiment. It was intended to determine: (1) if the time scale of the recovery of both the relaxation and the dynamic storage moduli were comparable (as indicated by earlier work<sup>37</sup>); (2) whether any change in the loss modulus accompanies the static straining; (3) the extent to which the initial association of the carbon-black aggregates influences the response of the rubber.

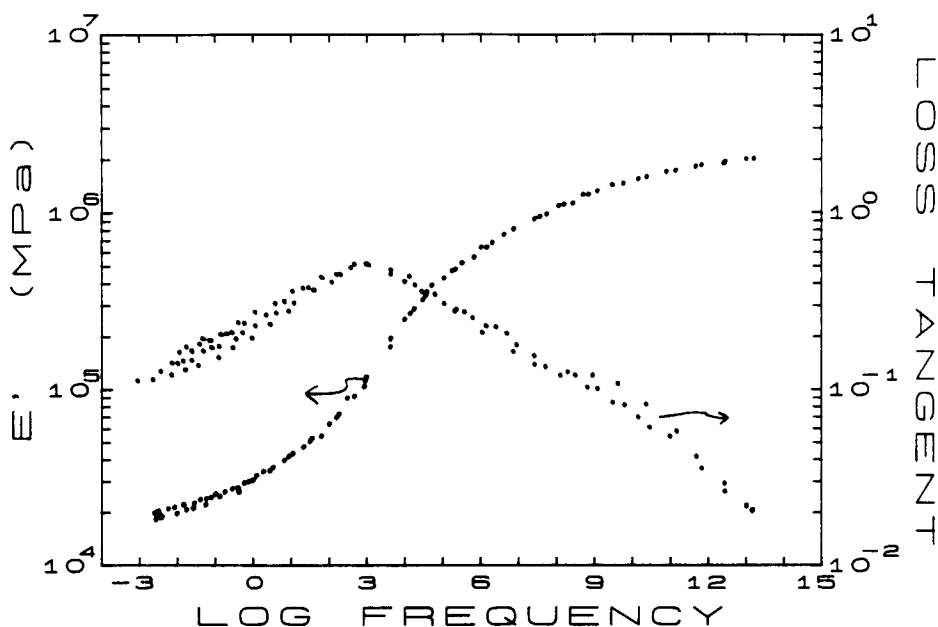


FIG. 8.—The superpositioned results for the acoustically measured storage modulus and loss tangent of BR-75F at a reference temperature of 15°C.

Displayed respectively in Figures 9 and 10 are the stress relaxation modulus and the dynamic storage modulus for the three rubbers measured after imposition of a static strain of 1.9%. The least mixed, and hence most agglomerated, stock (SBR-83-0) has the highest modulus, both transient and at equilibrium. This is expected, since the filler dominates at high loading. It is observed that the recovery of the storage modulus is transpiring at least as rapidly as measurements could be obtained (about 6 seconds after the static strain was imposed, which is more than an order of magnitude sooner than in any previous determinations). The kinetics of the relaxation and recovery were found to be insensitive to the initial extent of aggregate interaction. Repetition of these experiments at various temperatures within the rubbery regime confirmed that the response to a moderately large deformation proceeds independently of the nature of the carbon-black dispersion. This is consistent with determinations that time-temperature shift factors do not vary with carbon-black content, implying that while the filler network dominates the mechanical response, its recovery is controlled by configurational rearrangements of the polymer chains<sup>34</sup>. In all cases, the original value for the dynamic modulus was eventually recovered, as has previously been found for cured, but not for uncured, rubbers<sup>28,34,37</sup>.

The processes seen in Figures 9 and 10, as well as the recovery of the acoustic modulus after straining (data not shown), could be described, at least at long times, by a power-law relationship in time. The exponent [*i.e.*,  $d \log (E)/d \log (t)$ ] was significantly larger in absolute magnitude for the relaxation modulus than for the storage modulus. It appears that the recovery of the latter may transpire over a longer time scale. This suggests that the polymer segments have assumed their equilibrium configurations prior to complete healing of the filler network. Consistent with this is the extended time for complete recovery of the electrical resistivity after straining (Figure 11). The more agglomerated network experiences a smaller increase in resistivity after imposition and removal of a large (*circa* 10%) strain. The recovery for both SBR-83-0 and SBR-83-20 was longer than the terminal relaxation time inferred from stress-relaxation experiments. Unlike the recovery and relaxation of the modulus, there is

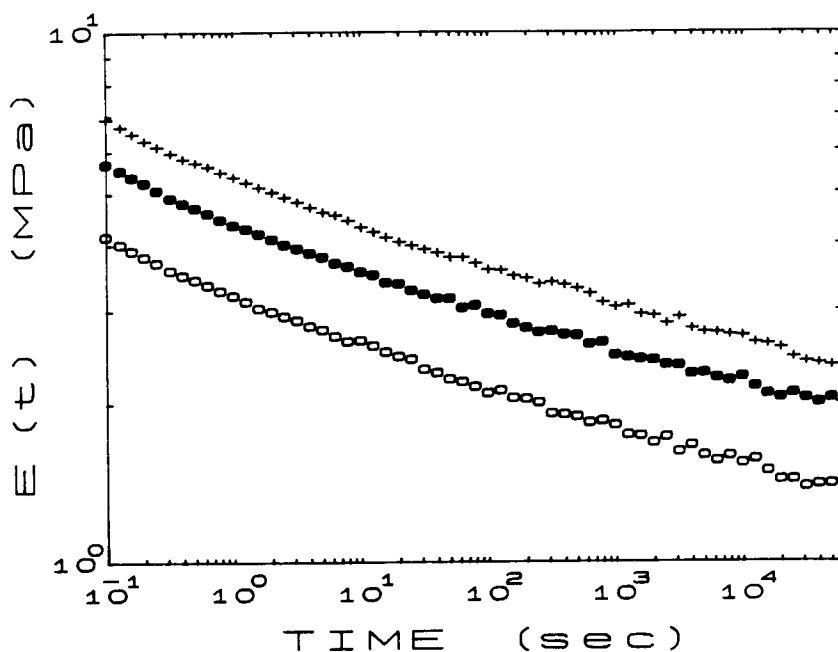


Fig. 9.—The change in the relaxation modulus after imposition of a 1.9% strain for SBR-83-0 (+), SBR-83-5 (●), and SBR-83-20 (○) at 25°C.

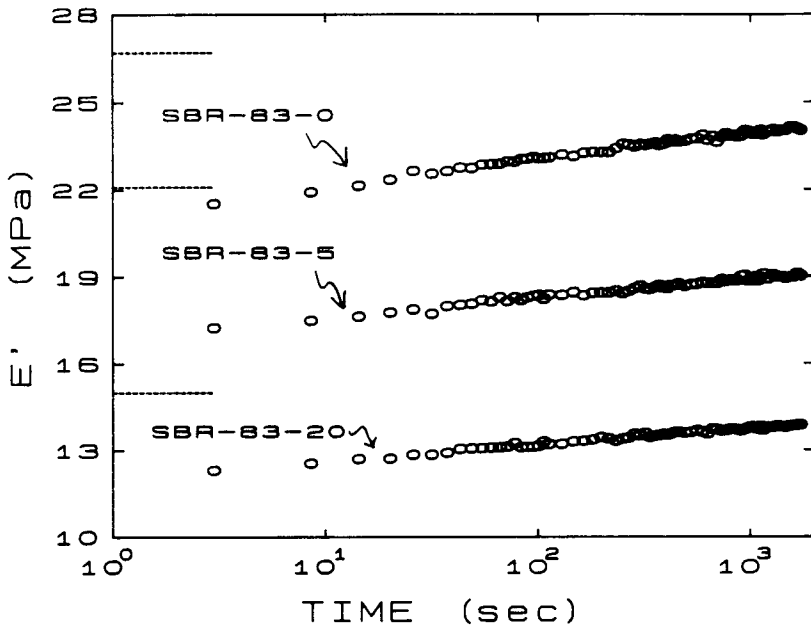


FIG. 10.—The recovery at 25°C of the low-strain storage modulus (40 Hz) after imposition of a static strain of 1.9% for the SBR-83 stock with varying degrees of carbon-black dispersion. The magnitude of  $E'$  after complete recovery (indicated by the dashed line) is equal to the value measured before the static deformation.

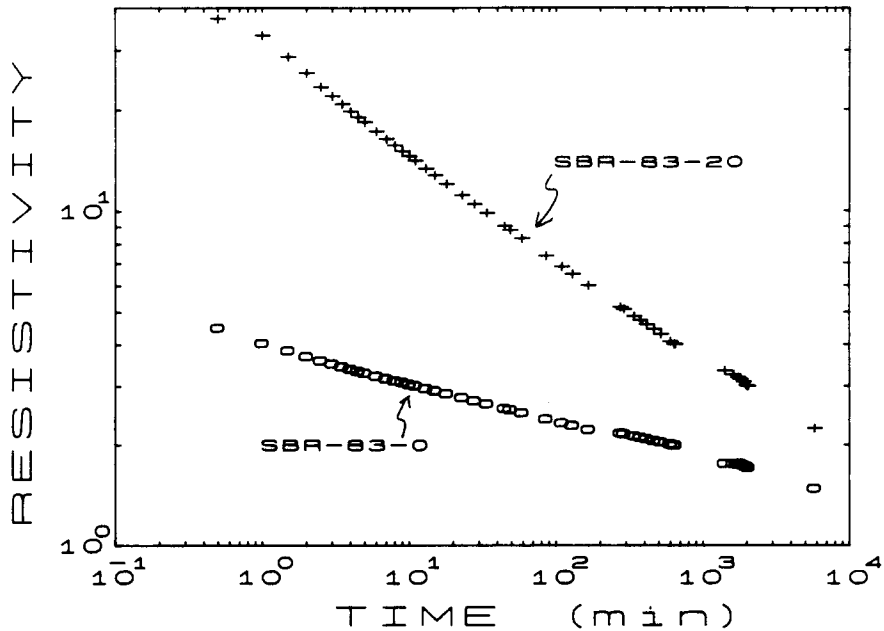


FIG. 11.—The electrical resistivity (divided by the initial value before deformation) after imposition and removal of a 10% tensile strain ( $T = 23^\circ\text{C}$ ). The sample with the more agglomerated network, SBR-83-0, was significantly more conductive (resistivity equal to 639 ohm-cm *versus* 23 700 ohm-cm for the SBR-83-20) and showed less relative sensitivity to deformation.

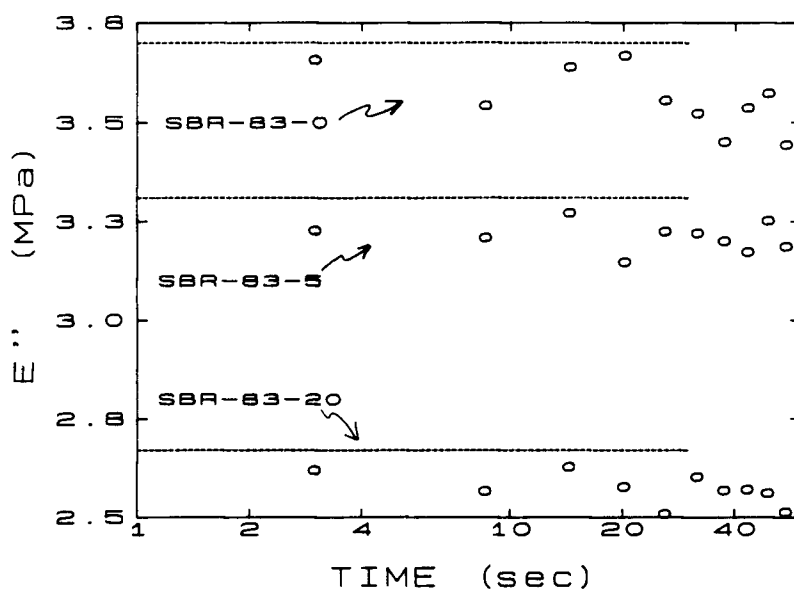


FIG. 12.—The initial recovery at 25°C of the low-strain loss modulus (40Hz) after imposition of a static strain of 1.9% for the SBR-83 stock with varying degrees of carbon-black dispersion. The original magnitude of  $E''$  (indicated by the dashed line) slightly exceeded the values measured after the static deformation.

some divergence between the rubbers of different carbon-black agglomeration with respect to recovery of their electrical conductivity.

For damping applications, the effect of deformation on the loss modulus is of primary concern. The out-of-phase component of the dynamic response is more difficult to measure, and consequently its response to a static deformation has been a point of contention<sup>34,37</sup>. Displayed in Figure 12 is a comparison to the initial (low strain) loss modulus with the values measured after a 1.9% static strain was imposed on the SBR-83 samples. For all degrees of carbon-black agglomeration, there is a slight decline in  $E''$  as a result of the deformation. The decrease is sufficiently small that it is not easily seen above the noise in these measurements. A similar effect was observed in analogous acoustic measurements of the dynamic properties upon static deformation. This reduction in hysteresis is expected, since the flocculated network has been disrupted by the moderately large static strain. For practical considerations, however, the loss of damping would be insignificant.

#### SUMMARY

Measurements of the dynamic properties of carbon-black-filled rubber can be carried out on most instrumentation at strains within the limits of linear behavior; thus, assessments of acoustic performance can readily be made. The equivalence of small-strain dynamic-mechanical testing and acoustic measurements has been demonstrated herein. Blends of NR with a high concentration of 1,2-BR are attractive candidates for damping applications because of the extended frequency range of the glass to rubber transition. One approach to improving the magnitude of the damping is to incorporate high levels of carbon black into the material. Significant interaggregate interaction, promoted for example by a low degree of carbon-black dispersion, will amplify the energy dissipation. The strain dependence of the dynamic properties implicit in such an approach can result in a damping performance sensitive to deformation. The loss tangent rises significantly after such a deformation, while the loss modulus experiences a barely measurable decline. This sensitivity to deformation will thus impact more on constrained layer damping applications than on simple extensional

damping. For the materials tested in the present study, complete recovery of the damage to the carbon-black network (which engenders the changes in dynamic mechanical properties) required more than a day at room temperature.

#### ACKNOWLEDGMENTS

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