

## Restricted Equilibrium Swelling—A True Measure of Adhesion Between Short Fibers and Rubber

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### Synopsis

The adhesion between rubber and short glass or asbestos fibers has been studied using restricted equilibrium swelling measurements. It has been demonstrated that with improved adhesion between short fiber and rubber,

$$V_r = \left( \frac{V_I - V_F}{V_I} \right)$$

decreases by more than 0.04 units, where  $V_I$  and  $V_F$  respectively are the volume fractions of rubber in the dry and swollen samples. Goodrich compression fatigue and tensile measurements have been used to substantiate the adhesion-promoting role of bonding agents. The preferential role of silica over black as an adhesion promoter has been questioned. The effect of fiber orientation in controlling the anisotropy of restricted swelling has also been demonstrated.

### INTRODUCTION

Resorcinol-formaldehyde and their derivatives have been used<sup>1-3</sup> in the rubber industry for promoting adhesion between fibers (cords) and rubber for a long time. Hundreds of U.S. and foreign patents<sup>1</sup> have been issued on the use of resinous reaction products of disubstituted benzene derivatives and modified aldehydes or ketones. Coated and impregnated fibrous particles have been used<sup>3-5</sup> for reinforcing elastomers. The technique of in situ polymerization has also been thoroughly explored<sup>1,2</sup> for bonding fibers to elastomers. Numerous techniques<sup>2</sup> such as H block, strip adhesion, U, T, and many others, both static and dynamic in nature, have been used to measure adhesion between fibers and rubber. While most of these give a good relative indication of adhesion, the time-dependent nature of viscoelastic materials sometimes overshadows the real effect. For example, compared to black, silica and silicate fillers (when used with bonding agents) appear to show a preferential effect<sup>5-8</sup> in promoting adhesion between fibers and rubber. Whether this is really so needs a careful examination. This is possible only when techniques based on equilibrium measurements are employed. Equilibrium swelling is one of such techniques in which the fibers, if bonded, are supposed to restrict the swelling of elastomers.

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It is, therefore, the intent of this publication to use the restricted equilibrium swelling (RES) as a means to measure the degree of adhesion. It is also the intent of this paper to present the effect of fiber orientation on the nature of restricted swelling. The effect of bonded versus unbonded fibers on properties such as heat buildup, static and dynamic compression, permanent set, rupture elongation, and low extension moduli will also be discussed.

## EXPERIMENTAL

The rubber compounds without and with fibers, whose formulations are given in Tables III and IV, respectively, were prepared using the mixing procedures shown in Tables I and II.

### Preparation of Samples

For low- and high-extension tensile properties, 6 in.  $\times$  6 in.  $\times$  0.075 in. sheets were vulcanized at 320°F for 14 min. For swelling and heat buildup measurements, the Goodrich Flex test specimens were vulcanized at 320°F for 20 min. These specimens were cylindrical in shape, having a diameter of  $0.700 \pm 0.005$  in. and a height of  $1.000 \pm 0.01$  in. In fiber-containing compounds, the fiber orientation was controlled in the following manner:

For test specimens with vertical fiber orientation, flat fiber-containing rubber sheets were rolled to make vertical cylinders before curing. For test specimens with horizontal fiber orientation, circular discs were cut from flat rubber sheets and were stacked up. The discs were so aligned as to have a zero-degree angle between the oriented fibers of the neighboring plies. The so-stacked cured cylinders were used as specimens having horizontal fiber orientation. Henceforth for simplicity, the results obtained from the vertically oriented fiber-containing specimens will be indicated by a ( $\updownarrow$ )

TABLE I  
Mixing Procedure for Compounds Without Fibers (For Formulation see Table III)

Time, min	Materials charged
	Initial Mix: Laboratory Model Banbury (80°C) <sup>a</sup>
0	rubber
1.0	lead oxide, stearic acid, 1/2 black
2.5	1/2 Black, HiSil-233, antioxidants plasticizers
4.5	dump
	Final Mix: 2-Roll, Open Mill (50°C)
0	charge maturated batch
1	resorcinol, zinc oxide
3	cut twice, left and right
3.5	accelerator, Hexa, sulfur
4.5	cut
6	batch off-sheet

<sup>a</sup> Maturing period 24 hr.

TABLE II  
Mixing Procedure for Compounds With Short Fibers (For Formulation see Table IV)

Time, min	Materials charged
Initial Mix: Laboratory Model Banbury (80°) <sup>a</sup>	
0	rubber, lead oxide, stearic acid
1.0	short fibers
2.0	1/2 Black
2.5	1/2 Black, HiSil-233, plasticizer, and antioxidant
4.5	dump
Final Mix: 2-Roll, Open Mill (50°C)	
0	charge maturated batch
1.0	resorcinol, zinc oxide
3.0	cut twice, left and right
3.5	accelerator, Hexa, sulfur
4.5	cut
6.0	batch off-sheet

<sup>a</sup> Maturing period 24 hr.

TABLE III  
Formulation of Rubber Compounds E-H Without Fibers<sup>a</sup>

	E	E <sub>1</sub>	F	F <sub>1</sub>	G	H
SMR-5	100	100	100	100	100	100
Stearic acid	3	3	3	3	3	3
Philrich #5	7	7	7	7	7	7
PBNA	1	1	1	1	1	1
Santocure MOR	1	1	1	1	1	1
HAF Black	45	45	45	45	30	30
HiSil-233	—	—	—	—	15	15
Resorcinol	3.0	—	3.0	—	3.0	3.0
Hexa	1.5	—	1.5	—	1.5	1.5
Zinc oxide	10	10	8	8	10	8
Lead oxide	—	—	2	2	—	2
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

<sup>a</sup> Curing conditions: 14 min/320°F for 6 in. × 6 in. × 0.075 in. tensile sheets; 20 min/320°F for Goodrich Flex and swelling test specimens.

double arrow, and those with horizontally oriented fibers will be indicated by a (↔) double arrow.

### Test Procedures

**Swelling.** To determine the volume fraction of rubber in the dry state, the test specimens were weighed both in air and water. The difference of the two weights gave volume of the samples. From the base formulation, the amount of rubber present in the air weight of each specimen was calculated. Dividing it by 0.92, the volume of rubber present in dry specimens was determined. The volume of each specimen, and the volume of rubber present in it, gave the initial volume fraction of rubber ( $V_r$ ). These dry specimens were then swollen in benzene for a week.

TABLE IV  
Formulations of Fiber-Containing Rubber Compounds A-D\*

	A	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	B	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	D	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>
SMR-5	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic Acid	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Phulrich #5	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
PBNA	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
HAF	45	45	45	45	45	45	45	45	30	30	30	30	30	30	30	30
HiSil 233	—	—	—	—	—	—	—	—	15	15	15	15	15	15	15	15
Santocure MOR	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Glass Fibers (PPG's-833)	25	25	—	—	25	25	—	—	25	25	—	—	25	25	—	—
Plastibest-20 (Asbestos Fiber)	—	—	20	20	—	—	20	20	—	—	20	20	—	—	20	20
Resorcinol	3	—	3	—	3	—	3	—	3	—	3	—	3	—	3	—
Hexa	1.5	—	1.5	—	1.5	—	1.5	—	1.5	—	1.5	—	1.5	—	1.5	—
Zinc oxide	10	10	10	10	8	8	8	8	10	10	10	10	8	8	8	8
Lead oxide	—	—	—	—	2	2	2	2	—	—	—	—	2	2	2	2
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

\* Curing conditions: 14 min/320°F, for 6 in. × 6 in. × 0.075 in. tensile sheets; 20 min/320°F, for Goodrich Flex and swelling test specimens.

Volumes of swollen samples were determined by the benzene displacement method. The displaced volumes of benzene were corrected for actual volumes of swollen samples by multiplying them with 0.879. The volume of rubber in dry and swollen samples was assumed unchanged. The volume of swollen samples, and the volume of rubber in them, gave the volume fraction of rubber in swollen samples ( $V_r$ ). A parameter

$$V_r = \left( \frac{V_I - V_F}{V_I} \right)$$

was used for a relative comparison. A highly bonded system would result in a higher restriction in swelling. Consequently,  $V_F$  would have a relatively higher and  $V_r$  a relatively lower value. On the other hand, if bonding was not adequate,  $V_F$  will be relatively lower, resulting in a higher  $V_r$  value.

**Heat Buildup and Compression Fatigue.** For comparing the rate of heat generation and the fatigue characteristics of bonded and unbonded fiber compounds, a Goodrich Flexometer (D-623) was used. This test consists of subjecting a cylindrical specimen of definite size (defined earlier) to a static compressive load and superimposing on it an additional high-frequency cyclic compression of a definite amplitude. The rate and amplitude of the used cyclic compression were  $1800 \pm 10$  rpm and 0.25 in., respectively. The machine was operated at room temperature. Tests were terminated after 25 min at which time the rise in temperature (heat buildup) was measured. After removing the specimens from the machine, they were cooled for 1 hr at room temperature before measuring the height to calculate the permanent set (D-395). The static compression was measured initially after applying the static load but before subjecting the sample to the cyclic compression. The change in height of the specimen during cyclic compression was also measured. While the static compression gives an indication of the initial stiffness of a specimen, the permanent set and the change in height indicates the degree of relaxation during cyclic compression. The heat buildup gives an indication of the dissipated energy.

**Tensile Test.** Dumbbell-shaped samples were used for testing the tensile properties at 20 in./min on the Scott tester. For slow-speed (2.0 in./min) tensile testing, however, 0.5 in.  $\times$  5.0 in. test specimens were pulled on the Instron. The extensometer was used to record low extensions to calculate the respective moduli.

## RESULT AND DISCUSSION

### Swelling Measurements

Tables V, VI, and VII summarize the swelling results of the rubber compounds having *no fiber*, *glass fiber*, and *asbestos fibers*, respectively. The following sections discuss their results.

TABLE V  
Change in Volume Fraction of Rubber due to Swelling of Control Rubber Compounds

A814-88 (no fiber)	E	E <sub>1</sub>	F	F <sub>1</sub>	G	H
Volume fraction of rubber in dry specimen ( $V_I$ )	0.71	0.73	0.71	0.73	0.72	0.72
Volume fraction of rubber in swollen specimen ( $V_F$ )	0.25	0.24	0.25	0.25	0.23	0.24
$\frac{V_I - V_F}{V_I} = V_r$	0.65	0.67	0.65	0.66	0.68	0.67

TABLE VI  
Change in Volume Fraction of Rubber due to Swelling of Glass Fiber Compound

Fiber-containing compound	Fiber orientation $\uparrow$			Fiber orientation $\leftrightarrow$		
	$V_I$	$V_F$	$(V_I - V_F)/V_I$	$V_I$	$V_F$	$(V_I - V_F)/V_I$
A	0.67	0.26	0.61	0.65	0.26	0.60
A <sub>1</sub>	0.68	0.21	0.69	0.67	0.23	0.66
B	0.67	0.27	0.60	0.67	0.26	0.61
B <sub>1</sub>	0.68	0.22	0.68	0.68	0.22	0.68
C	0.67	0.25	0.63	0.67	0.26	0.61
C <sub>1</sub>	0.68	0.20	0.71	0.68	0.20	0.71
D	0.67	0.25	0.63	0.67	0.26	0.61
D <sub>1</sub>	0.69	0.22	0.68	0.69	0.22	0.68

TABLE VII  
Change in Volume Fraction of Rubber due to Swelling of Asbestos Fiber Compounds

Fiber-containing compound	Fiber orientation $\uparrow$			Fiber orientation $\leftrightarrow$		
	$V_I$	$V_F$	$(V_I - V_F)/V_I$	$V_I$	$V_F$	$(V_I - V_F)/V_I$
A <sub>2</sub>	0.68	0.28	0.58	0.69	0.27	0.61
A <sub>3</sub>	0.69	0.24	0.65	0.70	0.20	0.70
B <sub>2</sub>	0.68	0.29	0.57	0.68	0.29	0.57
B <sub>3</sub>	0.70	0.26	0.63	0.69	0.26	0.62
C <sub>2</sub>	0.68	0.27	0.60	0.68	0.28	0.59
C <sub>3</sub>	0.69	0.22	0.68	0.69	0.22	0.68
D <sub>2</sub>	0.67	0.26	0.61	0.66	0.26	0.60
D <sub>3</sub>	0.69	0.24	0.65	0.69	0.24	0.65

**Swelling of Rubber Compounds with No Fibers.** The data in Table V indicate that the compounds with bonding agents (E and F) exhibit slight restriction in swelling compared to those with no bonding agents (E<sub>1</sub> and F<sub>1</sub>). The lower  $V_r$  values of the former compounds are indicative of this fact. This could partly be due to the presence of the rigid resorcinol-formaldehyde (RF) domains and partly because of newly introduced chroman ring-type crosslinks.<sup>9</sup> To demonstrate the fact that addition of silica instead of black with bonding agents does not contribute additional

restriction, the data on samples G and H are also included. The higher  $V_7$  values of G and H compared to E and F, respectively, indicate that silica has an antagonistic effect, if any, rather than synergistic effect.

**Swelling of Glass- and Asbestos-Containing Compounds.** Tables VI and VII summarize the swelling results of glass- and asbestos fiber-containing compounds, respectively. It is evident that the fiber-filled compounds containing bonding agents (A, B, C, and D and A<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, and D<sub>2</sub>) have substantially lower  $V_7$  values than those with fibers but no bonding agents (A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub>, and D<sub>1</sub> and A<sub>3</sub>, B<sub>3</sub>, C<sub>3</sub>, and D<sub>3</sub>). The magnitude of restriction in bonded fiber compounds was higher than that attributable to the presence of rigid RF domains or chroman rings only. The difference between  $V_7$  values of unbonded and bonded fiber compounds was in every case 0.04 or more, of which only 0.02 can be attributed to RF domains and chroman rings (Table V). It appears, therefore, that the bonding agents establish some sort of permanent bonds between fibers and rubber. These bonds appear to be permanent and not temporary in nature, particularly in all black compounds (A, B, A<sub>2</sub>, and B<sub>2</sub>) because during swelling the bonded specimens sustained a hydrostatic strain of the swelling solvent, at least for a week, without being ruptured. The bonds in silica-containing compounds (C, D, C<sub>2</sub>, and D<sub>2</sub>), however, did not exhibit that firmness. This comment is based on the observation that the bonded silica-containing fiber compounds, in some cases, opened up after swelling, whereas the all-black compounds did not. The magnitude of restricted swelling or its absolute value did not seem to be affected by whether it was all black or partly silica-containing compound. Even the direction of fiber orientation did not seem to affect the magnitude of restricted swelling, although it did affect the direction in which the samples experienced restriction. The vertically oriented bonded fiber samples swelled laterally, showing restriction in the vertical direction. The horizontally oriented bonded fiber samples, on the other hand, swelled vertically, exhibiting restrictions in the lateral direction. Even the unbonded fiber-containing compounds showed slight restriction. However, their restrictive effect was very nominal compared to that shown by bonded samples, particularly in glass-containing compounds. The unbonded asbestos-containing compounds showed slightly lower  $V_7$  values than the glass samples. This indicates that the unbonded asbestos shows slightly better adhesion to rubber than the glass fiber. Since the specific gravities of asbestos and glass are similar, with 20 phr of asbestos against 25 phr of glass (purely on volume fraction basis), one would expect greater restrictions from glass. But the result was just the opposite, particularly in those compounds where a lead oxide/zinc oxide acceleration system was used (formulation in Table IV).

### Goodrich Compression Fatigue Results

Fatigue results of *glass-* and *asbestos* fiber-containing compounds have been summarized in Tables VIII and IX, respectively. It is apparent from the data in these tables that as a general rule the bonded fiber-containing

specimens developed lower heat, lower permanent set, and lower change in heights compared to their unbonded counterparts. However, it is worthwhile recalling that in this test the cylindrical specimens were subjected to a static compressive load superimposed by a cyclic compression of a definite amplitude (25%). Therefore, those samples which were stiffer in the direction of compression experienced higher stress levels for equivalent amplitude of cyclic compression. Since the dissipated energy in viscoelastic materials depends on both the stress and the strain amplitudes,<sup>10</sup> the samples which need to be subjected to higher stresses (for equivalent compression) could generate more heat. Constrained under high stresses, the stiffer samples could undergo a rapid yield phenomenon, resulting in a higher permanent set. In view of the above, one should be careful in analyzing other data in Tables VIII and IX.

Since all samples, regardless of their fiber orientation, were compressed cyclically in the vertical direction, those with vertical fibers were relatively

TABLE VIII  
Goodrich Compression Fatigue Results of Glass Fiber-Containing Compounds

Fiber-containing compound	Fiber orientation ↓				Fiber orientation ↔			
	Heat buildup, °F	Static compression, %	Perm. set, %	Change in height, %	Heat buildup, °F	Static compression, %	Perm. set, %	Change in height, %
A	79	5.2	1.9	3.2	60	8.0	2.6	0.1
A <sub>1</sub>	96	7.7	7.4	12.4	60	16.1	4.8	2.2
B	89	4.3	4.1	7.5	51	8.0	1.8	0.2
B <sub>1</sub>	111	5.1	9.8	14.7	57	12.7	2.2	1.9
C	60	10.8	2.2	0.2	46	11.2	1.7	0.0
C <sub>1</sub>	70	15.2	4.7	5.1	56	16.3	3.3	2.8
D	55	10.5	1.7	0.0	38	10.5	2.2	0.2
D <sub>1</sub>	103	13.1	10.6	13.6	65	15.1	4.0	3.2

TABLE IX  
Goodrich Compression Fatigue Results of Asbestos Fiber Compound

Fiber-containing compound	Fiber orientation ↓				Fiber orientation ↔			
	Heat buildup, °F	Static compression, %	Perm. set, %	Change in height, %	Heat buildup, °F	Static compression, %	Perm. set, %	Change in height, %
A <sub>2</sub>	92	3.0	2.2	1.6	50	9.5	1.7	0.9
A <sub>3</sub>	103	7.9	6.2	9.4	53	14.1	2.3	1.2
B <sub>2</sub>	99	3.1	2.1	2.3	61	4.5	2.5	0.4
B <sub>3</sub>	111	5.0	6.2	9.1	72	10.8	3.4	2.3
C <sub>2</sub>	86	5.4	2.1	0.7	62	7.0	2.1	0.1
C <sub>3</sub>	89	12.9	6.4	10.0	63	15.2	6.1	—
D <sub>2</sub>	65	8.2	2.2	0.0	50	7.8	2.0	0.1
D <sub>3</sub>	86	10.8	4.6	7.5	65	12.5	5.4	2.2



stiffer compared to those with horizontal fiber orientation. Consequently, the former experienced lower static compression than the latter (Tables VIII and IX). The higher stiffness of vertically oriented fiber compounds also resulted in higher heat buildup, higher permanent set, and greater change in heights compared to their horizontally oriented counterparts. As indicated in the previous section, the heat buildup, the permanent set, and the change in heights of the bonded fibers were lower than their unbonded counterparts (both vertical and horizontal). This was despite the fact that the promoted bonding between fiber and rubber raised the stiffness of bonded specimens. The obvious reason for such an effect seems to be an increased elastic response of bonded rubber-fiber composites. The silica-containing compounds (C and D or C<sub>2</sub> and D<sub>2</sub>) which had higher static compression, indicating lower stiffness to start with, did show lower heat buildup, lower permanent set, and lower change in heights compared to their all-black counterparts (A and B or A<sub>2</sub> and B<sub>2</sub>). Whether this was due to lower stiffness or improved adhesion between fiber and rubber is difficult to say. It seems that if adhesion were improved it should have affected the restricted swelling, which it did not. Further, superior bonding should have resulted in higher-stiffness and consequently lower static compression, which silica-containing compounds did not show. Under these circumstances, the role of silica in promoting adhesion remains questionable. However, the role of bonding agents in promoting adhesion between fiber and rubber is very apparent. In every case, A versus A<sub>1</sub>, A<sub>2</sub> versus A<sub>3</sub>, B versus B<sub>1</sub>, B<sub>2</sub> versus B<sub>3</sub>, C versus C<sub>1</sub>, C<sub>2</sub> versus C<sub>3</sub>, D versus D<sub>1</sub>, and D<sub>2</sub> versus D<sub>3</sub>, and in either mode of fiber orientation, bonding agents did raise the stiffness and consequently decreased the static compression and did increase restriction in equilibrium swelling. In so doing it gave some extra bonuses such as lower heat buildup, lower permanent set, and smaller change in heights.

### Tensile Properties

The data in Tables X and XI give the tensile properties of glass and asbestos fiber compounds, respectively. Based on these properties, one can easily conclude that bonding agents increased the stiffness and lowered the elongation of fiber compounds. Comparison of A, B, C, and D with their unbonded A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub>, and D<sub>1</sub> counterparts or A<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, and D<sub>2</sub> with their unbonded A<sub>3</sub>, B<sub>3</sub>, C<sub>3</sub>, and D<sub>3</sub> counterparts, respectively, makes it apparent. The improved adhesion of the bonded over unbonded fiber compounds has been previously verified by swelling measurements. Whether silica plays a synergistic role in promoting adhesion over black needs a further examination. Looking at tensile properties alone, one would be tempted to suggest so. But in view of our previously discussed swelling and compression fatigue measurements, one should be cautious. Comparing the moduli of compounds A with C and B with D at low extensions (Table X), one finds that beyond 10% the moduli of silica-containing com-

TABLE X  
Tensile Properties of Glass Fiber-Filled Rubber Compounds  
(Fiber Orientation in Mill Direction)

Properties <sup>a</sup>	A	A <sub>1</sub>	B	B <sub>1</sub>	C	C <sub>1</sub>	D	D <sub>1</sub>
C.H.S. 20 in./min								
M <sub>100</sub> , psi	1275	750	1400	675	—	975	—	1000
Tensile, psi	2600	3200	2475	3225	2200	2400	1950	2450
Elongation, %	260	380	250	400	70	370	60	340
Shore A	80	71	75	74	75	66	75	74
C.H.S. 2.0 in./min								
M <sub>10</sub> , psi	429	210	420	275	323	200	420	220
M <sub>20</sub> , psi	665	342	650	375	620	350	790	366
M <sub>30</sub> , psi	810	420	836	405	995	500	1270	464
M <sub>40</sub> , psi	880	447	955	425	1315	550	1530	512
M <sub>50</sub> , psi	930	474	1000	450	1540	600	1700	560
M <sub>60</sub> , psi	950	500	1020	475	1665	625	1750	585
M <sub>70</sub> , psi	960	536	1060	500	1770	650	—	597
M <sub>80</sub> , psi	975	554	1045	525	—	655	—	610
M <sub>90</sub> , psi	1000	631	1070	550	—	675	—	635
M yield, psi	960	420	1060	405	Broke	655	1750	597
Elong. at yield, %	70	30	70	30	before yield point	80	60	70

<sup>a</sup>  $M_x$  = Modulus at  $x$  per cent elongation.

pounds are higher. One also finds that the elongation of compounds C and D dropped substantially to 70% and 60%, respectively, compared to that of their C<sub>1</sub> and D<sub>1</sub> counterparts having no bonding agents. The elongations of compounds A and B, containing black and bonding agents but no silica, also dropped compared to that of their A<sub>1</sub> and B<sub>1</sub> counterparts, but not as drastically as those of C and D. While decrease in elongation should indicate improved adhesion, such a drastic decrease could also mean either a very high degree of adhesion or a rapid dissipation of energy due to the initiation of a catastrophic rupture.<sup>11</sup> It is also interesting to note (Table XI) that in bonded asbestos compounds, while the moduli of compound C<sub>2</sub> (with silica) are higher than those of A<sub>2</sub> (no silica) beyond 30% elongation, in compounds B<sub>2</sub> and D<sub>2</sub> the pattern is just reversed. That is, in the latter case the silica-containing compound D<sub>2</sub> shows lower moduli than B<sub>2</sub>. The reason seems to be that in all these compounds, owing to some energy dissipation process, fracture initiates and forces a Gaussian to nonGaussian transformation<sup>12</sup> of stress/strain curves in an early stage of deformation. Thus, a rapid upturn in stress/strain curve occurs as the rupture elongation approaches.

While the preferential role of silica over black is questionable in promoting adhesion, the role of bonding agents is unquestionable. Comparison of tensile properties alone may not make it so apparent, but these coupled with swelling and compression fatigue measurements confirm the adhesion-promoting role of bonding agents beyond the shadow of doubt.

TABLE XI  
Tensile Properties of Asbestos Fiber-Filled Compounds (Fiber Orientation in Mill Direction)

Properties <sup>a</sup>	A <sub>2</sub>	A <sub>3</sub>	B <sub>2</sub>	B <sub>3</sub>	C <sub>2</sub>	C <sub>3</sub>	D <sub>2</sub>	D <sub>3</sub>
C.H.S. 20 in./min								
M <sub>100</sub> , psi	—	900	—	1250	—	1050	—	1100
Tensile, psi	2475	2925	2825	3175	2800	2225	2425	2325
Elongation, %	70	390	60	350	60	270	50	330
Shore A	81	75	86	79	84	70	85	74
C.H.S. 2.0 in./min								
M <sub>10</sub> , psi	495	270	965	520	495	264	710	400
M <sub>20</sub> , psi	855	393	1482	731	840	430	1080	667
M <sub>30</sub> , psi	1210	515	1830	865	1480	600	1340	775
M <sub>40</sub> , psi	1502	589	2070	915	1920	670	1575	825
M <sub>50</sub> , psi	1775	613	2260	965	2200	767	1735	880
M <sub>60</sub> , psi	1975	637	2360	990	2500	802	—	960
M <sub>70</sub> , psi	2105	663	—	1010	—	825	—	975
M <sub>80</sub> , psi	2240	687	—	1040	—	850	—	986
M <sub>90</sub> , psi	—	710	—	1060	—	875	—	1025
M yield, psi	broke	663	broke	915	broke	no	broke	975
Elong. at yield, %	before yield point	70	before yield	40	before yield point	apparent yield point	before yield	70

<sup>a</sup> M<sub>x</sub> = Modulus at x per cent elongation.

## CONCLUSIONS

Based on equilibrium swelling, compression fatigue, and tensile measurements, one can safely conclude the following:

1. The bonding agents promote adhesion between hydrocarbon-type rubber and glass or asbestos short fibers.
2. The bonded fibers restrict the swelling of rubber-fiber composites.
3. The bonds between fiber and rubber are permanent and not temporary in nature, particularly in all-black compounds.
4. While the orientation of bonded fibers does not affect the magnitude of restricted swelling, it does, however, control the swelling direction. The vertically oriented bonded fibers restrict the swelling in the vertical, and the horizontally oriented restrict it in lateral directions.
5. The heat buildup, the permanent set, and the change in heights of the bonded fiber compounds are always lower than those of their unbonded counterparts.
6. The horizontally oriented fibers, being softer in compression direction compared to their vertically oriented counterparts, exhibit lower heat buildup, lower permanent set, and lower change in heights during cyclic compression.
7. The bonded short fibers raise the stiffness and decrease the rupture elongation of the composites.
8. Whether one uses all-HAF black or replaces 15 phr of HAF by HiSil-233 does not seem to affect the real bonding between short fibers and rubber. This is clearly evidenced by RES measurements.

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