Effect of Adhesive-Coated Glass Fiber in Natural Rubber (NR), Acrylonitrile Rubber (NBR), and Ethylene–Propylene–Diene Rubber (EPDM) Formulations. II. Effect of Cyclic Loading, Abrasion, and Accelerated Aging

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ABSTRACT: Treated glass fibers (RICS, 3 and 6 mm in length) were added at a concentrations of 10, 20, and 30 phr in natural rubber (NR), nitrile rubber (NBR), and ethylene–propylene–diene comonomer (EPDM) formulations, in both plain and carbon black mixes. The compounds were mixed in two-roll mill and were evaluated for their resistance to hot-air aging, abrasion, compression set, Goodrich heat buildup, De Mattia fatigue, and for NR mixes, adhesion in the tensile mode. The vulcanizates of the three rubbers showed resistance to hot-air aging. Abrasion resistance was poor for NR, and it improved with carbon black addition in the presence of treated glass fiber in NBR. In carbon-black-added EPDM vulcanizates, the abrasion resistance and fatigue resistance were better. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1124–1135, 2004

Key words: short glass fiber; elastomers; rubber; NR; EPDM; NBR carbon black; vulcanization; adhesion; adhesives

INTRODUCTION

In part I of this series, cure and static stress–strain properties showed that the adhesive treatment given to the chopped glass fiber was suitable in ethylene–propylene–diene comonomer (EPDM) and nitrile rubber (NBR) in that order and was less preferred in natural rubber (NR). Fibers, particularly short fibers, are known for their limited compression fatigue. In a rubber matrix, one may overcome this problem by enabling interfacial interaction between the fiber and the rubber through a suitable adhesive coating and, in some cases, with a proper curing system.

The object of this study was to examine the effect of cyclic loading in generating new surface, heat buildup, and the stability of bonding, if any, between the rubber and the fiber; the stability of such interaction under accelerated air aging and abrasive conditions may provide additional information in compounding.

EXPERIMENTAL[1,2]

The formulations and the scheme of the evaluations were discussed in part I. The tests conducted to evaluate the test mixes were heat buildup, fatigue, abrasion resistance, aging properties, compression set, and adhesion (Table I).

The test equipment used included a Goodrich flexometer, a De Mattia flex tester, a Pico abrader, a hot-air aging oven, and a compression set apparatus (constant deflection).

Preparation of test specimens (Fig. 1)

Heat buildup

The test was run up to 15 min, and the time for blowout was also recorded (Tables II–IV). The initial temperature was set at 50°C.

Compression set

This test was done according to ASTM D 395 under accelerated conditions: 24 h at 70°C for NR-based specimens and 24 h at 100°C for NBR and EPDM-based specimens:

$$\text{Compression set } \% = [(t_i - t_o)/(t_i - t_s)] \times 100$$

where t_i is the thickness before set, t_o is the thickness after set, and t_s is the spacer thickness (9.4 mm)

Fatigue test

The fatigue test was conducted according to ASTM D 430. Crack growth was recorded in millimeters for

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TABLE I
Tests Used on the Various Specimens

Test	Specimen/standard	Vulcanization	
		Temperature (°C)	Time (min)
Heat Buildup	Flexometer/ASTM D 623	150	25
Fatigue	De Mattia fatigue strip/ ASTM D 430	150	25
Abrasion	Pico	160	15
Compression set	Button/ASTM D 395	150	25
Adhesion test	Insulator specimen	160	15

every 1000 cycles for NR specimens, 1000 cycles for NBR specimens, 100 cycles for non-carbon-black-reinforced EPDM specimens, and 500 cycles for carbon-black-reinforced EPDM specimens.

Abrasion

This test was done in a Pico abrader machine.

$$\text{Abrasion resistance index (\% Pico)} = \frac{\text{Volume loss of standard specimen} \times 100}{\text{Volume loss of test specimen}}$$

RESULTS AND DISCUSSION

Study of NR

Heat buildup

Heat buildup decreased for the 10-phr RICS loading nonblack NR compound (B2). However, it increased for the 20- and 30-phr loadings in non-black-reinforced NR (B3 and B4, Fig. 2). This may have been due to (1) polysulfide crosslink formation or (2) an increase in fiber loading affecting the type and degree of crosslinks formed. However, carbon-black-reinforced NR mixes (B5–B8) showed a greater tendency toward mechanical loss, that is, a higher heat buildup (Fig. 3). A fiber loading of 10 phr showed a higher heat buildup than 20 and 30 phr of fiber-loaded black-reinforced NR compounds (B6 and B7). It appeared that the influence by the carbon black was more than from the fiber loading to heat buildup. In plain vulcanizates at the higher loading of 30 phr of fiber, blowout occurred at 12.5 min. All of the other vulcanizates did not blowout until the conclusion of the test. This may have been due to (1) poor compression fatigue of the vulcanizates with 30 phr of fiber in the plain mix or (2) carbon black strengthening the matrix to support compression fatigue even in the presence of fiber at the highest content of 30 phr.

Fatigue

Fatigue life decreased with increasing fiber loading in both nonblack and black-reinforced NR compounds, as shown in Figures 4 and 5. This may have been due to (1) the low fatigue life of glass fiber or (2) the lack of bonding between the fiber and rubber. The role of carbon black was not much, at least in the relation with fatigue cycles and the crack growth. Fiber loading at 10 and 20 phr (B2 and B3) in nonblack NR mixes caused no significant increase in crack growth resistance. Further, carbon-black-reinforced NR compounds (B5–B8) showed a more pronounced decrease in crack growth resistance than non-black-reinforced NR compounds (B1–B4). That means carbon black in the presence of fiber restricted the strain-induced crystallization of NR and made the vulcanizates more vulnerable to fatigue cracking.

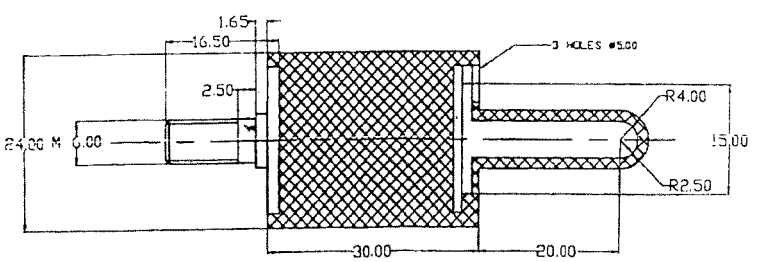

Figure 1 Test specimen for rubber-mild steel adhesion used to study the effect of treated glass fiber in NR compounds.

TABLE II
Blowout Times of NR Vulcanizates

	B1	B2	B3	B4	B5	B6	B7	B8
Blowout time (min)	Nil	Nil	Nil	12.5	Nil	Nil	Nil	Nil

Abrasion

Abrasion resistance in general was poor in plain and black-added vulcanizates (Figs. 6 and 7). However, the resistance improved notably on carbon black loading (Fig. 7). Within the given testing principle and the influential factors, the reduced abrasion resistance showed that the fiber was not compatible with NR under abrasive conditions because the values were less than 100% in all of the cases.

Hot-air aging

The charts (Figs. 8 and 9) show that resistance to aging improved with fiber in both non-black-reinforced (B1–B4) and black-reinforced compounds (B5–B8, Figs. 10 and 11). This trend revealed that under aggressive conditions (e.g., tear and tensile deformation in hot air), these vulcanizates were best suited. Further hardness (Fig. 11), a measure of shear modulus (at low strain), showed little variation after aging, suggesting that the vulcanizates may have been adequate for such purpose.

TABLE III
Blowout Times for NBR Vulcanizates

	B9	B10	B11	B12	B13	B14	B15	B16
Blowout time (min)	7	4.5	2.1	2.91	12.2	7	5.7	4.1

TABLE IV
Blowout Times for EPDM Vulcanizates

	B17	B18	B19	B20	B21	B22	B23	B24
Blowout time (min)	5.5	3.3	2	1.7	7.6	5.6	3.5	2.2

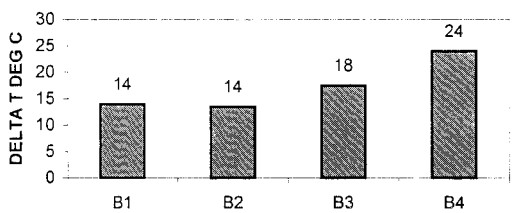

Figure 2 Effect of adhesive-coated glass fiber addition on the Goodrich heat buildup of NR nonblack compounds.

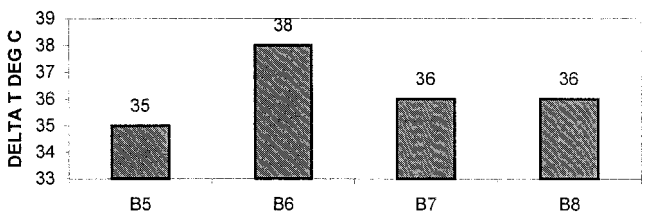

Figure 3 Effect of adhesive-coated glass fiber addition on the Goodrich heat buildup of NR black compounds.

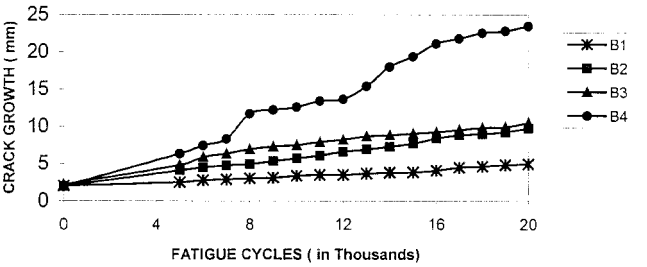

Figure 4 Effect of adhesive-coated glass fiber addition on the fatigue life of NR nonblack compounds.

Compression set

Compression set did not fit into a neat trend for both nonblack and black-reinforced NR compounds (Figs. 12 and 13). In nonblack mixes at a 10-phr fiber loading (B2), the compression set was not affected signifi-

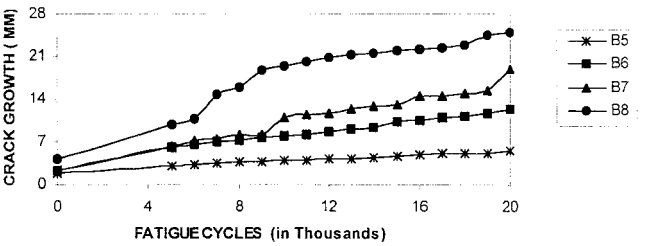

Figure 5 Effect of adhesive-coated glass fiber addition on the fatigue life of NR black compounds.

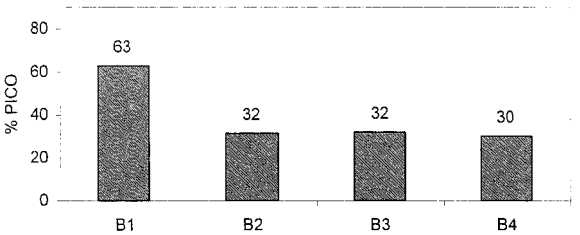

Figure 6 Effect of adhesive-coated glass fiber addition on the abrasion index of NR nonblack compounds.

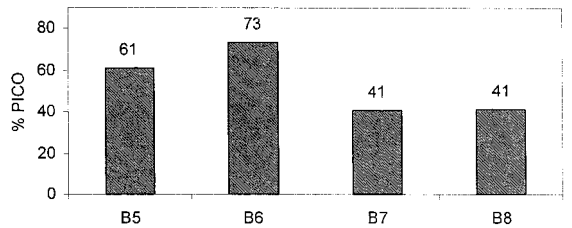

Figure 7 Effect of adhesive-coated glass fiber addition on the abrasion index of NR black compounds.

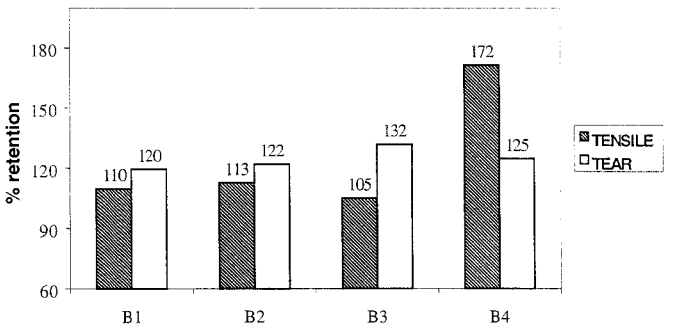

Figure 8 Effect of adhesive-coated glass fiber addition on the hot-air aging of NR nonblack compounds.

cantly. However, at the 20-phr level of fiber (B3), the set decreased considerably, and again, the set increased at 30 phr of fiber (B4). In carbon-black-reinforced NR, the variation was also similar, but it was lower compared to non-black-reinforced NR. This may have been due to carbon black interfering with the curing system.[3]

Adhesion properties

In nonblack formulations, an increase in fiber content increased the bond strength in pure tension (Fig. 14). A similar trend was also observed in black-reinforced NR compounds. For a given level of fiber loading, there was at least a 50-kg increase in bond strength on the addition of carbon black. This observation implied a synergistic effect of treated fiber and carbon black on adhesion. Nonblack compounds (B1 and B2) showed rubber–adhesive failure (Fig. 15). In black-filled compounds, the failure was rubber–rubber, that is, cohesive failure. Cohesive or matrix failure is not normally expected in black-reinforced vulcanizates. However, the observation here means that the effect of treated

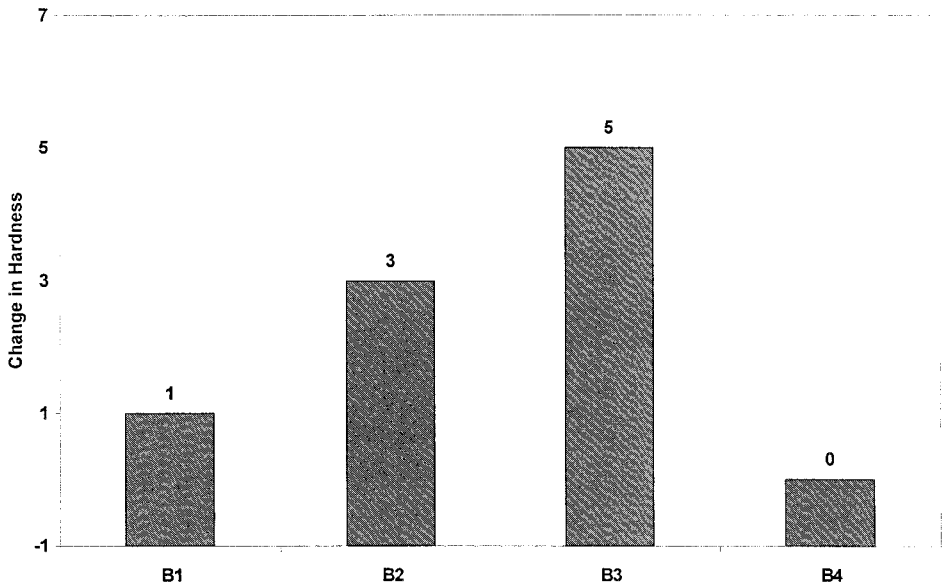

Figure 9 Effect of adhesive-coated glass fiber addition loading on the hot-air aging of NR nonblack compounds.

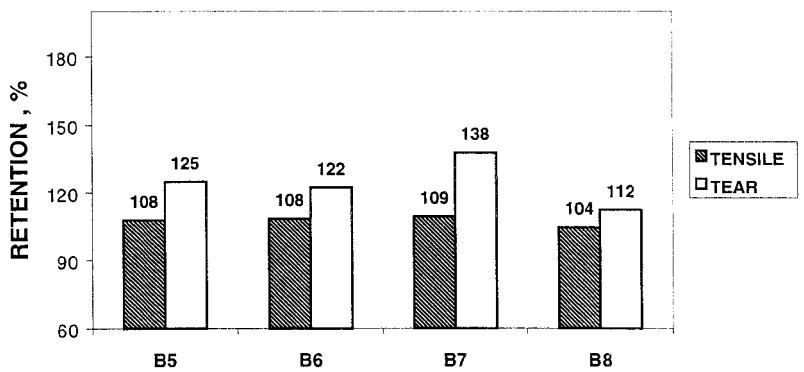

Figure 10 Effect of adhesive-coated glass fiber addition on the hot-air aging of NR black compounds, tensile strength, and tear strength.

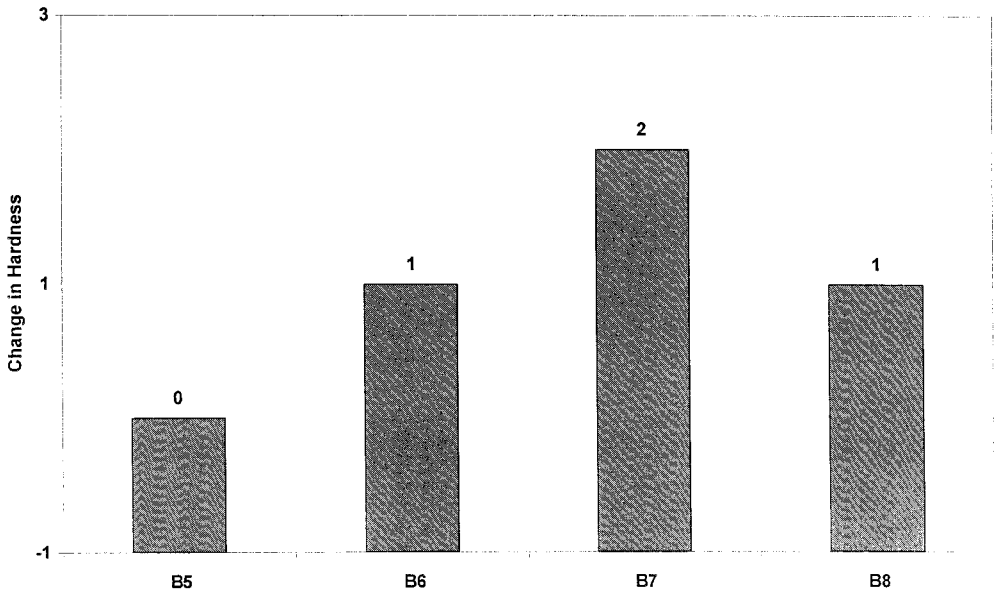

Figure 11 Effect of adhesive-coated glass fiber addition on the hot-air aging of NR black compounds; hardness.

fiber on rubber-to-metal adhesion overwhelmed the matrix.

Study of NBR

Heat buildup

Heat buildup remained unchanged on the loading of 10 phr of fiber in nonblack and black compounds (B10 and B14). In the presence of carbon black, fiber loading increased the heat buildup. The relative increase among the black mixes was marginal, except for the mix with 30 phr of fiber. This observation was similar to NR (Figs. 2 and 3). However, the set considerably decreased with the 20-phr RICS addition in both cases (B11 and B15, Figs. 16 and 17). In carbon black reinforcement, the rigid carbon black particles immobilized the rubber chains, which led to considerable intermolecular friction and caused higher mechanical loss, which resulted in a higher heat buildup than in the nonblack compounds.[3,4] All of the vulcanizates recorded a definite blowout time, unlike those seen in NR. However, the trend in data was different: B13 was the highest, and B11 was the lowest. This observation was contrary to that of the NR vulcanizates (B1–B8), which had better resistance to compression fatigue.

Fatigue

Increasing fiber loading led to poor fatigue life in both black-filled (B13–B16, Fig. 18) and non-black-filled (B9–B12, Fig. 19) compounds. This may have been due to the poor fatigue life property of the polymer, which was further weakened by the easy separation of the fiber from the rubber. However, for a given amount of fiber, the black-added vulcanizates showed a higher resistance to fatigue on the order of 2–3. Further, the crack growth with fatigue cycles was sluggish in

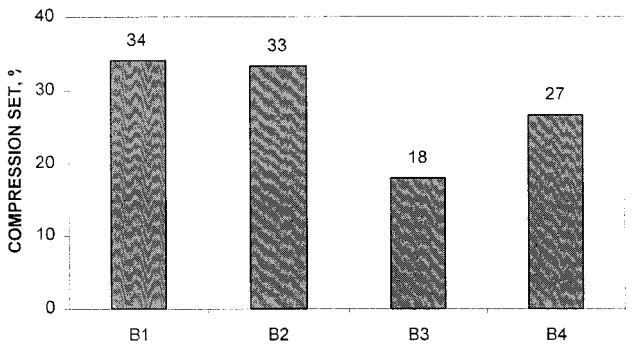

Figure 12 Effect of adhesive-coated glass fiber addition on the compression set of NR nonblack compounds.

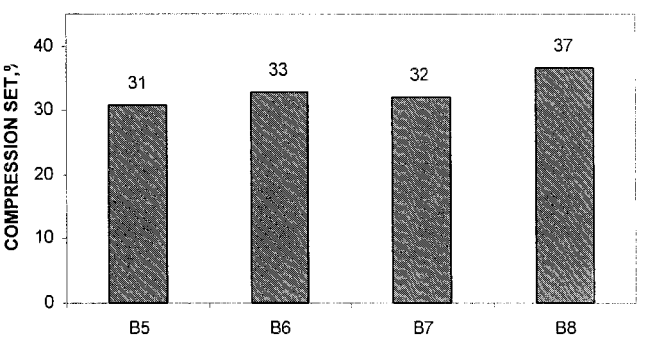

Figure 13 Effect of adhesive-coated glass fiber addition on the compression set of NR black compounds.

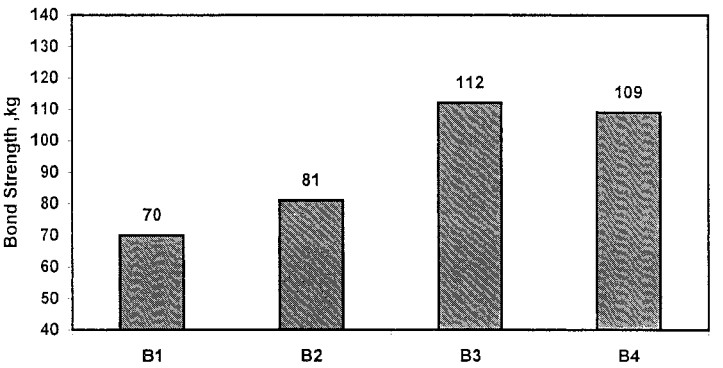

Figure 14 Effect of adhesive-coated glass fiber addition on the bond strength of NR nonblack compounds.

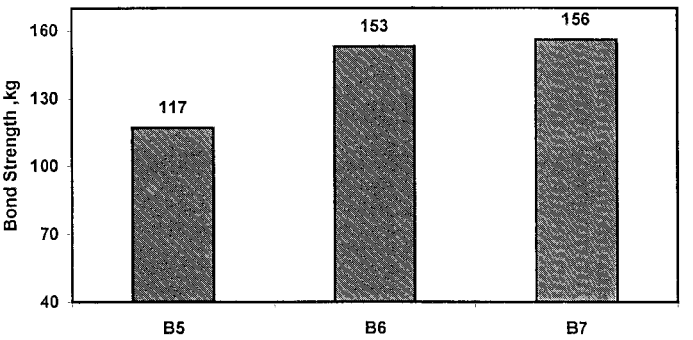

Figure 15 Effect of adhesive-coated glass fiber addition on the bond strength of NR black compounds.

black-added vulcanizates, which truly reflected the carbon black reinforcement of an amorphous rubber such as NBR. This observation was in contrary to what was seen for NR.

Abrasion resistance

All nonblack NBR vulcanizates showed poor abrasion resistance (low Pico index, Fig. 20). Within the trend observed, abrasion increased with increasing fiber loading. However, in carbon-black-added, the vulcanizates showed much better resistance to abrasion, unlike NR vulcanizates (Fig. 7). This particular observation suggests a preference to the addition of treated glass fiber in NBR under abrasive conditions. All of the NBR vulcanizates showed a much better resistance to abrasion with an anomalous increase in abrasion resistance on the 10-phr addition of treated glass fiber (B14, Fig. 21). This may have been due to fibers being positioned perpendicular to the abrading surface.[5]

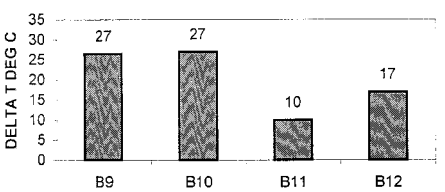

Figure 16 Effect of adhesive-coated glass fiber addition on the Goodrich heat buildup of NBR nonblack compounds.

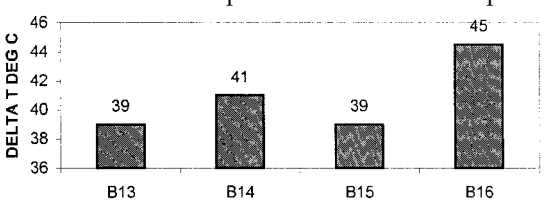

Figure 17 Effect of adhesive-coated glass fiber addition on the Goodrich heat buildup of NBR black compounds.

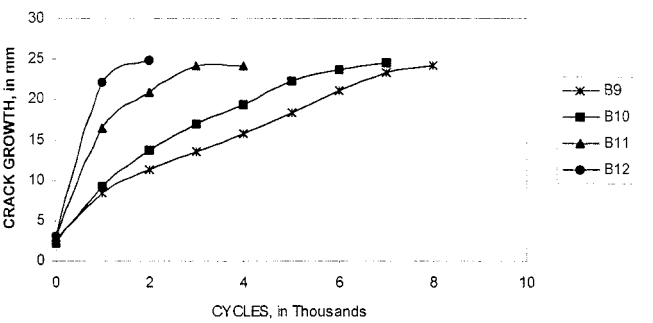

Figure 18 Effect of adhesive-coated glass fiber addition on NBR nonblack compounds; flex cracking.

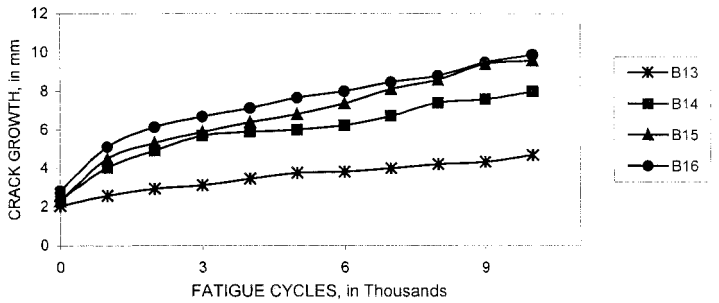

Figure 19 Effect of adhesive-coated glass fiber addition on NBR black compounds.

Effect of hot-air aging on NBR vulcanizates

In general, accelerated aging had a less deteriorating influence and, in some cases, a higher retention as well (Figs. 22–25). This may have been due to a stability and/or tightening of crosslinking supported by the treatment given to the glass fiber. Carbon-black-filled compounds with 20 and 30 phr of fiber (B15 and B16, Figs. 23 and 24) showed an increase in tear strength. This may also have been due to better retention. At the same time, hardness remained unaffected on aging for all nonblack and black-filled compounds (B9–B16, Figs. 24 and 25), which was similar to the NR vulcanizates.

Compression set

With increasing fiber loading, the samples showed a variation in a zigzag pattern for non-carbon-black compounds (B9–B12, Fig. 26). Black-filled compounds (B13–B16, Fig. 27) also did not show a smooth trend. In the 20-phr fiber-loaded black compound (B15), the set was more pronounced, which may have been due to the fiber being positioned at 90° to the compressive direction.[5] For B14 and B16 (10 and 30 phr of fiber), there was almost no change in set.

Study of EPDM

Heat buildup

Increasing fiber loading in both nonblack and black filled compounds resulted in reduced blowout times. The heat buildup was maintained around 15°C in nonblack (Fig. 28) and around 30°C in black compounds. For similar carbon black addition, the heat buildup was around 36°C in NR and 40°C in NBR. In plain compounds, the heat buildup was around 18°C in NR and 25°C in NBR. The vulcanizates of B23 and B24 showed a reduction in heat buildup (Fig. 29), which may have been due to the treated fiber possibly converting all of the mechanical energy into deformation (mostly elastic) and providing little room for hysteresis.

Fatigue resistance

The fatigue life for non-black-filled compound increased with increasing fiber loading (Fig. 30). The vulcanizate B17 failed immediately after the startup of the test. Therefore, it is not shown in Figure 30. Fatigue failure was more significant in B18 than in B19 and B20 (Fig. 31). The fatigue life for carbon-black-filled compounds also increased with increasing fiber loading (Fig. 31). The vulcanizates became insensitive to the fatigue cycles with increasing fiber loading, contrary to what was observed for the NR and NBR vulcanizates. The reduction in crack growth was substantial with the initial 10 phr of fiber loaded in black vulcanizates (B21 and B22, Fig. 31). The further addition of fiber, however, did not alter the crack sizes much, and the rate remained almost unaffected. This observation was important, considering the poor fatigue life of similar NR vul-

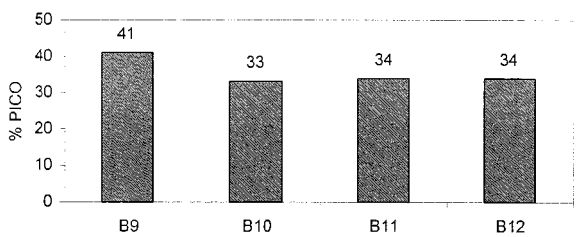

Figure 20 Effect of adhesive-coated glass fiber addition on NBR nonblack compounds; abrasion resistance.

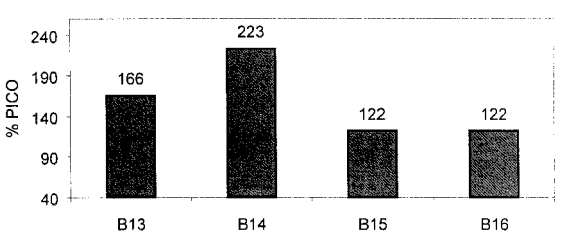

Figure 21 Effect of adhesive-coated glass fiber addition on NBR black compounds; abrasion resistance.

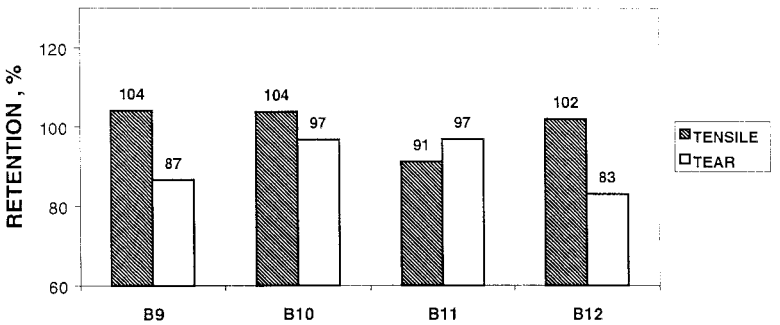

Figure 22 Effect of hot-air aging with adhesive-coated glass fiber addition in NBR nonblack compounds; tensile strength and tear strength.

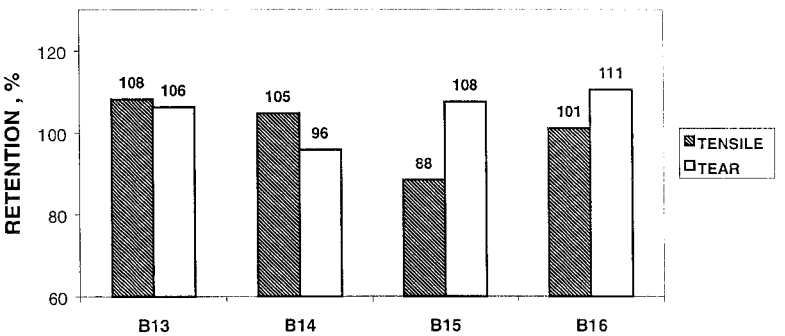

Figure 23 Effect of hot-air aging with adhesive-coated glass fiber addition in NBR black compounds; tensile strength and tear strength.

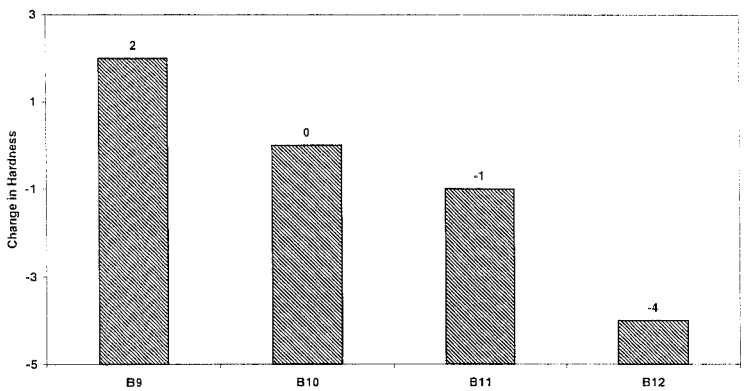

Figure 24 Effect of adhesive-coated glass fiber addition on the hardness on hot-air aging in NBR nonblack compounds.

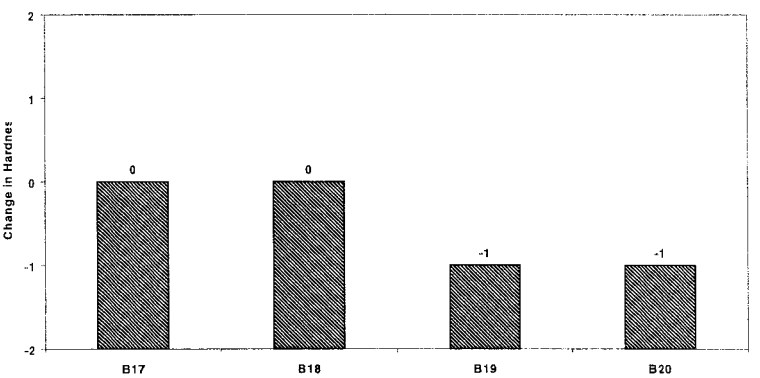

Figure 25 Effect of adhesive-coated glass fiber addition on the hardness on hot-air aging in NBR black compounds.

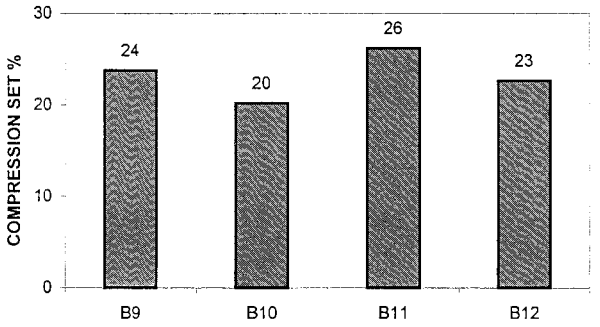

Figure 26 Effect of adhesive-coated glass fiber addition on the compression set of NBR nonblack compounds at 100°C for 24 h.

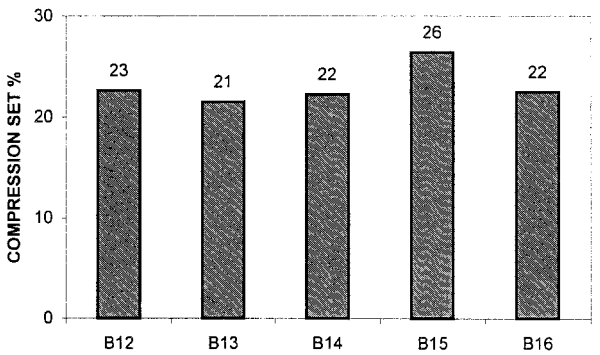

Figure 27 Effect of adhesive-coated glass fiber addition on the compression set of NBR black compounds at 100°C for 24 h.

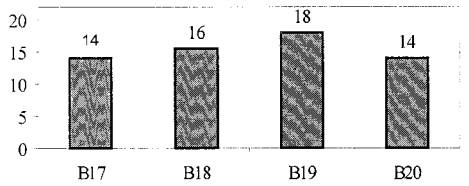

Figure 28 Effect of adhesive-coated glass fiber addition in EPDM nonblack compounds.

canizates discussed in the previous section. The reduction in fatigue failure may have been due to (1) the reduction of microscopic flaws, (2) the molecular

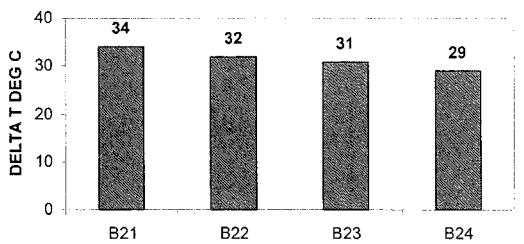

Figure 29 Effect of RICS loading in EPDM black compounds.

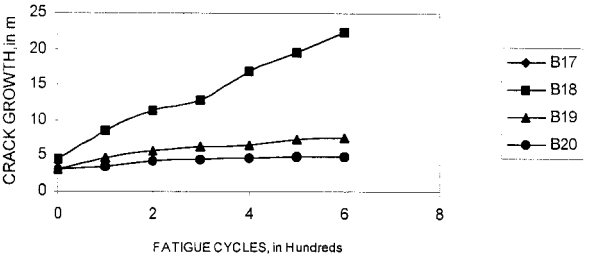

Figure 30 Effect of adhesive-coated glass fiber addition in EPDM nonblack compounds; flex cracking.

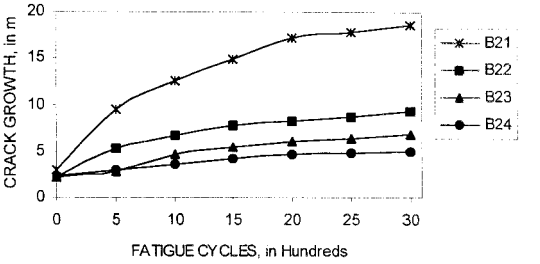

Figure 31 Effect of adhesive-coated glass fiber addition in EPDM black compounds; flex cracking.

orientation of the fiber in the EPDM matrix, or (3) good compatibility between coated glass fiber and the EPDM matrix.[3]

Abrasion resistance

In general, the abrasion resistance index did not show any smooth trend with increasing fiber loading in carbon-black-filled compounds (Fig. 32). However, fiber loading reduced the abrasion resistance index. Comparatively, B23 showed a higher index than B22 and B24. Due to experimental difficulty, the abrasion data for nonblack EPDM compounds are not reported.

Effect of hot-air aging on EPDM vulcanizates

In case of accelerated aging, the presence of oxygen was likely to cause additional crosslinks in sulfur-cured EPDM rubber. The result showed better retention of this property; that is, the vulcanizates

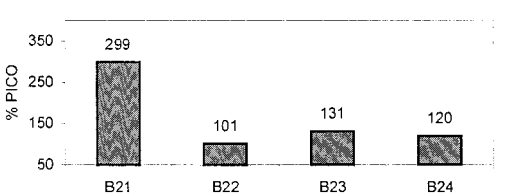

Figure 32 Effect of adhesive-coated glass fiber addition in EPDM black compounds; abrasion resistance.

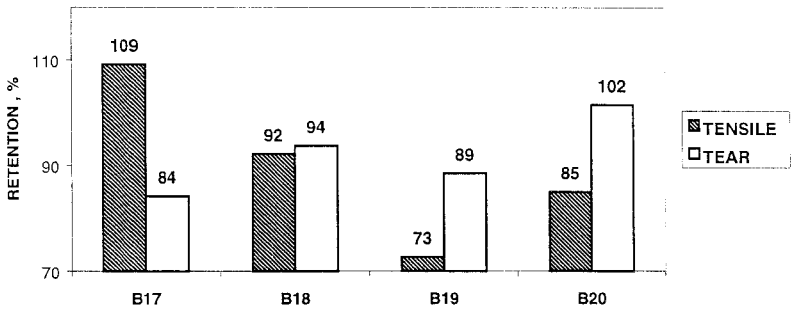

Figure 33 Effect of adhesive-coated glass fiber addition on the hot-air aging of EPDM nonblack compounds; tensile strength and tear strength.

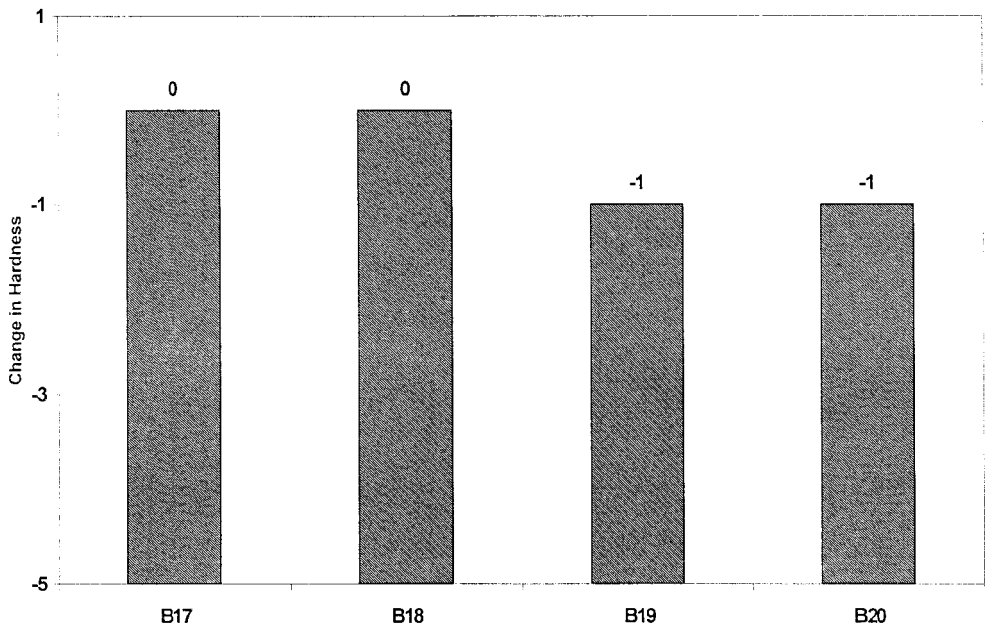

Figure 34 Effect of adhesive-coated glass fiber addition on the hot-air aging of EPDM nonblack compounds; hardness.

retained their unaged properties, which may have been due to better dispersion of the fiber (Figs. 33 and 34). The fiber dispersed through out the bulk of mix added to the thermal stability of the vulcanizates. The decrease in the retention of properties in carbon-black-filled compounds may have been due to the carbon black interfering with the fiber–EPDM matrix. B23 (20 phr of fiber) showed better retention in the black-filled compound. Hardness also remained unchanged in all of the vulcanizates (B17–B24, Figs. 35 and 36), which was similar to the NR and NBR vulcanizates.

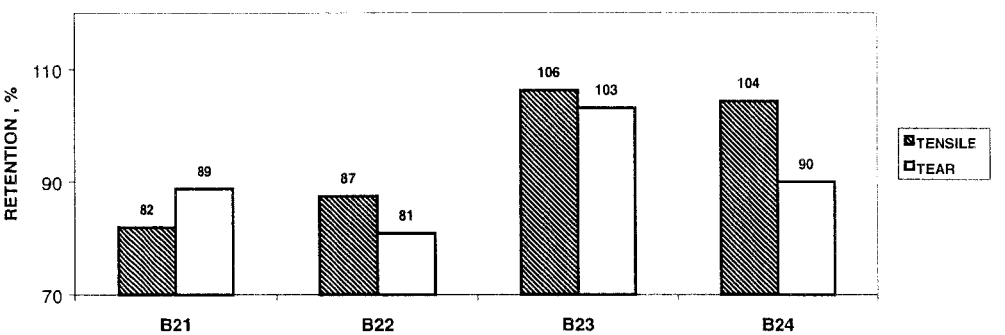

Figure 35 Effect of adhesive-coated glass fiber addition on the hot-air aging of EPDM nonblack compounds; tensile strength and tear strength of black compounds.

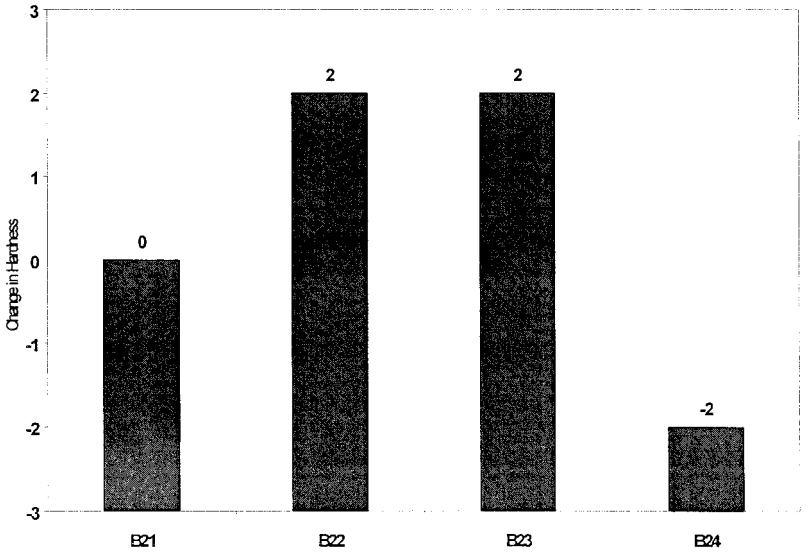

Figure 36 Effect of adhesive-coated glass fiber addition on the hot-air aging of EPDM black compounds; hardness.

Compression set resistance

The compression set initially decreased for B18 (Fig. 37) and increased marginally with increasing fiber loading in nonblack compounds. For the carbon-black-filled compounds (Fig. 38), B21 and B22 (0 and 10 phr of fiber) showed almost the same set properties. For the B23 and B24 (20 and 30 phr of fiber) vulcanizates, an increase in set was noticed. The increase in the set property may have been due to the fiber being positioned at 90° to the compressive force direction.[5] The optimum dosage of treated glass fiber for the low compression set may have been 10 phr (B18 and B22).

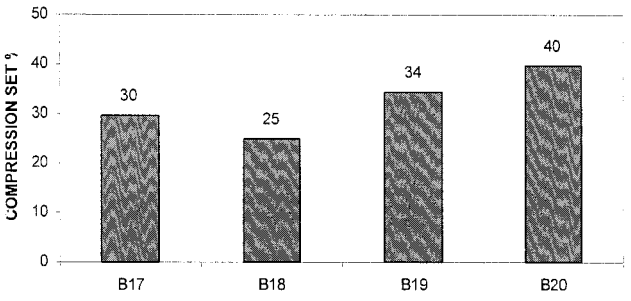

Figure 37 Effect of adhesive-coated glass fiber addition on the compression set of EPDM nonblack compounds at 100°C for 24 h.

CONCLUSIONS

All of the vulcanizates showed increased stiffness with increasing treated glass fiber, with EPDM exhibiting a greater tendency. Under similar heat buildup conditions, NR vulcanizates had better resistance to blowout compared to NBR and EPDM. EPDM vulcanizates were superior in flex fatigue. All of the vulcanizates (NR, NBR, and EPDM) had resistance to accelerated aging and exhibited irregular trends in compression set. NR vulcanizates had limited abrasion resistance. However, carbon-black-added NBR and EPDM vulcanizates showed re-

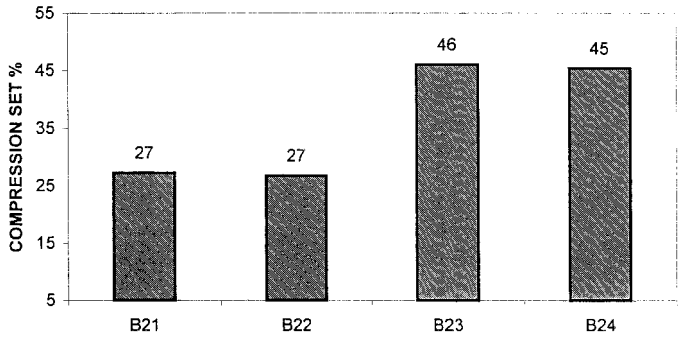

Figure 38 Effect of adhesive-coated glass fiber addition on the compression set of EPDM black compounds at 100°C for 24 h.

markable resistance to abrasion. Our overall conclusions are (1) carbon-black-treated glass fiber–NR vulcanizates are fit for applications such as engine mounts and tire treads (where resistance to compression fatigue is important) and (2) carbon-black-treated glass fiber–NBR and EPDM–carbon black–fiber are suitable for such technical rubber goods as hoses, dust covers, bellows, and O-rings, where flex fatigue and abrasion are significant.

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