

# High-Strain Hysteresis of Rubber Vulcanizates over a Range of Compositions, Rates, and Temperatures

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**ABSTRACT:** Hysteresis loss of natural rubber (NR) and styrene–butadiene rubber (SBR) vulcanizates having variations of loading of carbon black, silica, clay, resin, and curatives has been measured over a wide range of strain rates and temperatures as well as under swollen conditions. Hysteresis loss increases with an increase in strain rate, filler loading, resin loading (at high rates), crosslink density, and strain level. Hysteresis decreases with an increase in temperature, particle diameter of filler, and resin loading at high testing temperature. All the data of hysteresis loss of filled NR and SBR compounds have been found to be superimposable on single master curves with the help of the WLF shift factor. The master curves can be divided into three regions. The slope of the intermediate region,  $\Delta\log(\text{hysteresis})/\Delta\log(Ra_T)$  has been found to be 0.1 for almost all the vulcanizates. Similar master plots have been obtained when the hysteresis loss has been measured at higher cycles and higher extensions and also by using the data of the hysteresis loss ratio. The hysteresis loss ratio of all the vulcanizates follows a similar trend, except for the highly crosslinked system, which shows a lower value. Carbon black contributes significantly to the hysteresis loss even when the energy dissipation is minimized by swelling. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1429–1439, 1997

**Key words:** hysteresis loss; rubber; WLF equation; carbon black; natural rubber; styrene–butadiene rubber

## INTRODUCTION

Hysteresis of rubber, defined as the amount of energy dissipated during cyclic deformation, is an important topic of investigation. Hysteresis loss measured at low strain (<10%) using dynamic mechanical instruments at various frequencies and temperatures for natural rubber (NR) and styrene–butadiene rubber (SBR) vulcanizates has been reported by several authors.<sup>1–7</sup> The effect of carbon black and a few other compounding ingredients on the dynamic properties of rubber vulcanizates at low strain is well known. Caruthers,

Medalia, and Cohen<sup>8</sup> attributed several simultaneous processes as the cause of hysteresis loss in filled vulcanizates. Compared with the number of studies at low strain, investigations of hysteresis loss at high strain are few and far between. Notable work in this area has been done by Payne and Whittaker,<sup>9</sup> Harwood and Payne,<sup>10</sup> and Harwood et al.<sup>11–13</sup> The main thrust of their work was to correlate hysteresis loss at high strain with failure properties such as tensile strength and rubber fatigue. They studied the influence of carbon black filler on the hysteresis loss at break and energy input to break at different temperatures. Meinecke et al.<sup>14,15</sup> proposed that the hysteresis loss is proportional to the square of the strain amplification factor in extension or compression. It has been demonstrated that the mechanisms of

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**Table I** Formulation of Mixes

	Mix Number											
	A <sub>i</sub>	B <sub>i</sub>	C <sub>i</sub>	D <sub>i</sub>	E <sub>i</sub>	F <sub>i</sub>	G <sub>i</sub>	H <sub>i</sub>	I <sub>i</sub>	J <sub>i</sub>	K <sub>i</sub>	L <sub>i</sub>
NR	100	0	100	0	100	0	100	0	100	0	100	0
SBR	0	100	0	100	0	100	0	100	0	100	0	100
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TMQ	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
6PPD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ISAF black	A <sub>i=0-60</sub>	B <sub>i=0-60</sub>	40	40	40	40	40	0	0	0	0	0
Silica	0	0	0	0	0	0	0	0	20	20	0	0
Clay	0	0	0	0	0	0	0	0	0	0	20	20
Aromatic oil	5.0	5.0	5.0	5.0	5.0	5.0	0	0	0	0	0	0
Si-69	0	0	0	0	0	0	0	0	2.0	2.0	0	0
Resin	0	0	C <sub>i=0-20</sub> <sup>j=0-20</sup>	D <sub>i=0-20</sub> <sup>j=0-20</sup>	0	0	10	10	0	0	0	0
BSM	0.8	0.8	0.8	0.8	E <sub>i=1-4</sub>	F <sub>i=1-3</sub>	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2.5	2.5	2.5	2.5	E <sub>i=1-4</sub>	F <sub>i=1-3</sub>	2.5	2.5	2.5	2.5	2.5	2.5
PVI	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

A<sub>i=0-60</sub> : A<sub>0</sub>, A<sub>20</sub>, A<sub>40</sub>, A<sub>60</sub>, suffix indicates loading of filler.

B<sub>i=0-60</sub> : B<sub>0</sub>, B<sub>20</sub>, B<sub>40</sub>, B<sub>60</sub>, suffix indicates loading of filler.

C<sub>i=0-20</sub><sup>j=0-20</sup> : C<sub>0</sub><sup>0</sup>, C<sub>0</sub><sup>10</sup>, C<sub>0</sub><sup>20</sup>, C<sub>10</sub><sup>0</sup>, C<sub>10</sub><sup>10</sup>, C<sub>10</sub><sup>20</sup>, C<sub>20</sub><sup>0</sup>, C<sub>20</sub><sup>10</sup>, C<sub>20</sub><sup>20</sup>, i indicates loading of filler, and j indicates loading of resin.

D<sub>i=0-20</sub><sup>j=0-20</sup> : D<sub>0</sub><sup>0</sup>, D<sub>0</sub><sup>10</sup>, D<sub>0</sub><sup>20</sup>, D<sub>10</sub><sup>0</sup>, D<sub>10</sub><sup>10</sup>, D<sub>10</sub><sup>20</sup>, i indicates loading of filler, and j indicates loading of resin.

E<sub>i=1-4</sub> : E<sub>1</sub> (BSM/S = 0.8/2.5), E<sub>2</sub> (BSM/S = 1.5/1.5), E<sub>3</sub> (BSM/S = 1.0/1.0), E<sub>4</sub> (BSM/S = 3.0/3.0).

F<sub>i=1-3</sub> : F<sub>1</sub> (BSM/S = 0.8/2.5), F<sub>2</sub> (BSM/S = 1.5/1.5), F<sub>3</sub> (BSM/S = 1.0/1.0).

hysteresis loss of rubber vulcanizates at low and high strains are clearly different.<sup>6</sup>

The literature survey indicates that several questions on the hysteresis loss at high strain still remain unanswered. In many cases, hysteresis loss has been ascribed to the viscoelastic energy losses in a complex manner. However, there is no work to demonstrate whether the data of hysteresis loss at high strain obtained at different rates and temperatures are superimposable by any technique. What would be the effect of a number of ingredients added in rubber on the master curve of hysteresis loss, if there is any? This article attempts to answer these questions. The purpose of the present investigation is to understand the high strain hysteresis behavior of NR and SBR vulcanizates over a range of compositions, strain rates ( $1.9 \times 10^{-2} \text{ s}^{-1}$  to  $2.8 \times 10^{-1} \text{ s}^{-1}$ ), and temperatures (25–125°C). The variations in composition include nature and level of filler, resin, and vulcanization system.

## EXPERIMENTAL

The formulations of the various mixes are given in Table I. The nature of polymers (mixes A<sub>i</sub> to

L<sub>i</sub>), the loading of filler (mixes A<sub>i</sub> and B<sub>i</sub>), the nature of filler (mixes I<sub>i</sub>, J<sub>i</sub>, K<sub>i</sub> and L<sub>i</sub>), the loading of resin (mixes C<sub>i</sub> and D<sub>i</sub>), and the crosslink density (mixes E<sub>i</sub>, F<sub>i</sub>, G<sub>i</sub> and H<sub>i</sub>) were varied.

Natural rubber (RMA-4), SBR-1502, stearic acid, Si-69 (Degussa, AG), silica, and aromatic oil were supplied by Birla Tyres, Ltd., Balasore. ISAF (N220) was supplied by Phillips Carbon Black, Ltd., Durgapur. Zinc oxide was obtained from the local market. High styrene resin and sulfur were supplied by Bengal Waterproof, Ltd., Panihati. Polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (TMQ), *N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine (6-PPD), *N*-cyclohexyl thiophthalimide (PVI), and 2-(4-morpholinyl mercapto)benzthiazole sulphenamide (BSM) were supplied by ICI, Ltd., Rishra.

### Mixing

The ingredients were mixed with rubber on a two-roll mill (0.15 m × 0.33 m, Schwabenthan, Germany) at a temperature of 50°C and a friction ratio 1 : 1.1.

### Curing

The curing characteristics of the mixes were evaluated from a Rheometer R-100 according to ASTM

D-2084-81. The molding of the tensile sheets was carried out at a temperature of 150°C, 4 MPa pressure, and at an optimum cure time ( $t_{90}$ ) using David Bridge Press, Castleton, Rocchdale, England.

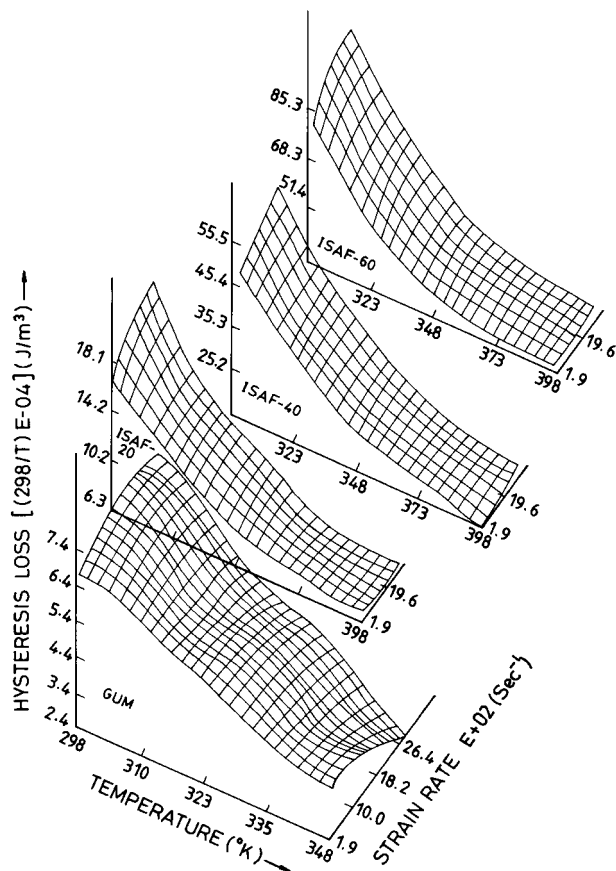
### Measurements

**Hysteresis.** Hysteresis loss was determined on the tensile dumbbells (ASTM D-412-80) over a range of temperatures (25–125°C) and strain rates ( $1.9 \times 10^{-2} \text{ s}^{-1}$  to  $2.8 \times 10^{-1} \text{ s}^{-1}$ ) and extensions (50 to 300%), using Zwick Universal Testing machine 1445 equipped with an environmental chamber. The samples were mounted in mechanical clamps 44 mm apart, and the crosshead was adjusted to give zero tension. The temperature was controlled to  $\pm 0.5^\circ\text{C}$ . The samples were preconditioned in the Zwick heating chamber for 10 min before testing. For the purpose of obtaining hysteresis energy loss continuously, the stress–strain curves were recorded on tape and fed into the attached computer. The measurements were continued up to eight cycles. The hysteresis ratio ( $Hy$ )<sub>r</sub>, which is defined as the energy dissipated relative to the energy supplied in stretching, was determined from the areas  $w_1$  (work done during extension) and  $w_2$  (work done during retraction) when the specimens were stretched to varying extents and rates of elongation and then allowed to retract at the same rate to the unstretched state.

$$(Hy)_r = (w_1 - w_2)/w_1 \quad (1)$$

**Glass Transition Temperature.** The glass transition temperature and  $\tan \delta$  of rubber vulcanizates were measured using a Dynamic Mechanical Thermal Analyzer (DMTA, Rheometric Scientific, MK-II) over a range of frequencies (0.01 to 100 Hz), temperatures ( $-100$ – $150^\circ\text{C}$ ), and a peak-to-peak displacement of  $4 \times 64 \mu\text{m}$  with a heating rate of  $2^\circ\text{C}/\text{min}$  under shear mode.

**Swelling.** A few samples were swollen in paraffin oil and xylene up to seven days for equilibrium swelling at room temperature. The samples for hysteresis testing were cut from the unswollen and swollen vulcanizates by using a type-2 die (ASTM D412).

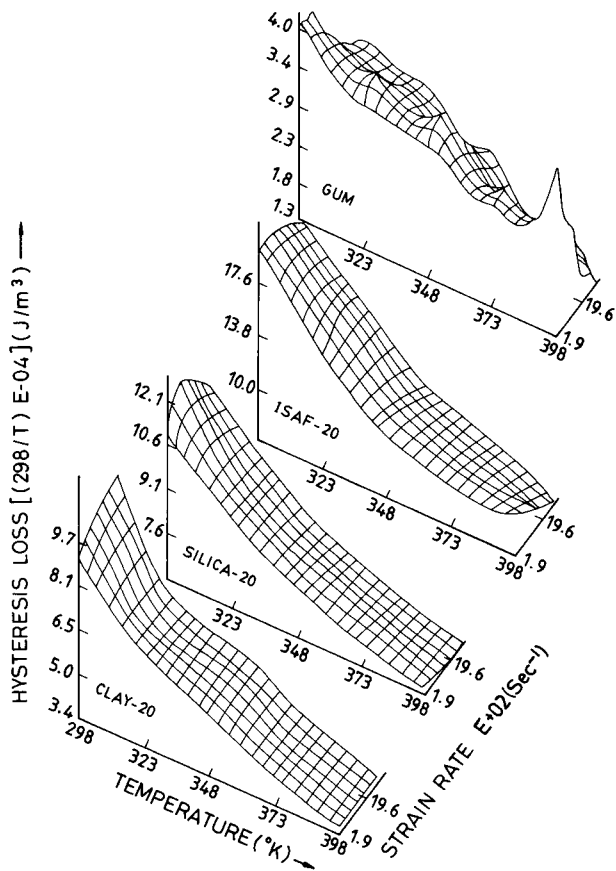


**Figure 1** Three-dimensional plots of hysteresis loss at 100% strain against temperature and strain rate for SBR vulcanizates having variations of filler loading.

## RESULTS AND DISCUSSION

### Hysteresis Over a Range of Rates and Temperatures

Measurement of hysteresis was carried out over a wide range of strain rates ( $1.9 \times 10^{-2} \text{ s}^{-1}$  to  $2.8 \times 10^{-1} \text{ s}^{-1}$ ) and temperatures (25–125°C) for all the NR and the SBR vulcanizates. The hysteresis loss data have been multiplied by  $298/T$  to take into account the change of modulus caused by change in temperature ( $T$ ).<sup>9</sup> Representative plots of hysteresis loss of the first cycle at 100% strain versus temperature and strain rate of the SBR vulcanizates—gum and filled with 20, 40, and 60 phr carbon black; of the NR vulcanizates filled with 20 phr carbon black, silica, and clay; of the NR vulcanizates blended with resin; and of the black-filled NR vulcanizates crosslinked to varying degrees are shown in Figures 1–4. Most of these plots show expected behavior of the depen-

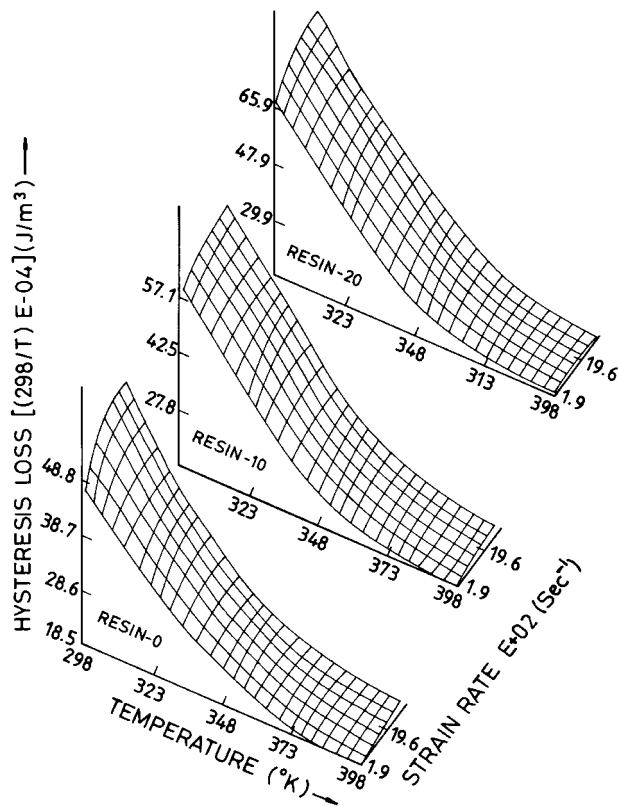


**Figure 2** Three-dimensional plots of hysteresis loss at 100% strain against temperature and strain rate for NR vulcanizates having various types of filler.

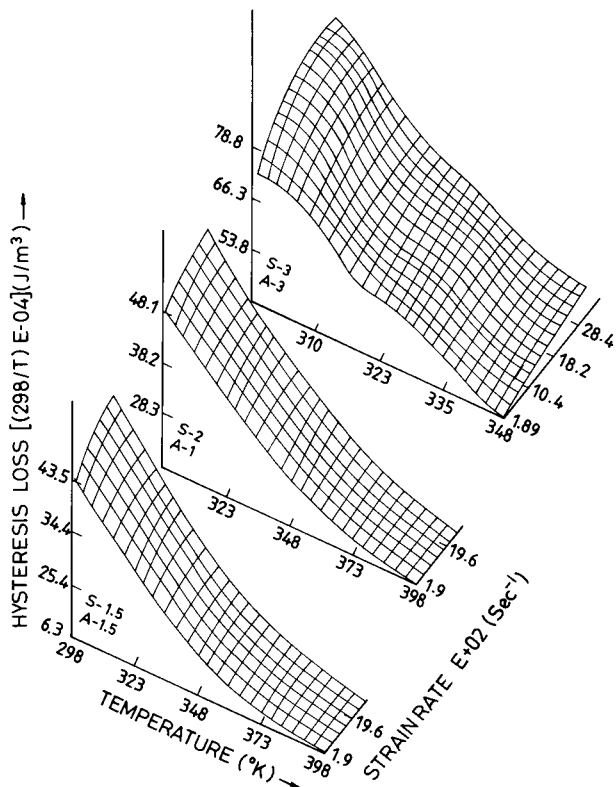
dence of hysteresis loss on rates and temperatures (i.e., the hysteresis decreases with an increase in temperature and with a decrease in strain rate). With the increased loading of carbon black filler, the hysteresis increases. For example, at a temperature of 25°C and strain rate of  $1.9 \times 10^{-2} \text{ s}^{-1}$ , the hysteresis loss of NR increases by about 5 fold, 11 fold, and 25 fold on additions of 20 phr, 40 phr, and 60 phr ISAF filler respectively. Two-, six- and ten-folds increases are observed for the corresponding SBR vulcanizates. Raising the temperature from 25 to 125°C decreases the hysteresis loss of these filled vulcanizates by about 2 to 3 times. It was shown that the hysteresis of NR is lower than that obtained for the amorphous rubber at the same energy input at break between 80 and 140°C.<sup>11</sup> It is, however, interesting to note that there is no abnormal behavior over the temperatures and strain rates studied in the case of filled NR and SBR vulcanizates, although anoma-

lous behavior is observed with NR-gum compounds.

The increased loss at low temperatures and high rates occurs because the gum and the filled rubbers are viscoelastic materials and show pronounced energy dissipation under these conditions.<sup>3</sup> As the temperature is increased, the segmental mobility of the chain is increased, and the viscosity is decreased. As a result, less energy is dissipated. Hysteresis loss of carbon black filled rubbers, shown in Figures 1–4, may be attributed to (1) molecular frictions accompanying deformation of the gum phase, (2) polymer–filler detachment, and (3) breakdown of filler structure and weak rubber chains. At very low strain under dynamic conditions, it has also been proposed that filler–filler bonding may take place.<sup>8</sup> All these processes are rate, temperature, and strain dependent. Similarly, hysteresis loss of resin-filled systems, shown in Figure 3, may be attributed to molecular frictions in the gum phase along with the breakdown of loose network, filler–rubber, and filler–filler bonds and slippage of resin–rub-



**Figure 3** Three-dimensional plots of hysteresis loss at 100% strain against temperature and strain rate for NR vulcanizates having variations of resin loading.



**Figure 4** Three-dimensional plots of hysteresis loss at 100% strain against temperature and strain rate for NR vulcanizates having variations of crosslink density.

ber bonds. Again, these processes are rate and temperature dependent. The data of hysteresis loss ratio, when plotted against rates and temperatures (not shown here) are in accord with the above results.

The most important observation in this investigation is that the change of energy loss with temperature and rate follows a systematic trend even in the case of highly filled strain-crystallizing rubbers. Natural rubber gum compound shows deviation perhaps because of the different rates of strain crystallization at different temperatures and rates. Though these processes have been shown above to be rate and temperature dependent, a question remains now about the nature of the dependence. In other words, how can these changes be quantified, especially in the case of filled vulcanizates?

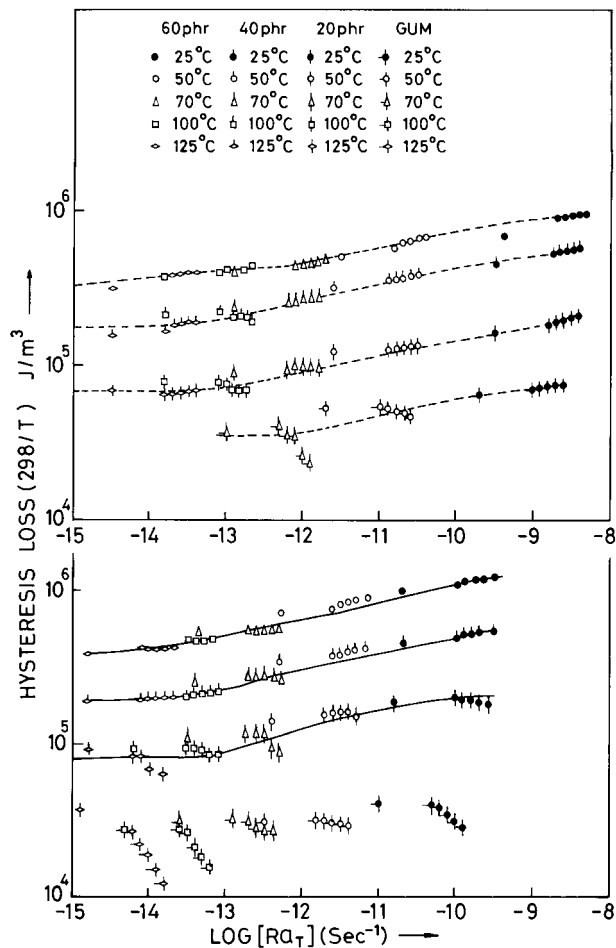
**Master Curves of Hysteresis Loss**

The data obtained at different rates and temperatures, as discussed in the earlier section, are plot-

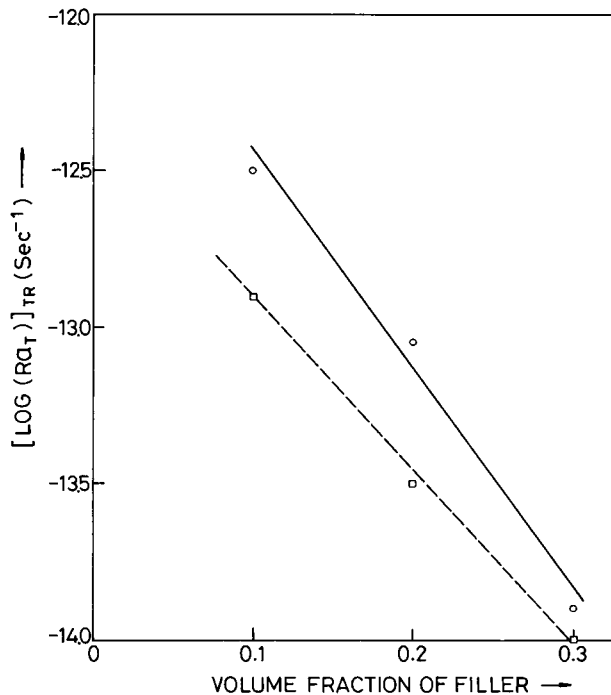
ted against the reduced rates in Figures 5–9. The reduction factor  $a_T$  used to transform the results corresponds to the universal form of the WLF rate temperature equivalence relation<sup>3</sup> as follows:

$$\log a_T = \frac{-17.5(T - T_g)}{52 + T - T_g} \quad (2)$$

where  $T$  is the temperature of the measurement and  $T_g$  is the glass transition temperature obtained from the  $\tan \delta$  plot of the dynamic mechanical thermal analysis. Glass transition temperature values are given in Table II. Figures 5–9 show that the data points at different temperatures and rates superpose to form a single master curve for each system. The gum and the 10 phr



**Figure 5** Data of hysteresis loss at 100% strain at various rates and temperatures replotted against reduced strain rate at a reference glass transition temperature of NR vulcanizates (—) and SBR vulcanizates (— —), using universal WLF shift factor.



**Figure 6** Effect of volume fraction of filler on the onset of the intermediate zone of NR vulcanizates (○) and SBR vulcanizates (□) from Figure 5.

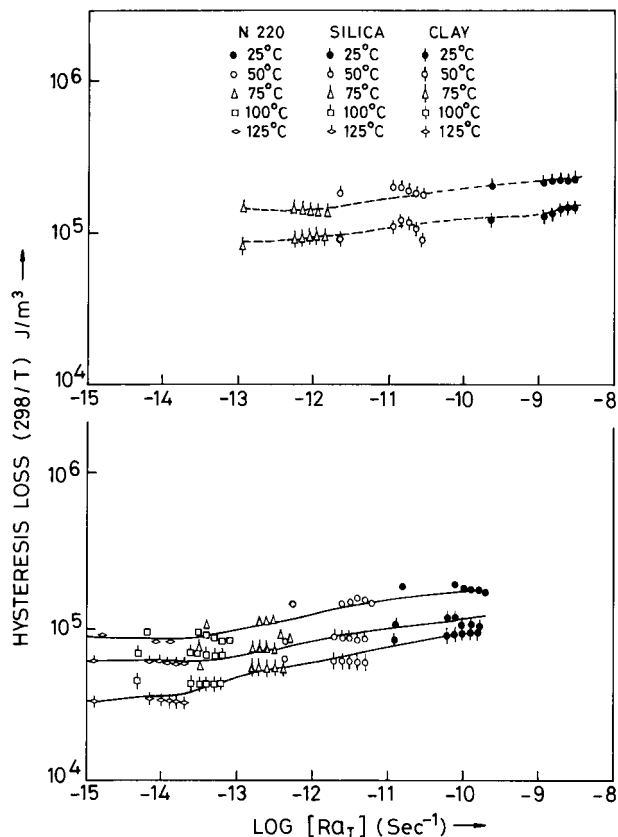
resin-filled NR vulcanizates are exceptions. Otherwise, the hysteresis is the same for all the elastomers filled with various loadings of filler under the conditions of equal segmental mobility. As far as we are aware, this is the first report of this behavior at high strain on such filled polymers. The hysteresis increases with reduced rates for all the elastomers. The master curves shift upward on the hysteresis axis with an increase of filler loading. At equal loading of 20 phr filler, N220-filled vulcanizate shows higher hysteresis loss than the silica- and clay-filled vulcanizates over the whole range of reduced rates (Fig. 7).

Hysteresis loss master curves can be divided into three regions: a low-rate region, where the hysteresis does not change with reduced rate and approaches a limiting value; an intermediate-rate region, where the changes in hysteresis values with rates are quite significant; and a high-rate region, where the hysteresis values marginally increase with rates. In all the regions, the hysteresis increases with the increase in carbon black loading for both the NR and the SBR vulcanizates, as shown in Figure 5. In the low-to-intermediate regions, when the data are plotted against the reduced rate on a semilogarithmic plot, a transi-

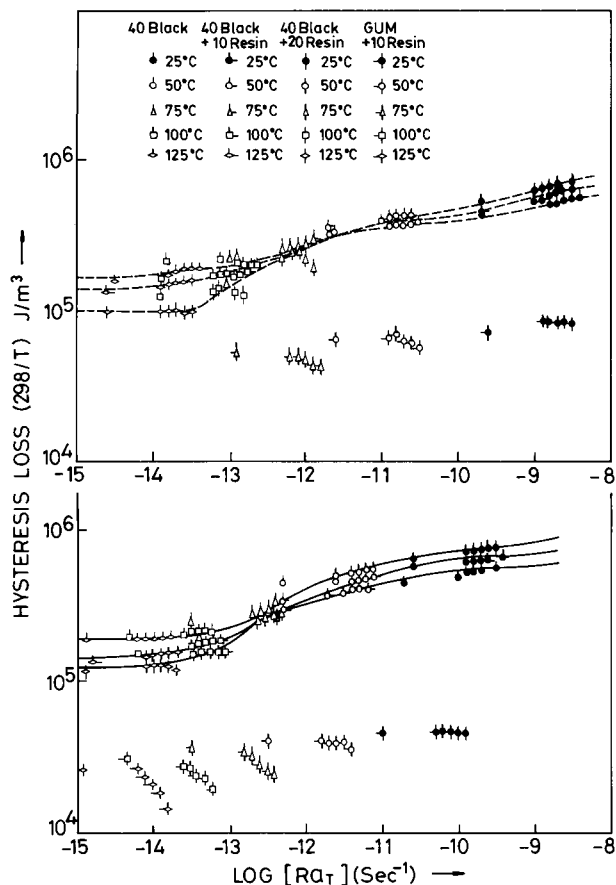
tion at a distinct rate is observed that is possibly caused by a change in the mechanism of hysteresis loss. As shown in Figure 6, this transition rate decreases as the loading of the carbon black is increased. This rate is also higher for the natural rubber vulcanizates.

In the low-rate region, an increase in resin loading decreases the hysteresis loss (Fig. 8). The hysteresis loss values at the transition region are almost similar for resin-filled systems, and there is a crossover with the data points of the control system. At higher rates, however, the hysteresis loss increases with the resin loading. Under low strain condition, Aubrey<sup>16</sup> made similar observations on unvulcanized NR blends with a 67-phr resin system.

The most obvious effects of resin loading are (1) displacement of the intermediate region toward lower reduced rates and (2) a reduction in the width of the plateau region in the intermediate zone. These effects may be interpreted in molecular terms as a restriction of the segmental motion,



**Figure 7** Master curves of hysteresis loss at 100% strain versus reduced strain rate at a reference glass transition temperature of NR vulcanizates (—) and SBR vulcanizates (---) having various types of filler.



**Figure 8** Master curves of hysteresis loss at 100% strain versus reduced strain rate at a reference glass transition temperature of filled NR vulcanizates (—) and SBR filled vulcanizates (— —) having variation of loading of resin.

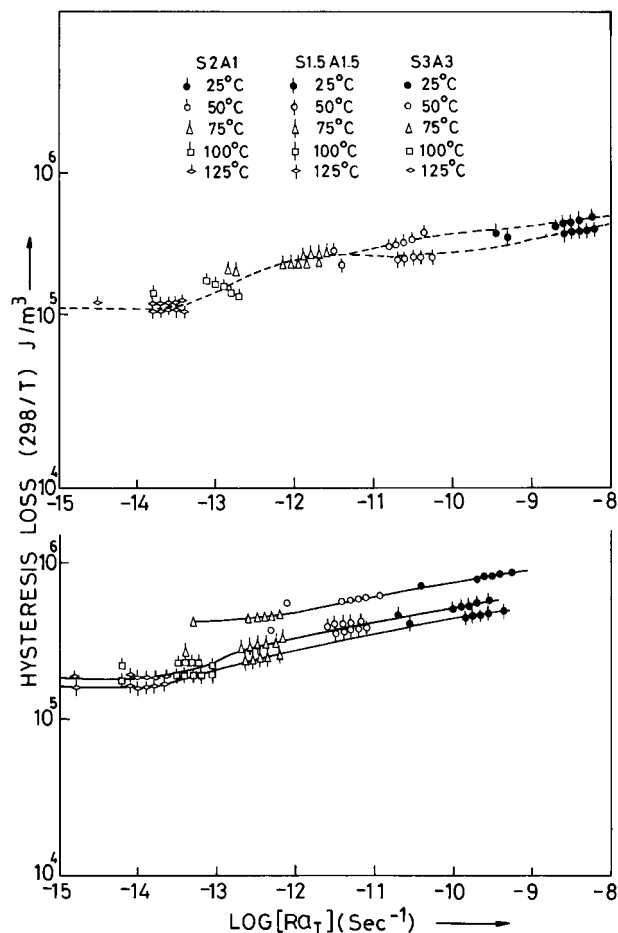
resulting in reduced fractional free volume and an increased monomeric friction coefficient. In the low-rate and high-temperature region, a decrease in hysteresis loss, as compared with the control sample, is observed with the resin-filled systems. To explain this, the melting point of the resin has been checked with dynamic mechanical thermal analysis and found to be 56°C. The log-reduced rate corresponding to this value is -12.2. Hence, below a value of the (reduced rate) of -12.2, the hysteresis loss is decreased owing to melting of the resin.

With increasing sulfur and curatives, the hysteresis loss increases, especially at high rates. This surprising result will be explained in the next section.

It is also interesting to note that the slope of the plot in the intermediate region  $\Delta \log [(Hysteresis) / \Delta \log (Ra_T)]$  is always found to be 0.1, ex-

cepting the system with the highly filled resin. This finding is independent of the composition and true for the range of hysteresis loss values over which the present data fall. This clearly indicates that the physical mechanism of the hysteresis loss for the systems studied here is almost the same. It was observed by Gent and Lai<sup>17</sup> that the slope over the central region was 0.3 when the tear strength was plotted against the reduced rate and was 0.6 in the plot of dynamic shear modulus versus effective frequency of oscillation. These findings are probably related to the characteristic dimension for the dissipative region, which are different in different measurements. Further studies are in progress in this laboratory to unravel this phenomenon.

Data of hysteresis loss ratio, defined in eq. (1),



**Figure 9** Master curves of hysteresis loss at 100% strain versus reduced strain rate at a reference glass transition temperature of filled NR vulcanizates (—) and SBR filled vulcanizates (— —) at different cross-link densities.

**Table II** Glass Transition Temperatures of Mixes A<sub>i</sub> to L<sub>i</sub> Obtained from DMTA

Mix Number	$T_g$ (°C)
A <sub>0</sub>	-34
A <sub>20</sub>	-31
A <sub>40</sub>	-30
A <sub>60</sub>	-30
B <sub>0</sub>	-19
B <sub>20</sub>	-17
B <sub>40</sub>	-17
B <sub>60</sub>	-16
C <sub>0</sub> <sup>0</sup>	-34
C <sub>0</sub> <sup>10</sup>	-33
C <sub>40</sub> <sup>0</sup>	-30
C <sub>40</sub> <sup>10</sup>	-29
C <sub>40</sub> <sup>20</sup>	-29
D <sub>0</sub> <sup>0</sup>	-19
D <sub>0</sub> <sup>10</sup>	-18
D <sub>40</sub> <sup>0</sup>	-17
D <sub>40</sub> <sup>10</sup>	-19
D <sub>40</sub> <sup>20</sup>	-19
E <sub>1</sub>	-30
E <sub>2</sub>	-30
E <sub>3</sub>	-28
E <sub>4</sub>	-26
F <sub>1</sub>	-17
F <sub>2</sub>	-15
F <sub>3</sub>	-16
G <sub>i</sub>	-29
H <sub>i</sub>	-19
I <sub>i</sub>	-32
J <sub>i</sub>	-18
K <sub>i</sub>	-32
L <sub>i</sub>	-18

have been plotted against reduced rate for representative samples of NR and SBR vulcanizates in Figure 10. It is observed that the trend with respect to filler loading remains the same. The filled vulcanizate always show higher hysteresis loss ratio than the gum vulcanizates. However, the system having high sulfur accelerator shows a reverse trend (i.e., the hysteresis loss ratio decreases with increases in sulfur and accelerator) because the work done during extension is higher (cf. 37% higher at 25°C and at a strain rate of  $1.9 \times 10^{-2} \text{ s}^{-1}$ ) than the lower-crosslinked system.

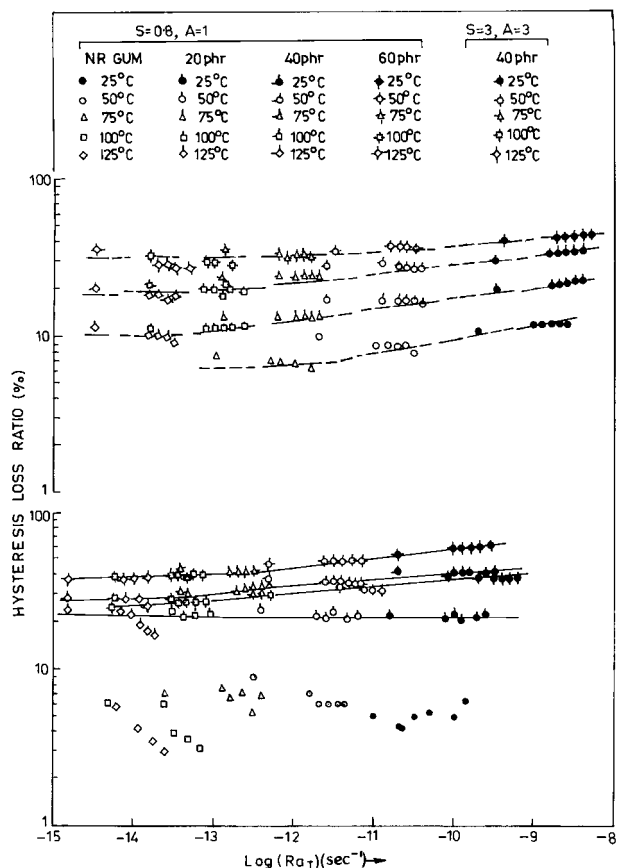
### Hysteresis at Different Strains

The hysteresis loss results discussed in earlier sections were obtained at 100% strain. To understand the hysteresis loss over a range of strains,

experiments were carried out at 200 and 300% strains over a range of strain rates ( $1.9 \times 10^{-2} \text{ s}^{-1}$  to  $2.8 \times 10^{-1} \text{ s}^{-1}$ ) and temperatures 25 to 125°C. The data for the SBR and the NR vulcanizates filled with 60 phr black are plotted on a master curve shown in Figure 11. At high strains, the hysteresis loss is more, as expected, owing to greater breakdown of filler–filler and rubber–filler bonds and higher energy dissipation. It is interesting to note that the hysteresis loss increases with increasing reduced rates even at high strains and follows the same trend. The slope of the plot of log (hysteresis) versus log (reduced rate) in the intermediate region remains the same [i.e., 0.1, and is independent of the extent of extension (from 100–300%)].

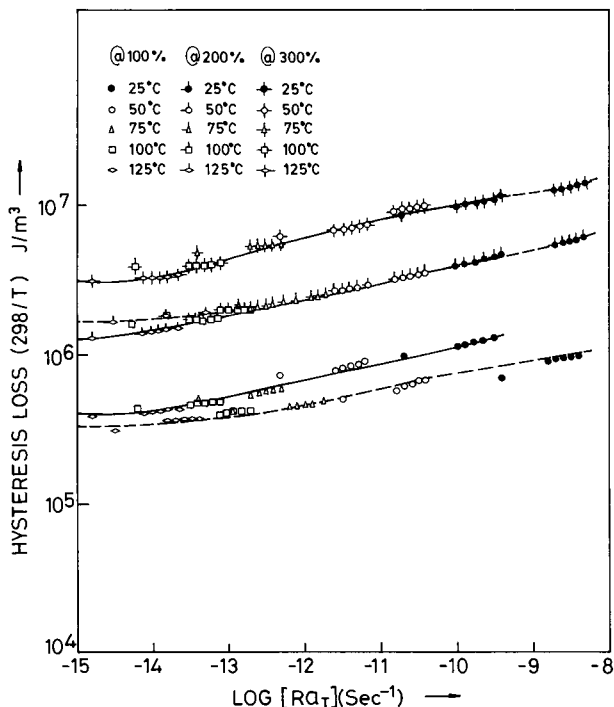
### Hysteresis Versus Number of Cycles

Hysteresis loss of all the samples was measured over a number of cycles to investigate their behav-



**Figure 10** Master curves of hysteresis loss ratio at 100% strain versus reduced strain rate at a reference glass transition temperature of NR (—) and (— —) SBR vulcanizates at different loadings of filler and crosslinking densities.



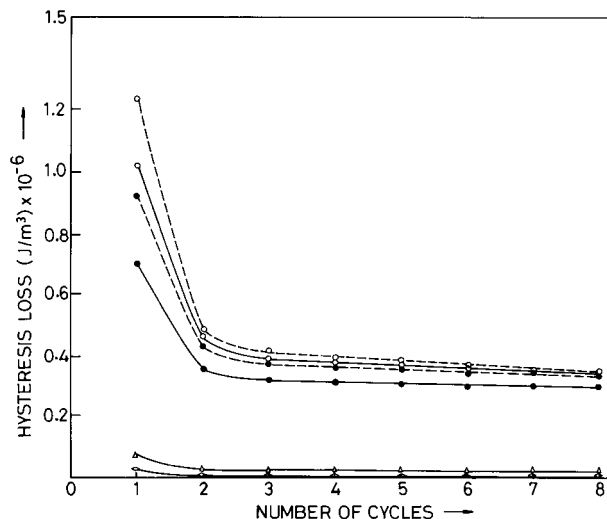


**Figure 11** Master curves of hysteresis loss versus reduced strain rate at a reference glass transition temperature of 60-phr ISAF filled NR vulcanizates (—) and 60-phr ISAF filled SBR vulcanizates (— —) at different strain levels (100, 200, and 300%).

ior. As shown in Figure 12, the hysteresis loss decreases drastically in the second cycle and attains a plateau value at the fourth cycle. The change is insignificant after this. The loss is more at higher loadings or at higher rates of testing, as expected. It may be mentioned here that similar master curves (not shown here) may be drawn using the hysteresis loss values obtained from fourth to eighth cycles. The cumulative hysteresis loss of SBR having various loadings of carbon black and tested at different temperatures is plotted against time (proportional to the number of cycles) in Figure 13. The loss increases linearly with time. With increased loading of black, the slope of these lines increases owing to the increased energy dissipation. At higher temperature, the slope decreases. These slopes,  $k$ , when plotted against  $1/T$ , yield the following equation:

$$\ln k = \ln A + (\Delta E/T) \quad (3)$$

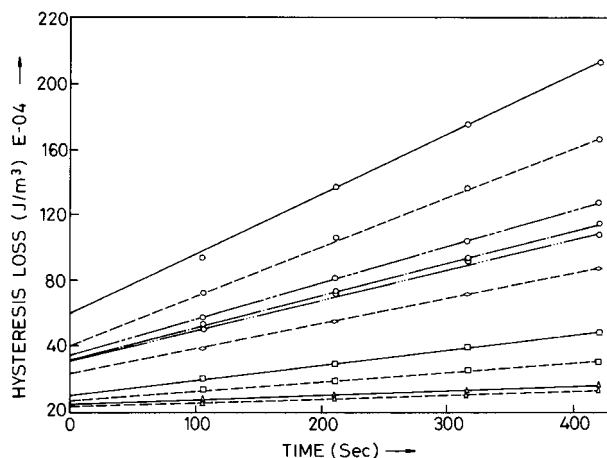
The value of  $\Delta E$  is  $0.07-0.08 \text{ J m}^{-3} \text{ s}^{-1} \text{ K}^{-1}$  and is independent of the loading of filler.



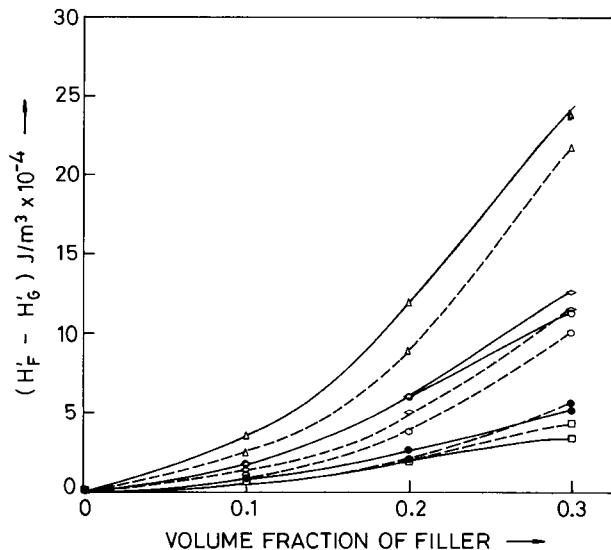
**Figure 12** Effect of number of cycles on hysteresis loss at 100% strain of 60-phr ISAF-filled SBR (○), 60-phr ISAF-filled NR (●), NR-gum (◇), and SBR-gum (△) at a strain rate of  $1.9 \times 10^{-2} \text{ s}^{-1}$  (—) and  $2.84 \times 10^{-1} \text{ s}^{-1}$  (— —).

### Hysteresis Loss Under Minimum Energy Dissipation

As discussed earlier, the hysteresis loss arises for several reasons, including the viscoelasticity in the rubber matrix as well as breakdown of rubber-filler and filler-filler bonds. The contribution of viscoelasticity of the rubber could easily be lowered by swelling the samples in good solvents. Fig-



**Figure 13** Effect of time on hysteresis loss at 100% strain of 60-phr ISAF-filled SBR (○), 40-phr ISAF-filled SBR (◇), 20-phr ISAF-filled SBR (□), and gum (△) vulcanizates at a strain rate of  $2.8 \times 10^{-1} \text{ s}^{-1}$  at different temperatures (— 25°C, --- 50°C, - - - 75°C, - · - 100°C, and - · · - 125°C).



**Figure 14** Effect of volume fraction of filler on the difference of hysteresis loss (filled-gum) at 50% strain of NR vulcanizates (—) and SBR vulcanizates (----) under different experimental conditions. [ $\Delta$ , unswollen of first cycle; ( $\diamond$ ) unswollen of fourth cycle; ( $\circ$ ), first-fourth cycles unswollen; ( $\bullet$ ), first-fourth cycles swollen in paraffin liquid, and ( $\square$ ), first-fourth cycles swollen in xylene].

ure 14 shows the hysteresis loss values (first cycle, fourth cycle) of the unswollen samples and of the samples swollen with paraffin oil and xylene versus volume fraction of fillers. The difference between first- and fourth-cycle values increases with increasing loading of filler. With swelling, the difference also increases with filler loading. The maximum difference in hysteresis values ( $H_{1\text{st cycle}} - H_{4\text{th cycle}}$ ) for 0.3 volume fraction of filler of the xylene-swollen NR vulcanizate is  $3 \times 10^4 \text{ J/m}^3$ , whereas the difference in hysteresis values for the unswollen sample is  $11 \times 10^4 \text{ J/m}^3$ , which is a four-fold increase in the absence of swelling. SBR and NR vulcanizates show comparable values. It can be concluded from these results that most of the hysteresis loss arises owing to the viscoelastic contribution from the rubber matrix and that the values are greater when the samples are modified with carbon blacks. It is, however, interesting to note that carbon black contributes to the hysteresis loss even when an attempt has been made to minimize the energy loss. The possible mechanism for this may be breaking of the filler–filler bonds as well as detachment of weak rubber–filler bonds.<sup>18</sup>

## CONCLUSIONS

The aim of this research has been to understand the hysteresis behavior of NR and SBR vulcanizates over a range of compositions, strain rates ( $1.9 \times 10^{-2} \text{ s}^{-1}$  to  $2.8 \times 10^{-1} \text{ s}^{-1}$ ), and temperatures (25–125°C) and under swollen conditions. The following conclusions have been reached:

1. Hysteresis loss increases with an increase in strain rate, filler loading, resin loading at high testing rates, and strain level.
2. Hysteresis decreases with an increase in temperature, particle diameter of filler, resin loading at high testing temperature, and swelling in xylene and paraffin liquid.
3. Hysteresis loss data of unswollen vulcanizates can be superimposed onto a single master curve by using the WLF reduced variables technique.
4. The master curves consist of three regions: a low-rate region, where the hysteresis does not change with reduced rate and approaches a limiting value; an intermediate-rate region, where the changes in hysteresis loss are quite significant; and at high-rate region, where the hysteresis value marginally increases with rates.
5. The slope of the intermediate region  $\Delta \log(\text{hysteresis})/\Delta \log(\text{reduced rate})$  has been found to be 0.1 for almost all the vulcanizates.
6. The onset of the intermediate region is shifted to a lower reduced strain rate with an increase of volume fraction of filler or resin content in the filled NR and SBR vulcanizates.
7. Similar master curves can be obtained at higher strains and higher cycles and also by using data of hysteresis loss ratio.
8. Carbon black contributes significantly to the hysteresis loss even when the samples are swollen in xylene and paraffin oil.

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