Impact of Halobutyl Rubber Innerliners on Tire Durability

Halobutyl rubber · Innerliner · Durability · Tire

Halobutyl rubber is the polymer of choice in the tire innerliner compound due to its excellent air and moisture impermeability, and flex-fatigue resistance. The inflation pressure of the tire generally impacts the rolling resistance, treadwear, handling, and durability. The Tire Inflation Pressure Retention (IPR) loss rate is a key predictive parameter used to improve tire durability. Results will compare innerliner compounds made with varying amounts of halobutyl rubber and natural rubber, to road wheel performance of tires made with these compounds. Use of 100 phr of bromobutyl rubber in the innerliner compound leads to a tire with desirably low Inflation Pressure Retention values, low Intracarcass Pressure (ICP) values, and increased tire Durability as measured in hours to failure on indoor road wheels. Analysis of failed tires demonstrates the effectiveness of halobutyl rubber in protecting other select internal components of the tire.

Einfluss von Halobutyl-Innerlinern auf die Lebensdauer von Reifen

Halobutylkautschuk · Innerliner · Lebensdauer · Reifen

Halobutylkautschuk ist aufgrund seiner ausgezeichnet geringen Luft- und Feuchtigkeitspermeabilität und der guten Biegeermüdungsfestigkeit das Polymer der Wahl für Reifen-Innerliner. Der Reifendruck hat im allgemeinen einen Einfluss auf den Rollwiderstand, den verschleiß, das Handling und die Lebensdauer. Die Reifendruckänderungsrate ist ein Schlüsselparameter um die Lebensdauer von Reifen zu verbessern. Die Meßergebnisse vergleichen Innerlinercompounds mit unterschiedlichen Mischungsverhältnis von Halobutyl und Naturkautschuk bezüglich des Verschleißes auf der Straße. Die Verwendung von 100 phr Brombutylkautschuk in den compounds führt zu niedrigen Reifendruckänderungsraten, durch einen niedrigen Intrakarkassendruck und damit zu einer erhöhten Lebensdauer im „indoor“ Test. Die Analyse der ausgefallenen Reifen stellt den durch Halobutyl gesicherten Schutz anderer Reifenkomponenten unter Beweis.

The innerliner is a thin layer of rubber laminated to the inside of a tubeless tire whose primary function is vapor retention. It is formulated to also provide flex fatigue resistance, aging resistance and adhesion to the ply coat compound [1–2]. It has been shown that of the elastomers studied, butyl rubber has the lowest permeability coefficient [3], see Figure 1.

Butyl rubber [4–8] (IIR) is the copolymer of isobutylene and about 2 % of isoprene. It has excellent impermeability for air barrier and good flex fatigue properties. These properties result from low levels of unsaturation in between the long polyisobutylene chain segments. Tire innertubes were the first major use of butyl rubber. The development of halogenated butyl rubbers greatly extended the usefulness of butyl rubbers by providing faster curing rates, which enabled co-vulcanization with general-purpose tire rubbers such as NR, SBR and BR, without affecting the desirable impermeability and fatigue properties. This permitted development of tubeless tires in which the innerliner compound is chemically bonded to the carcass ply.

The impermeability of polyisobutylene is thought to be the result of the close packing of the geminal-dimethyl side groups along the polymer backbone which results in slow movement of the chains [9]. As an example, three repeat units of cis-polyisoprene totaling fifteen carbon atoms occupy more space than do four repeat units of polyisobutylene which contain sixteen carbon atoms, see Figure 2. This is a result of the Sp^3 hybridization of each carbon atom in polyisobutylene affords a tetrahedral arrangement of the backbone, compared to the planar arrangement of the Sp^2 hybridized carbon atoms in the C=C double bond of each segment in polyisoprene.

Bromobutyl rubber is used extensively in innerliner formulations for several reasons [10–22]:

- superior adhesion and balance of properties,
- increasing use of ultra-low profile, speed-rated tires having higher surface area to air volume ratios,
- requirement for lighter tires to reduce rolling resistance and improve vehicle fuel economy,
- use of high-pressure space-saver spare tires requiring a more impermeable innerliner,
- better flex-cracking resistance after aging, and
- bromobutyl innerliners, at half the gauge, are cheaper in material costs

We present results of the effect that the bromobutyl rubber content in the innerliner formulation has upon tire durability performance as measured on laboratory road wheels. Innerliners with 100-phr BIIR and 80/20 and 60/40 blends of BIIR/NR were studied in high-performance radial passenger tires.

Experimental

Bromobutyl rubber used is BIIR 2222 (ExxonMobil Chemical). Natural rubber is SMR 20. All other ingredients are commercial materials. Formulations are shown in Table I. Compounds were mixed in a factory using a conventional two-step mixing sequence in internal mixers equipped with tangential rotors. Masterbatch mixing was completed using a GK400 mixer followed by sheeting out on an extruder with roller die. Finalization was completed in a GK160 mixer and stocks sheeted out on a two-roll mill. A cold-feed pin extruder

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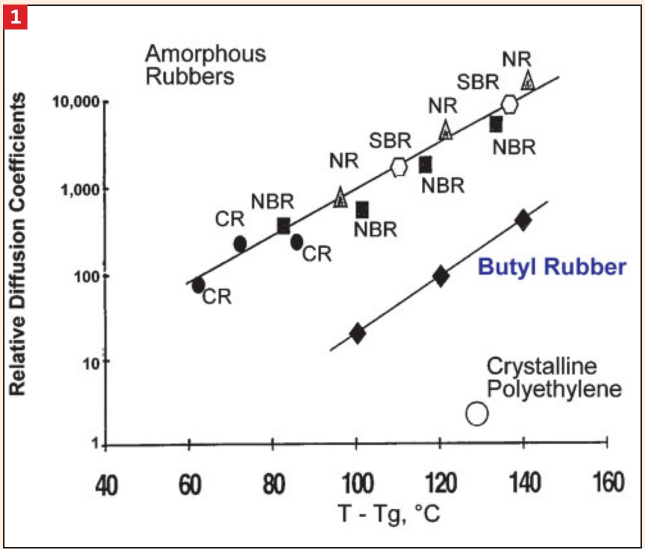
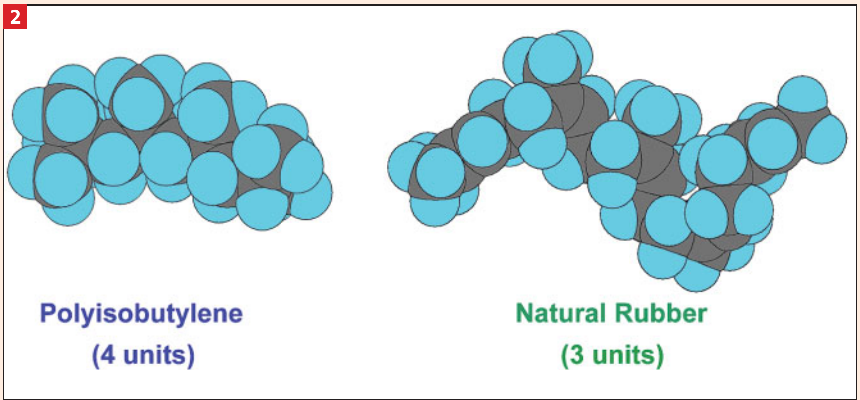


1 Relative Diffusion Coefficients of Elastomers [3]



2 Space-filling Models of Polyisobutylene and Natural Rubber

1 Innerliner Compound Formulations

Ingredient	1	2	3
Bromobutyl Rubber, 2222	100	80	60
Natural Rubber, SMR 20	0	20	40
Processing Aid, SP1068	4	4	4
Carbon Black, N660	60	60	60
Processing Aid, Struktol 40 MS	7	7	7
Processing Oil, TDAE	8	8	8
Stearic Acid	1	1	1
Zinc Oxide	1	1	1
Sulfur	0.5	0.5	0.5
Accelerator, MBTS	1.25	1.25	1.25

3 Peel Adhesion Test Specimen

was used to profile each innerliner compound [23–24] (Table 1).

P205/60 HR15 tires were built using automatic building machines in order to test the effect that changes in the bromobutyl rubber content in the innerliner compound have upon tire performance. Cured innerliner thicknesses averaged 1.0 mm. Tire Inflation Pressure Retention (IPR) loss rate was tested in accordance to ASTM F-1112 and is reported as the percent pressure loss per month. Tire Intracarcass Pressure (ICP) was measured for tires on standard rims inflated to 240 kPa. Typically five calibrated gauges with hypodermic needles are inserted with the needle tip set on the cords. Readings are taken until the pressure equilibrates, normally two months, and is reported as the average of at least two tires.

A Tread Separation Test was run for tires (steel rims) inflated to 240 kPa using 50/50 O_2/N_2 against a 28.5 cm wheel running at 80 km/hr in a room at 21°C. The load was set using the 100 % load for 207 kPa inflation [25], which normally gave a deflection of 30 % to 35 %. Pressure was adjusted daily to maintain as constant. Tires were tested until failure.

The Federal Motor Vehicle Safety Standards (FMVSS) 139 Endurance Test was run for tires inflated to 180 kPa with air against a 1.7 m wheel of an All Well Tire Testing Machine Model AW-TT-2A-M4 running at 120 km/hr in a room at 38°C. The procedure was to run the tire for four hours at 85 % load, followed by six hours at 90 % load, and followed by 24 hours at 100 % load. Tires were inspected visually for failures, and if none were visible testing was continued until failure. Tires were inspected and failures determined after dissection.

The Akron Rubber Development Laboratory (Akron, Ohio, USA) was employed to dissect new and tested tires and to analyze specific components in order to obtain samples of the Natural Rubber skim coat and shoulder wedge compounds. Crosslink density was determined by solvent swelling [26]. Fixed oxygen contents were determined by elemental analysis using a LECO CHNS-932. Tensile properties (ASTM D412) were determined for the Natural Rubber wedge compound. One-inch wide strips were used to determine the peel adhesion strengths (ASTM D413) for the wedge and skim composites, see Figure 3.

Modulus profiles [27–29] were generated for the shoulder area, see Figure 4 as an example.

SAS JMP 4.0 software was used to statistically analyze all data.

2 Tire Performance Properties

Polymer Composition	Inflation Pressure Retention	Intracarcass Pressure	Durability	Durability
			Tread Separation	FMVSS 139 Endurance, to Failure
BIIR/NR	% Loss/Month	kPa	Hours to Failure	Hours to Failure
100/0	1.48	57.9	797.2	539.4
80/20	2.05	82.5	668.0	384.8
60/40	2.75	116.8	610.6	349.9

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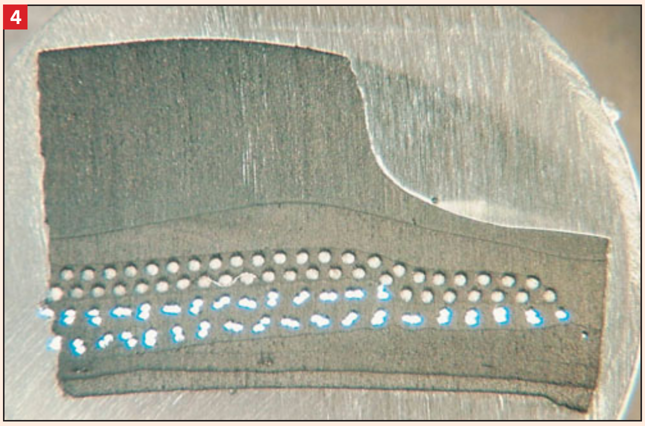

4 Modulus Profile Test Specimen

Results and discussion

Cure, cured physical and aged physical properties of innerliner compounds have been reported [24]. Aged properties were adversely changed by replacing bromobutyl rubber in the innerliner formulation. Modulus values increased, and tensile strength, elongation at break, and energy to break values all decreased for all three compounds upon being aged in an air oven at 125°C for 72 hours. Fatigue to failure values decreased upon increasing natural rubber content. Air permeability increased linearly ($R^2 = 0.99$) with increasing natural rubber content in the innerliner compound. The 100-phr BIIR compound has the desirably lowest permeability and is the most age resistant.

Tire Inflation Pressure Retention, Intracarcass Pressure, and Durability were determined in duplicate. Results are summarized in Table 2 Inflation Pressure Retention loss rates (Figure 5; $R^2 = 0.9965$) and ICP (Figure 6; $R^2 = 0.991$) increased linearly with increasing natural rubber content in the innerliner compound. The tire having a 100-

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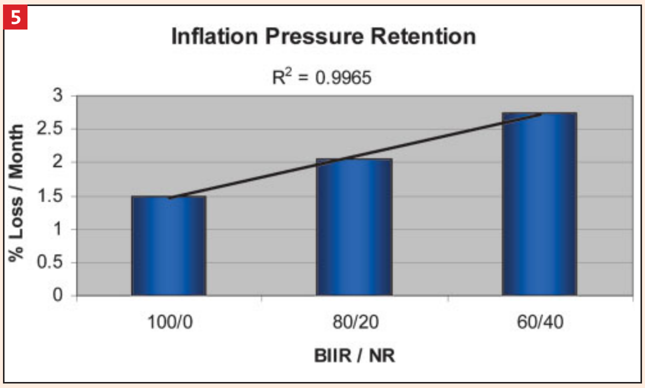

5 Inflation Pressure Retention versus the Bromobutyl Rubber Content in Innerliner

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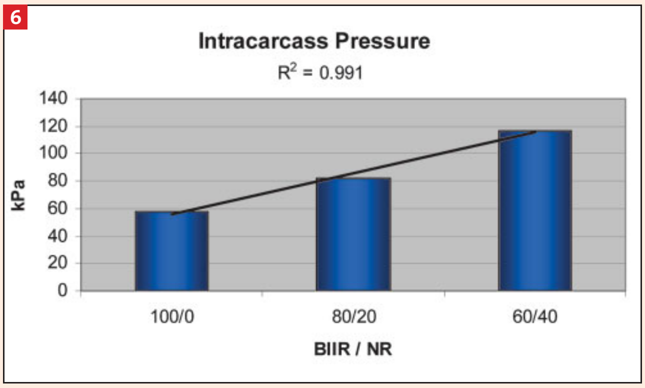

6 Intracarcass Pressure versus the Bromobutyl Rubber Content in the Innerliner

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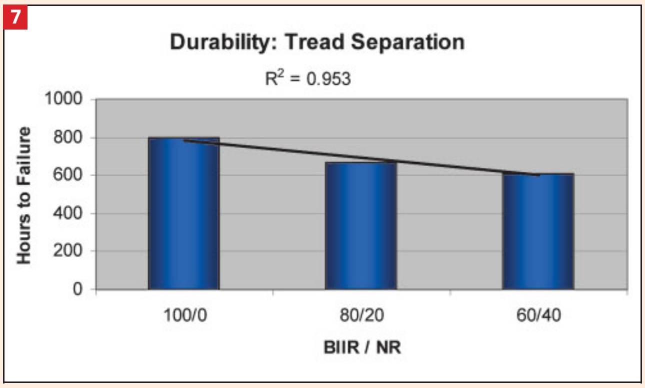

7 Durability on a 28.5 cm Wheel versus Bromobutyl Rubber Content in Innerliner

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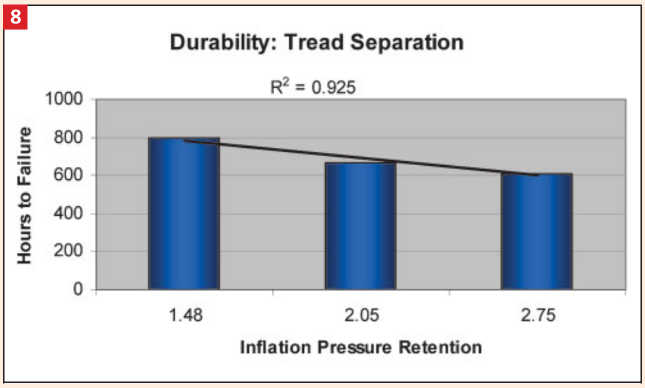
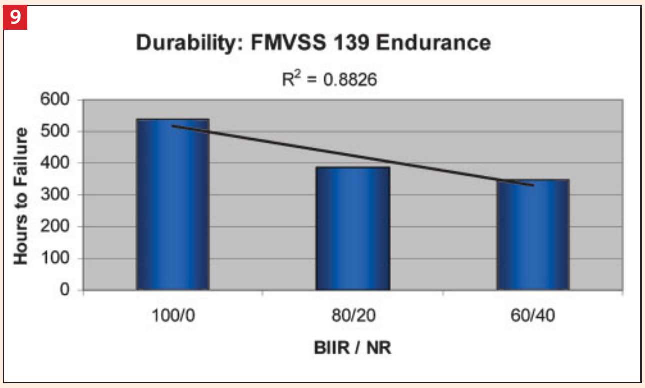
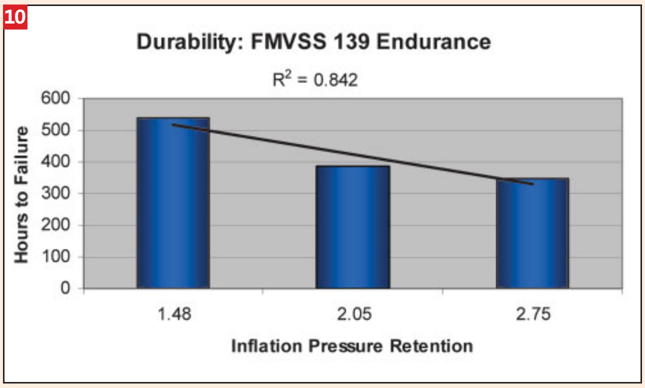


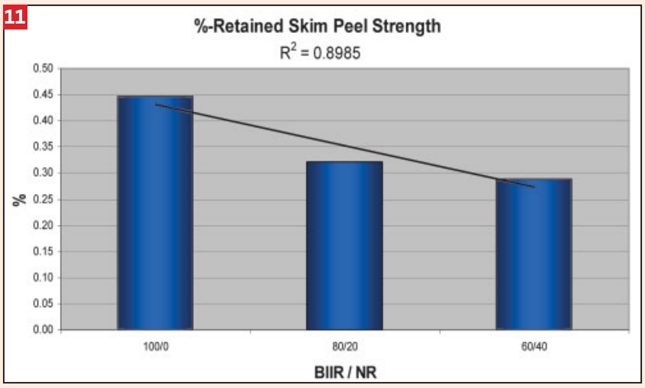
8 Durability on a 28.5 cm Wheel versus Inflation Pressure Retention Loss Rate



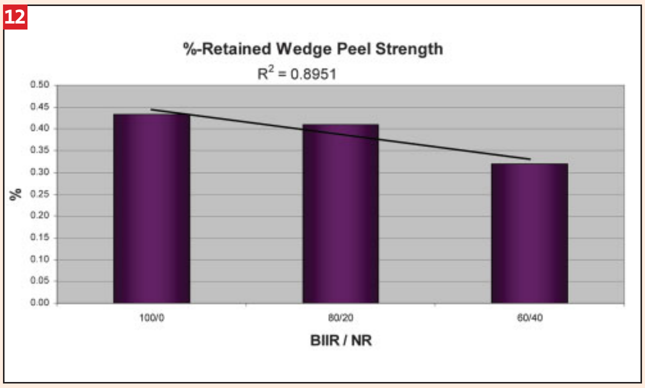
9 Durability on a 1.7 m Wheel versus Bromobutyl Rubber Content in the Innerliner



10 Durability on a 1.7 m Wheel versus Inflation Pressure Retention Loss Rate



11 %-Retained Skim Peel Strength versus Bromobutyl Rubber Content in the Innerliner



12 %-Retained Wedge Peel Strength versus Bromobutyl Rubber Content in the Innerliner

phr bromobutyl rubber innerliner has the desirably lowest Inflation Pressure Retention and ICP values (Table 2).

Two tire durability tests were performed: Tread Separation, and FMVSS 139 Endurance but testing until tire failure. All tires failures were the result of belt-to-belt separations. Tires run on the small (28.5 cm) test wheel at 80 km/h until failure showed a high correlation to both Bromobutyl Rubber content in the innerliner compound ($R^2 = 0.953$) and to the Inflation Pressure Retention loss rate values ($R^2 = 0.925$), see Figures 7 and 8.

Tires were run on the 1.7 m test wheel according to Federal Motor Vehicle Safety Standards 139 Endurance at 120 km/h until the 34-hour test period had elapsed. Tires were inspected, had no visible flaws, and were run until failure. Figures 9 and 10 show a good correlation of hours to failure versus Bromobutyl Rubber content in the innerliner ($R^2 = 0.8826$) and to Inflation Pressure Retention loss rates ($R2^2 = 0.842$). For each road wheel durability test, the tire having the lowest Inflation Pressure Retention loss values, which contained the 100 phr bromobutyl rubber innerliner, performed best as determined by the longest number of hours run before failure by a belt-to-belt separation.

Tires that had run until failure on the Tread Separation Tester (28.5 cm wheel) were dissected and specific components analyzed. They were tires with a 100 phr Bromobutyl Rubber innerliner, and tires with an 80/20 and 60/40 blend of Bromobutyl Rubber/Natural Rubber. A new tire was used as a control to obtain original values.

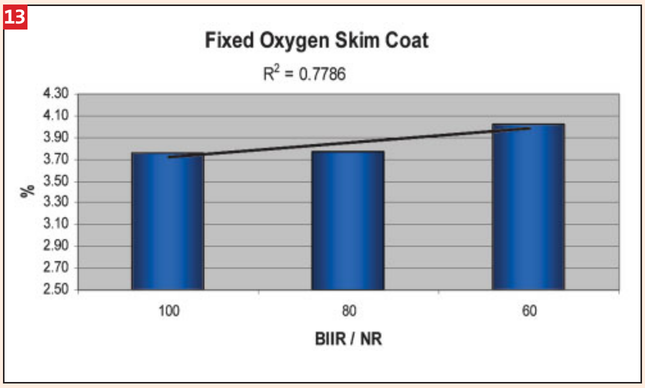
The 100 % modulus values of the wedge compounds did not correlate to either Bromobutyl Rubber content in the innerliner or to Tire Inflation Pressure Retention loss values. Elongation to break values did show a qualitative correlation to Bromobutyl Rubber content ($R^2 = 0.829$) and to Tire Inflation Pressure Retention ($R^2 = 0.77$). Crosslink density of either the skim or wedge compounds did not correlate to either Bromobutyl Rubber content in the innerliner or to Tire Inflation Pressure Retention values.

Belt-to-belt peel strength values of the skim composites shows good correlations to the Bromobutyl Rubber content in the innerliner ($R^2 = 0.8985$) or to Tire Inflation Pressure Retention values ($R^2 = 0.845$), see Figures 11 and 12. Similar good correlations were also obtained for the wedge composite ($R^2 = 0.8951$ to BIIR and $R^2 = 0.895$ to Inflation Pressure Retention, see Figure 12.

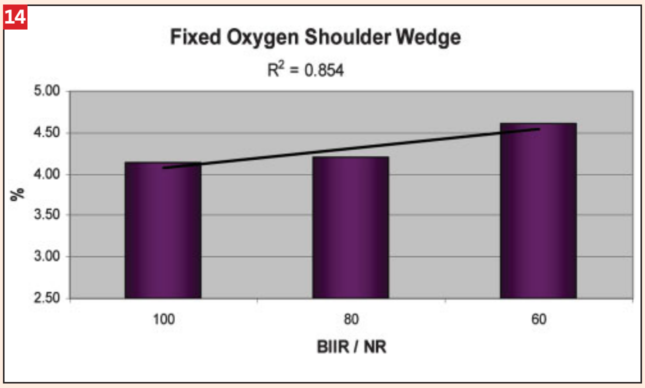
Fixed oxygen contents showed a good correlation to the Bromobutyl Rubber content for both the skim coat ($R^2 = 0.778$) and shoulder wedge ($R^2 = 0.854$) compounds; Figures 13 and 14.

When normalized for the differences in the number of hours run until failure on the Tread Separation Tester, quantitative correlations were obtained for the Fixed Oxygen contents of the skim coat ($R^2 = 0.99999$) and shoulder wedge compounds ($R^2 = 0.9996$) to Tire Inflation Pressure Retention loss rates. Also, normalized Fixed Oxygen contents of the skim coat ($R^2 = 0.9985$) and shoulder wedge compounds ($R^2 = 0.9997$) quantitatively correlated to Tire Intracarcass Pressure values.

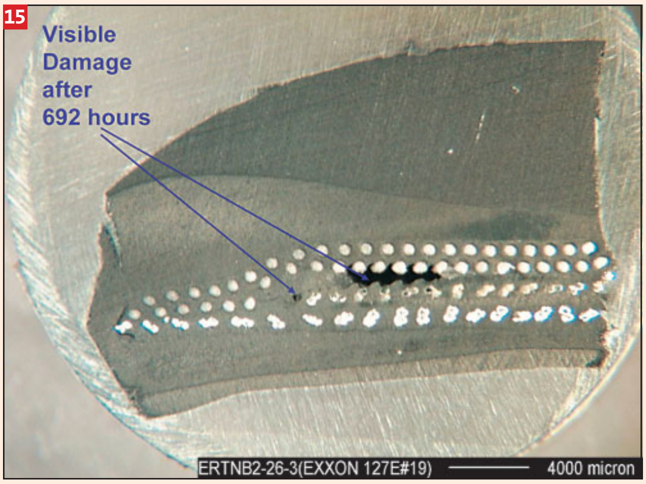
Modulus profiling of the shoulder region was performed on a new tire with an innerliner having a Bromobutyl Rubber/Natural Rubber ratio of 60/40, and three tires



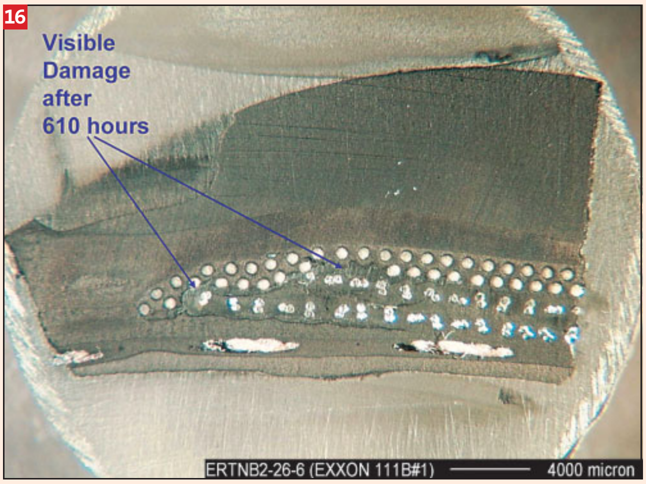
13 Fixed Oxygen Content of the Skim Coat versus Bromobutyl Rubber Content in the Innerliner



14 Fixed Oxygen Content of the Shoulder Wedge versus Bromobutyl Rubber Content in the Innerliner



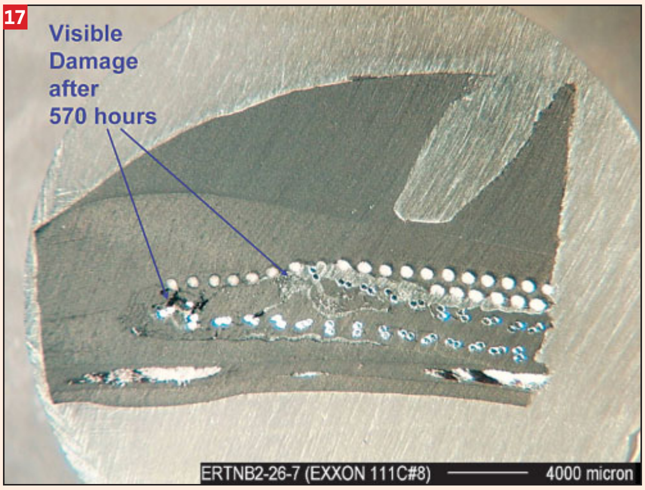
15 Modulus Profile Specimen for the Tire having a 100 phr Bromobutyl Rubber Innerliner



16 Modulus Profile Specimen for the Tire having an 80/20 Bromobutyl Rubber/Natural Rubber Innerliner

that had been tested to failure on the Tread Separation Tester. They were a 100 phr Bromobutyl Rubber and an 80/20 and 60/40 Bromobutyl Rubber/Natural Rubber blend innerliner. Figures 15–17 shows the belt-to-belt separations that were observed for three tested tires. Figure 18 shows the Modulus Profiles.

Average modulus values of each tire component were plotted, see Figure 19, and when normalized for differences in the failure times of the three tires it is seen that the tire with the 100phr Bromobutyl Rubber innerliner best protected all other internal rubber components of the tire from age hardening, see Figure 20.



17 Modulus Profile Specimen for the Tire having a 60/40 Bromobutyl Rubber/Natural Rubber Innerliner

Summary

Halobutyl rubber innerliners are the best at retaining pressure, both air and moisture, and minimizes the temperature-dependence of air permeability. Butyl rubber is approximately an order of magnitude less permeable than the other elastomers studied [3]. The quality of the innerliner compound is improved by using a 100 phr bromobutyl rubber formulation, since it affords the highest percentage of retained tensile properties upon air-oven aging [24].

The integrity of the tire is improved significantly by using a 100 phr bromobutyl rubber formulation in the innerliner, since it minimizes Tire Inflation Pressure Retention loss rates, minimizes the development of Tire Intracarcass Pressure, and maximizes Tire Durability as determined by measuring

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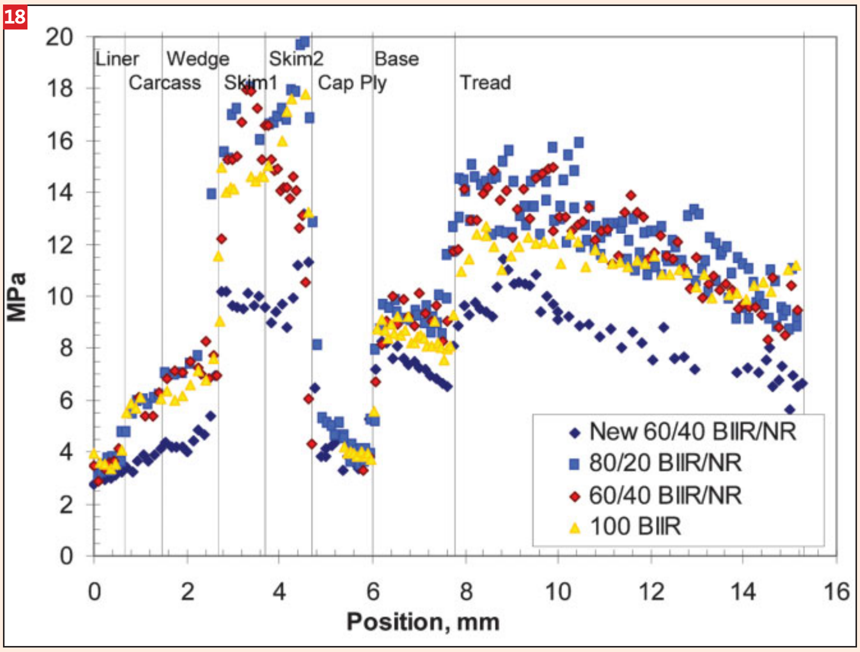

18 Modulus Profile plots of new and three tested tires

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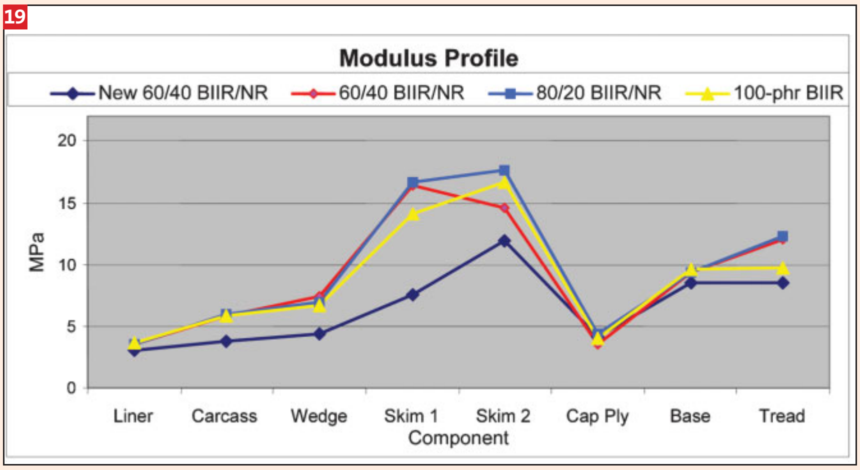

19 Plots of the average Modulus values of each tire component in the shoulder region.

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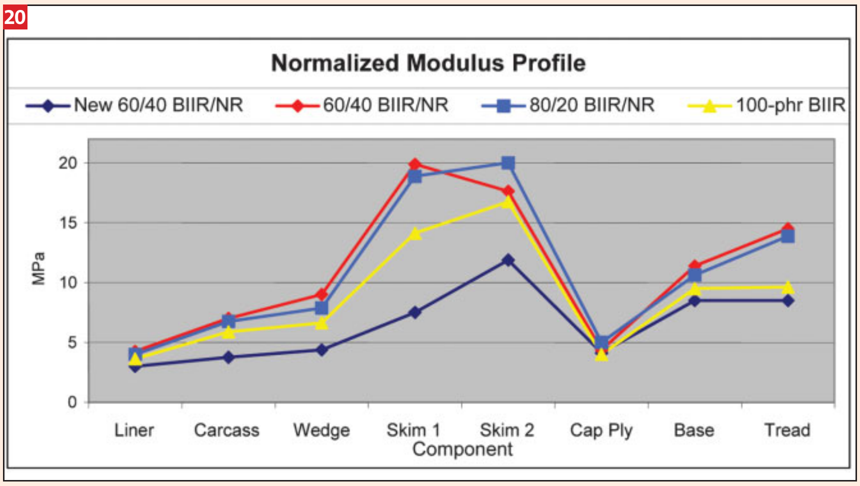

20 Plots of the normalized Modulus values of each tire component in the shoulder region.

the hours to failure by a belt-to-belt separation on indoor road wheels.

Statistical analysis of Tire Durability test results to the Bromobutyl Rubber content of the innerliner, to the Tire Inflation Pressure Retention loss rates, and to Tire Intracarcass Pressure values showed quantitative correlation to Tread Separation Test results and good correlations to modified FMVSS 139 Endurance test (run to tire failure) results. Good statistical correlations of the belt-to-belt Peel Strengths and the Fixed Oxygen contents of the skim and wedge composites are obtained to the Bromobutyl Rubber content in the innerliner and to the Inflation Pressure Retention loss rates of the tire. Modulus Profiling studies shows that the tire with the 100 phr Bromobutyl Rubber innerliner best protects the other internal rubber components of the tire from age hardening.

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