SHEAROGRAPHIC ANALYSIS OF TIRE AGING

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ABSTRACT

Inflation pressure retention (IPR) is a key predictive parameter to improving tire durability. Improved Tire IPR, manifested as reduced percent pressure loss per month values, has statistically been shown to be a direct result of innerliner compounds made with increasing amounts of halobutyl rubber when other potential variables are constant. Roadwheel performance of tires is best when using 100-phr of halobutyl rubber in the innerliner compound. This affords a tire with desirably low IPR loss rate values, desirably low tire intracarcass pressure (ICP) values, and increased tire durability as measured in hours until failure on laboratory roadwheels. Analysis of failed tires demonstrates the effectiveness of halobutyl rubber in protecting other select internal components of the tire such as the natural rubber skim coat compound. Shearography is used to measure the crack growth at the belt edge of oven-aged tires that had been prepared with varying amounts of bromobutyl and natural rubbers in the innerliner when these tires are run on a laboratory roadwheel. Statistically significant results are obtained as a function of both roadwheel time and bromobutyl rubber content in the tire innerliner.

INTRODUCTION

The innerliner is formulated to provide flex fatigue resistance, aging resistance and adhesion to the ply coat compound for radial tires[1-2]. Butyl rubber[3-5] (IIR) is the copolymer of isobutylene and about 2% of isoprene, and has about an order of magnitude lower vapor transmission than other elastomers including natural rubber, styrene-butadiene rubber, nitrile rubber and chloroprene rubber[6]. 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 used in carcass coat stocks such as natural rubber, styrene-butadiene rubber and butadiene rubber, 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[7]. As an example, three repeat units of cis-polyisoprene totaling fifteen carbon atoms occupy greater 3-dimensional space than do four repeat units of polyisobutylene which contains a total of sixteen carbon atoms. This is a result of the sp^3 hybridization of each carbon atom in polyisobutylene affording 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 repeat unit in natural rubber.

Previously, we[8-11] have presented statistically quantitative results of the effect that the bromobutyl rubber content in the innerliner formulation has upon the tire performance properties of inflation pressure retention (IPR), intracarcass pressure (ICP) and durability as measured in hours to failure on laboratory roadwheels. Innerliners with 100-phr bromobutyl rubber (BIIR) and 80/20 and 60/40 blends of BIIR/natural rubber were studied in P205/60 HR15 and P205/60 SR15 radial passenger tires. Tires with a 100-phr bromobutyl innerliner had the lowest IPR (Figure 1), lowest ICP (Figure 2) and highest laboratory roadwheel durability values (Figure 3).

In addition, we[11] previously presented results using shearography[12] as a non-destructive test in order to quantify the cracks that are formed in the belt edge areas of aged tires. Now we extend those results by showing the effect that Tire IPR loss rate values, resulting from the varying amounts of bromobutyl rubber used in the innerliner formulations, has upon the oxidative aging process of the belt area of tires that are oven aged followed by testing on a laboratory roadwheel.

EXPERIMENTAL

Bromobutyl rubber used is BIIR 2222 (ExxonMobil Chemical) and the natural rubber grade is SMR 20. All other ingredients were the commercial tire factory materials. Model innerliner formulations affording different IPR values were used, see Table I. Compounds were mixed in the factory using a two-step sequence in internal mixers having tangential rotors. First stage masterbatch mixing was completed using a GK400 mixer followed by sheeting out on an extruder with roller die. Second step finalization was completed in a GK160 mixer and stocks were sheeted out on a two-roll mill. A cold-feed pin extruder was used to profile each innerliner compound. P205/60 SR15 tires were built with the three model innerliner compounds using automatic building machines, and tires were cured as usual. Optical analysis showed that cured tire innerliner thicknesses averaged 1.0 mm for all tires.

Inflation pressure retention loss rate values were measured in duplicate following ASTM F-1112-00 procedures[13], but was modified by using electronic transducers to continuously monitor tire pressures. Use of this procedure effectively shortens the total test period to 42 days, which included a 14-day stabilization period primarily needed due to the tire intracarcass pressure effect. IPR loss rate data for the first 14 days of testing was recorded and analyzed, but was not used in calculating IPR loss rate values to afford a 28-day actual test time period. Tire IPR loss values are reported as the percent pressure loss per month.

Intracarcass Pressure was measured in duplicate for tires on standard commercial rims inflated to 240 kPa. Typically five or six calibrated gauges with hypodermic needles were inserted with the needle tip set on the cords. Readings were taken daily until the pressure equilibrated, normally two months, and are reported as the average of at least four gauges each for at least two tires.

The Federal Motor Vehicle Safety Standards (FMVSS) 139 test procedures[14] were performed in duplicate using a 1.707-m diameter laboratory roadwheel of an All Well Tire Testing Machine Model AW-TT-2A-M4 running at 38°C in the ExxonMobil Chemical laboratory in Bangalore, India. Briefly, the FMVSS 139 Endurance test procedure is to run the air-inflated (cold inflation pressure = 180 kPa; 26 psi) tire at 120 km/h (80 m/h) for four hours at 85% of maximum rated load, followed by running for six hours at 90% load, which is followed by running for 24 hours at 100% load. Tires are inspected visually for any flaws.

New tires were aged in an over after inflating with dry air to 240 kPa cold inflation pressure, checking for leaks, placing them vertically on a mobile tire rack, and rolling the rack into a walk-in air-circulating temperature-controlled room that had been pre-equilibrated at 60^{o}C. Tires were aged for eight weeks without checking the air pressure or reinflating.

Shearography[13] was performed using an ITT Compact (SDS Systemtechnik GmbH) instrument in the Akron Rubber Development Laboratory in Akron, Ohio. Measurements, for example see Figure 4, were taken for new tires, oven-aged tires, and oven-aged tires that were run on the roadwheel by following the FMVSS 139 Endurance / SUL procedure until tire failure. A complete 360 degree view of the tire is obtained in nine consecutive 40^{o} pictures, see Figure 5.

Measurements were made for oven-aged tires: (1) after four-hour of running at 85% load (first step of FMVSS 139 Endurance), (2) after completing the required six-hour run at 90% load (ten hours of total roadwheel time), (3) after each of four six-hour time periods of running at 100% load corresponding to the required 24 hours run at 100% load (respectively 16, 22, 28 and 34 hours of total roadwheel time), and (4) after each four-hour run time period during which a +10% increase in load was applied beyond 100% (called stepped-up load (SUL)) until tire failure occurred on the roadwheel. Roadwheel testing was performed at the Akron Rubber Development Laboratory using a servo- hydraulically controlled horizontal 6-station 1.7-meter drum. The mounting dismounting of tires was facilitated by careful slow speed unseating of the tire rim assembly using a Rhino TC 850 machine to release the tire for shearographic measurements reducing the severity of the stresses on the bead area by prying and/or bending at each step.

SAS JPM 6.0 software was used to statistically analyze all data.

RESULTS AND DISCUSSION

Innerliner Compounds

Physical and aged physical properties of innerliner compounds have previously been reported[9]. Aged properties were adversely changed by replacing bromobutyl rubber with natural rubber in this innerliner formulation, see Table I. Air permeability showed a quantitative, linear (R^2 = 0.99) decrease with increasing bromobutyl rubber content in the innerliner compound.

New Tires

Tire inflation pressure retention loss rate values (IPR; see Figure 1, R^2>0.99) and intracarcass pressure (ICP; see Figure 2, R^2>0.96) values for both the P205/60 HR15 and P205/60 SR15 sets of radial passenger tires decreased linearly with increasing bromobutyl rubber content in the innerliner compound. Statistically significant quantitative correlations were obtained. The tire having a 100-phr bromobutyl rubber innerliner has the desirably lowest Tire IPR loss rate and Tire ICP values regardless of the speed rating[8-11].

Three laboratory roadwheel durability tests were performed on new tires until failure:

(1) Tread Separation (28.5 cm diameter laboratory drum) at 80 km/h, see Figure 3[11],

(2) FMVSS 109 Endurance (1.7 m diameter laboratory wheel) at 80 km/h, but modified by continuing to test until failure after that tire had successfully completed the specified 34-hour roadwheel test and was inspected, see Figure 6, and

(3) FMVSS 139 Endurance (1.7 m diameter laboratory wheel) at 120 km/h, but modified by continuing to test until failure after that tire had successfully completed the specified 34-hour roadwheel test and was inspected, see also Figure 6.

All tire failures were the result of belt area separations such as belt-to-belt, belt-to-carcass and/or belt-to-tread cracking. Tires were visually inspected and were also cut and analyzed as needed to determine primary failures.

For each of the three laboratory roadwheel durability tests, the tire having the highest bromobutyl rubber content affording the lowest tire inflation pressure retention loss values performed best as determined by the longest number of hours run on the roadwheel before failing by a belt area separation. For Tread Separation and FMVSS 109 roadwheel durability testing at 80 km/h, a statistical correlation (R^2 ~0.95) was obtained for Tire IPR (or bromobutyl rubber level in phr) to hours run until failure. No correlation was obtained for these P205/60 SR15 tires when tested at 120 km/h.

Oven-aged Tires

New P205/60 SR15 tires were inflated with dry air to 240 kPa (35 psi), placed vertically on a rack and aged in an air-circulating walk-in oven for 56 days at 60^{o}C. Tire inflation pressures were not monitored nor were they re-inflated during this time period. Tires were dismounted and shipped to the Akron Rubber Development Laboratory for testing according to the FMVSS 139 Endurance / SUL procedure, but modified by measuring shearography at various time periods during roadwheel testing (see

Experimental). After completing the 34-hour test period corresponding to FMVSS 139 Endurance, tires were inspected and had no visible flaws.

Shearography analysis showed no internal laser Interferometry fringe patterns that are typically representative of defects larger than 1 mm^2 for either a new tire or the oven aged tire set prior to running on a roadwheel. Thus, simple oven aging of a tire does not result in any measurable cracking in the belt edge area detectable by shearography even though the dissection and analysis of oven-aged tires not run on a roadwheel had shown statistically significant changes in essentially all chemical and physical properties as a function of the %-oxygen in the filling gas, the inflation pressure of the tire, aging time in the oven, and oven temperature[8-11,15]. Chemical and physical property changes essentially show a quantitative correlation to the amount (phr) of bromobutyl rubber used in the innerliner formulation and to Tire IPR loss rate values when all other compounding and tire variables are kept constant[8-11].

Shearographic Analysis

Shearography measurements showed that there was no detectable internal cracking for tires simply oven aged or for tires run on the roadwheel for short time periods. Internal cracking in the belt edge area was first detected by shearography for the tire made with a 60/40 BIIR/NR innerliner after 16 hours of running on the roadwheel. The tire made with an 80/20 BIIR/NR innerliner first displayed detectable belt edge area cracking after 22 hours of running on the roadwheel. The tire made with a 100-phr bromobutyl rubber innerliner first displayed belt edge area cracking after 34 hours of running on the roadwheel. After 34 hours of total roadwheel testing, no flaws were observed for any tires by visual inspection; however, shearographic measurements show that extensive internal cracking is already occurring in the higher IPR tires, particularly the tire with IPR = 2.65 %-loss/month. Figure 7 shows an example of the shearography pattern obtained for each oven-aged tire (IPR = 1.45 (100-phr bromobutyl rubber), IPR = 2.0 (80/20 BIIR/NR), and IPR = 2.65 (60/40 BIIR/NR). After 34 hours of running on a roadwheel, there is essentially no cracking detectable by shearography for the tire with IPR = 1.45 (top picture), while belt edge cracking is detected for the tire with IPR = 2.0 (middle). Extensive cracking at the belt edge growing in-between the two belts is observed for the tire with the highest IPR = 2.65 loss rate value (bottom). Similar results were observed after 22, 28, 34, 38, and 42 hours of roadwheel testing.

Crack areas were determined for 24 circumferential sections, each spanning a 15 degree angle window around the tire to afford a 360-degree view of the cracking. Each window was integrated as a function of the roadwheel running time periods to obtain a time-dependent history of crack formation. Figure 8 is an example radar chart plotting the total cracking in each of the 24 windows measured after 34 hours of total roadwheel running time, which is the time period to complete the FMVSS 139 Endurance test. Recall that no flaws were observed for any tire by visual inspection.

Tire roadwheel testing was continued by applying the additional 10% load and running for another four-hour time period. The tire with the highest IPR = 2.65 %-loss/month value failed at 39.7 hours of total roadwheel running time at the 120% load step in the FMVSS 139 Endurance / Stepped-Up-Load test. The tire with IPR = 2.0 loss rate failed at 49.0 hours of total roadwheel running time at the 140% load step. The tire with the lowest IPR = 1.45 %-loss/month failed at 55.8 hours of total roadwheel running time at the 160% load step. All three tires failed by a belt edge separation, see Figure 9.

The crack areas in each of the 24 windows was integrated for each roadwheel time period in order to obtain a total crack area for the three oven-aged tires differing only in Tire IPR values as a result of the differing bromobutyl rubber levels used in the innerliner formulation, see Figure 10. Statistical analysis of cracking as a function of any specific roadwheel running time period clearly shows that belt area cracking can be quantitatively correlated (R^2>0.98) to Tire IPR loss rate values, for example see Figure 11. Similar results were observed after 22, 28, 34, 38, and 42 hours of roadwheel testing, but are not shown. Results were not obtained at longer time periods since the tire with IPR = 2.65 loss rate value failed at 39.7 hours of total testing time. Finally, statistical analysis also shows that the total time to failure on the laboratory roadwheel can also be quantitatively correlated (R^2=0.99) to Tire IPR loss rate values, see Figure 12.

Aging Mechanism

The present results are consistent with our previous work[8-11] and indicate that the probable mechanism of tire aging is (1) the natural rubber skim coat compound is oxidized by inflating the tire with air which contains about 21% oxygen and storing at elevated temperatures based upon fixed oxygen measurements[11], (2) the modulus of the belt coat natural rubber compound increases as a result of chemical oxidative aging based upon indentation modulus[16-18] measurements[11], and (3) measurable cracking occurs in the natural rubber compound at the belt edge and extends in-between the two steel belts for the aged tires only after mechanical exercising on the roadwheel. Tire failure eventually occurs as a result of growth in the belt edge cracking due to the continued running of the tire.

The tire with the lowest IPR loss rate values affords the measured lowest natural rubber skim coat oxidation, and the lowest modulus value increases in the skim coat compound, and significantly lower total belt-edge area cracking after roadwheel testing.

SUMMARY

The performance of new tires is improved significantly by using a 100-phr bromobutyl rubber in the innerliner formulation, since it desirably minimizes tire inflation pressure retention (IPR) monthly loss rate values, desirably minimizes the development of tire intracarcass pressure (ICP) values, and also desirably maximizes durability as measured by time to failure on a laboratory roadwheel. Statistically significant correlations ($R^2 > \sim 0.95$) for durability are obtained for new S-rated radial passenger tires when run on laboratory roadwheels at a speed of 80 km/h based upon both the Tread Separation test or the FMVSS 109 Endurance test (modified by testing until tire failure). There is no correlation to Tire IPR loss rate values or to the halobutyl rubber content in the innerliner when roadwheel testing is performed at a speed of 120 km/h according to FMVSS 139 Endurance conditions (until failure).

For inflated (240 kPa air), oven-aged (56 days in an air-circulating oven at 60^{o}C), roadwheel tested P205/60 SR15 tires, statistically significant quantitative correlations ($R^2 \sim 0.99$) are obtained between Tire IPR loss rate values and the total area of belt-edge cracking areas as measured by shearography.

Crack area results can be correlated for time periods totaling 28, 34, 38 and 42 hours of roadwheel running in this study. R^2 ~0.99 were obtained for correlations of shearography crack areas in the belt areas to Tire IPR loss rate values.

The present results are consistent with our previous work[8-11] and indicate that the probable mechanism of tire aging is (1) the natural rubber skim coat compound is oxidized by inflating the tire with air and storing at elevated temperatures based upon fixed oxygen measurements[11], (2) the modulus of the belt coat rubber compound increases as a result of chemical oxidative aging based upon indentation modulus measurements[11], and (3) cracking measurable by shearography occurs in the rubber compound at the belt edge and extends in-between the two belts for the aged tires only after mechanical exercising on the roadwheel. Tire failure ultimately occurs as a result of belt edge failures due to the continued running of the tire. The tire with the lowest IPR loss rate values affords the measured lowest skim coat oxidation, and lowest compound modulus value increases, and significantly lower total belt edge area cracking after roadwheel testing.

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Table I.
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

Figure 1. Inflation Pressure Retention Tire Test Results.

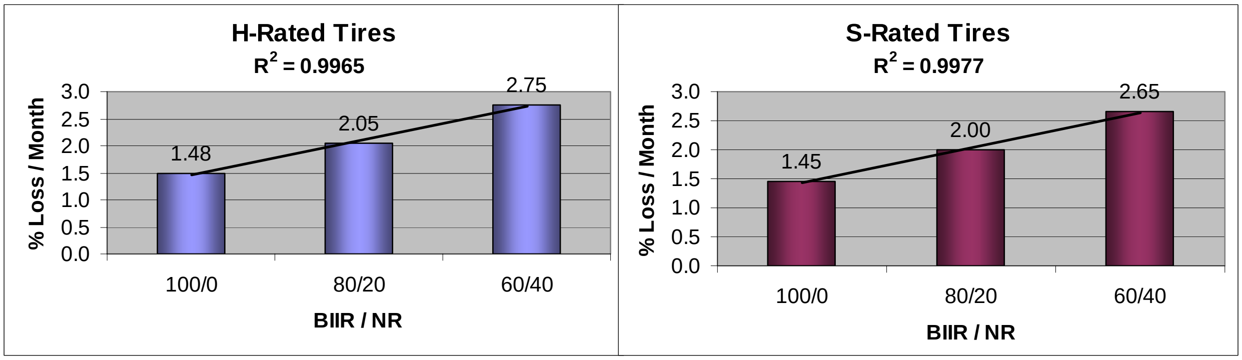

Figure 2. Intracarcass Pressure Tire Test Results.

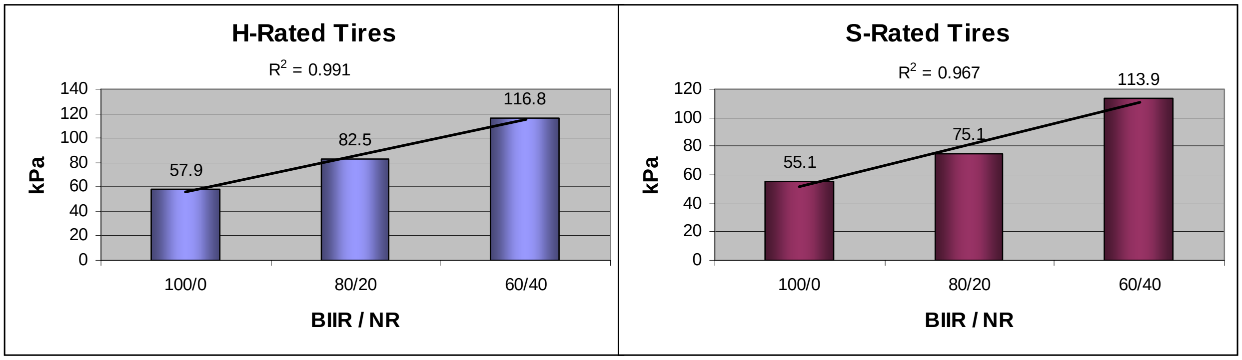

Figure 3. Tread Separation Tire Roadwheel (28.5 cm) Durability Test Results.

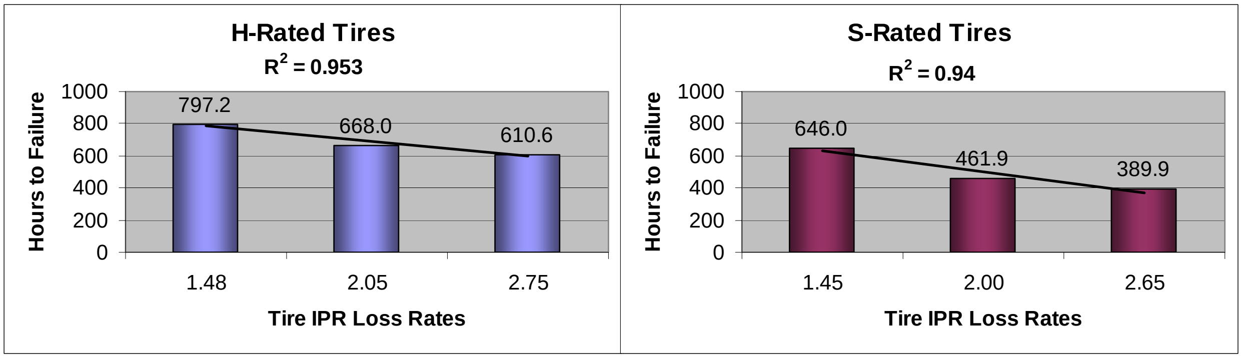

Figure 4. Tire Cross Section Highlighting the Belt-Edge Area of Interest and Showing an Example of a Shearography Pattern Obtained (see insert).

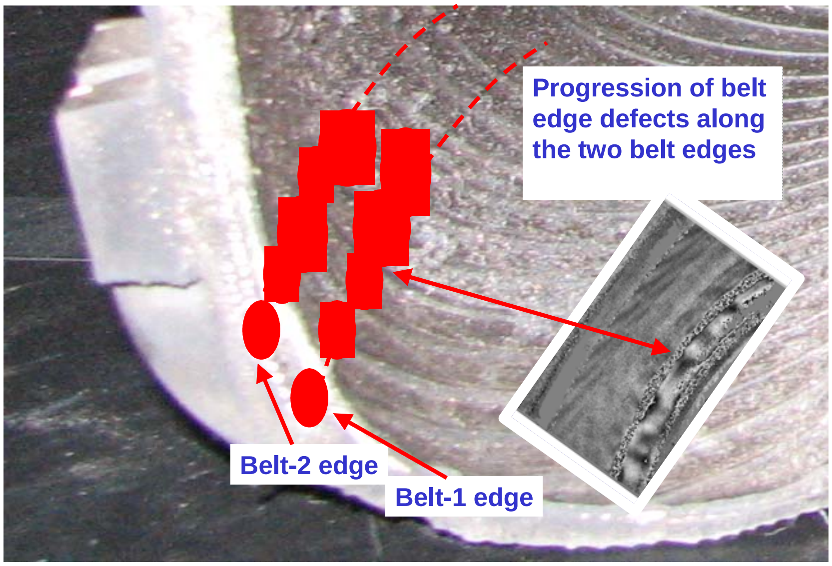

Figure 5. Nine 40-degree Shearographic Sections of the Belt-Edge Areas Showing a 360-degree View of Surface Deformations (denoted by boxes) Representing Internal Defects.

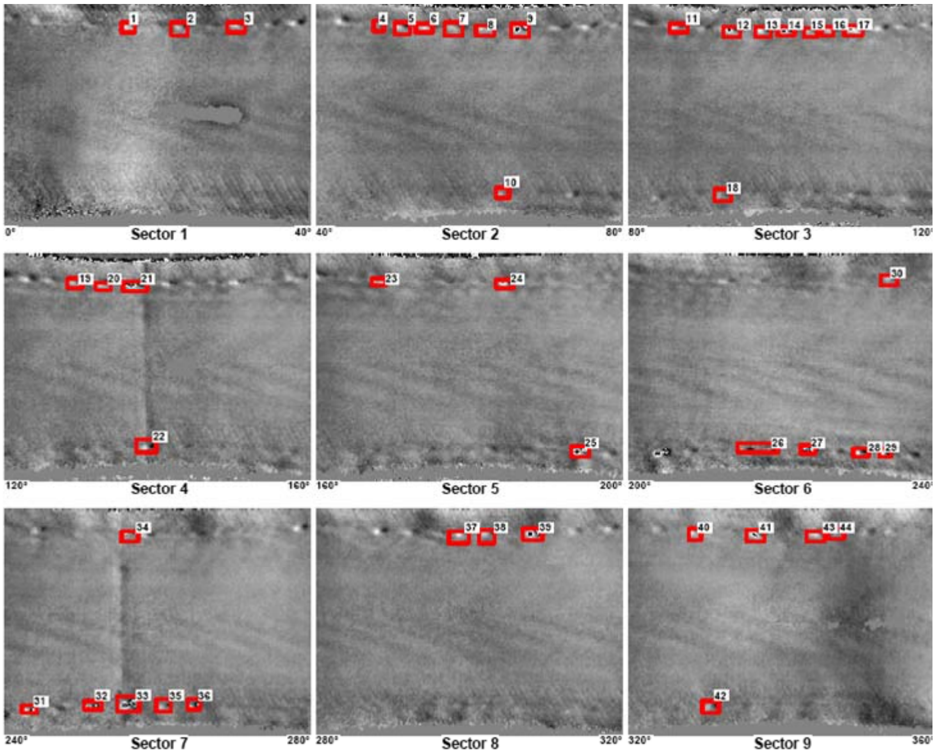

Figure 6. FMVSS 109 (to failure) and FMVSS 139 Endurance (to failure) Roadwheel (1.7 m) Durability Test Results for P205/60 SR15 Tires.

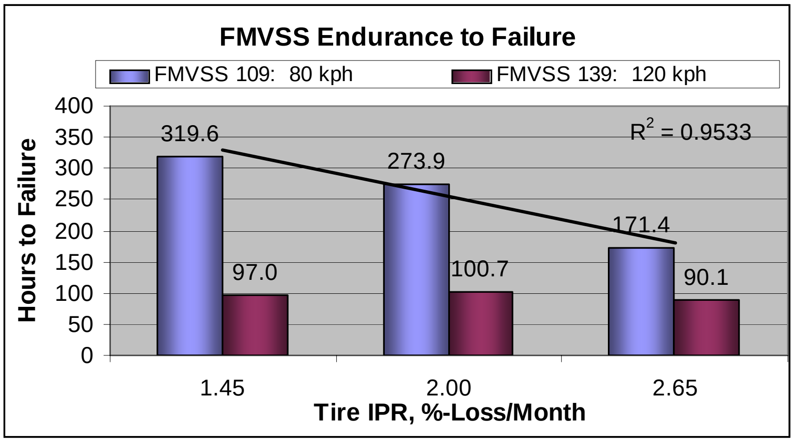

Figure 7. Example Shearography Patterns for Tires After 34 Hours of Total Roadwheel Run Times: Tire with IPR = 1.45 (100-phr bromobutyl rubber) is top picture; Tire with IPR = 2.0 (80/20 BIIR/NR) is middle; and Tire with IPR = 2.65 (60/40 BIIR/NR) is bottom.

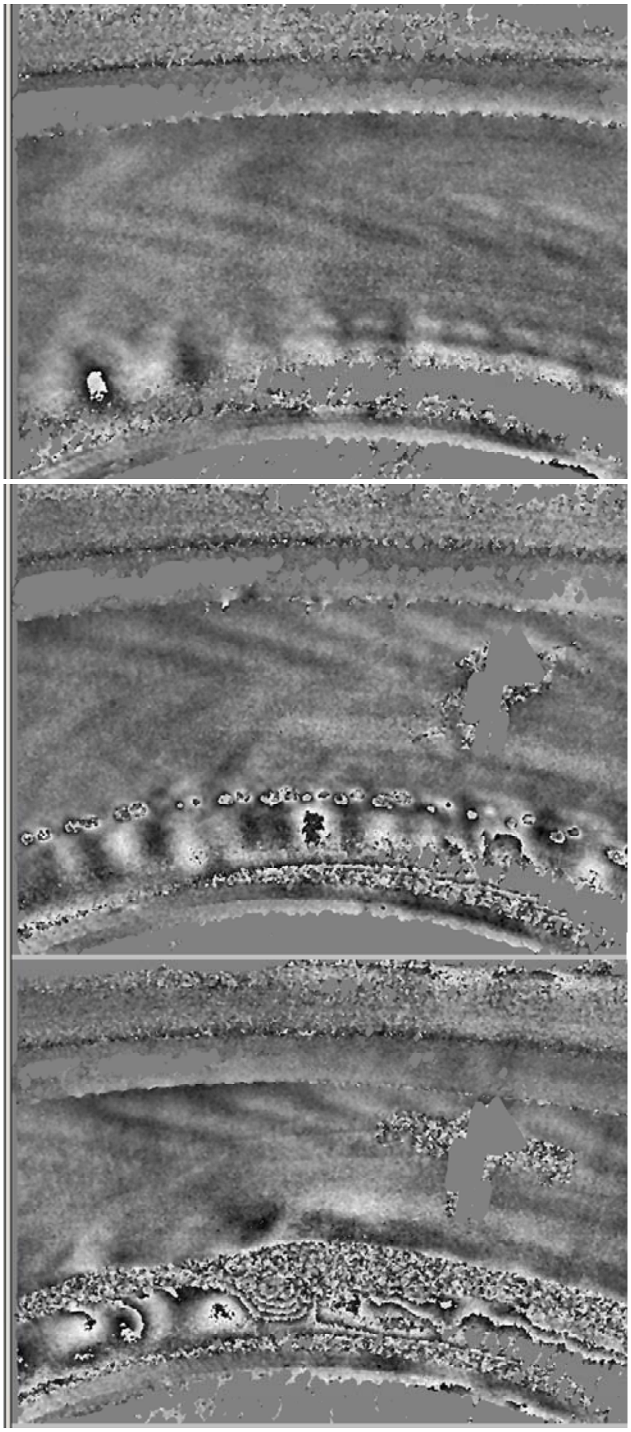

Figure 8. Radar Chart of Integrated Cracking Obtained by Shearography of Oven-aged Tires after 34 Hours of Total Roadwheel Run Time: Tire with IPR = 1.45 (100-phr bromobutyl rubber) is represented as green triangles; Tire with IPR = 2.0 (80/20 BIIR/NR) is blue x symbols; and Tire with IPR = 2.65 (60/40 BIIR/NR) is red diamonds.

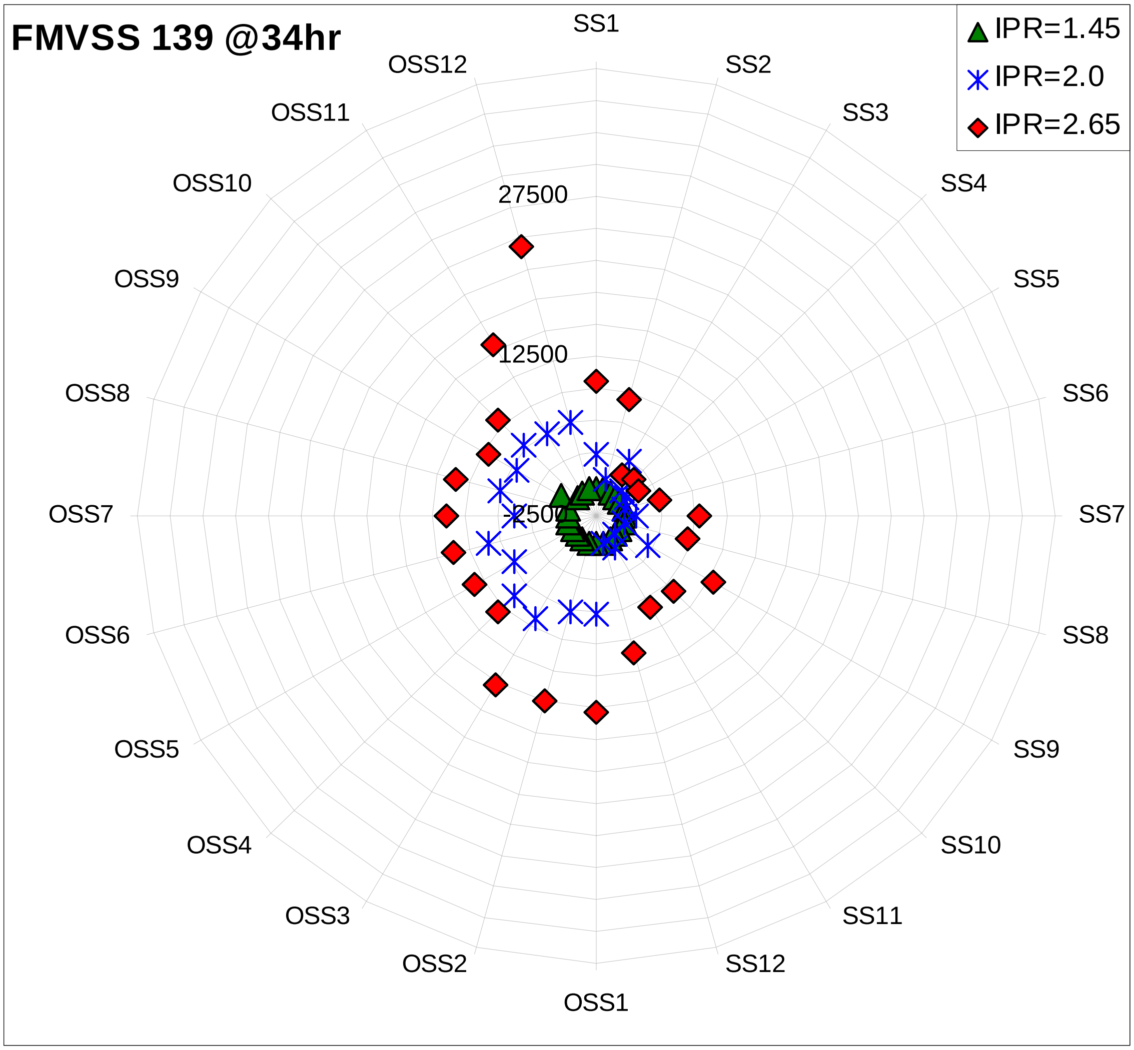

Figure 9. Photograph of Tire Section After Failure: Tire with IPR = 1.45 (100-phr bromobutyl rubber) failed at 55.8 hours (top picture); Tire with IPR = 2.0 (80/20 BIIR/NR) failed at 49.0 hours (middle); and Tire with IPR = 2.65 (60/40 BIIR/NR) failed at 39.7 hours (bottom).

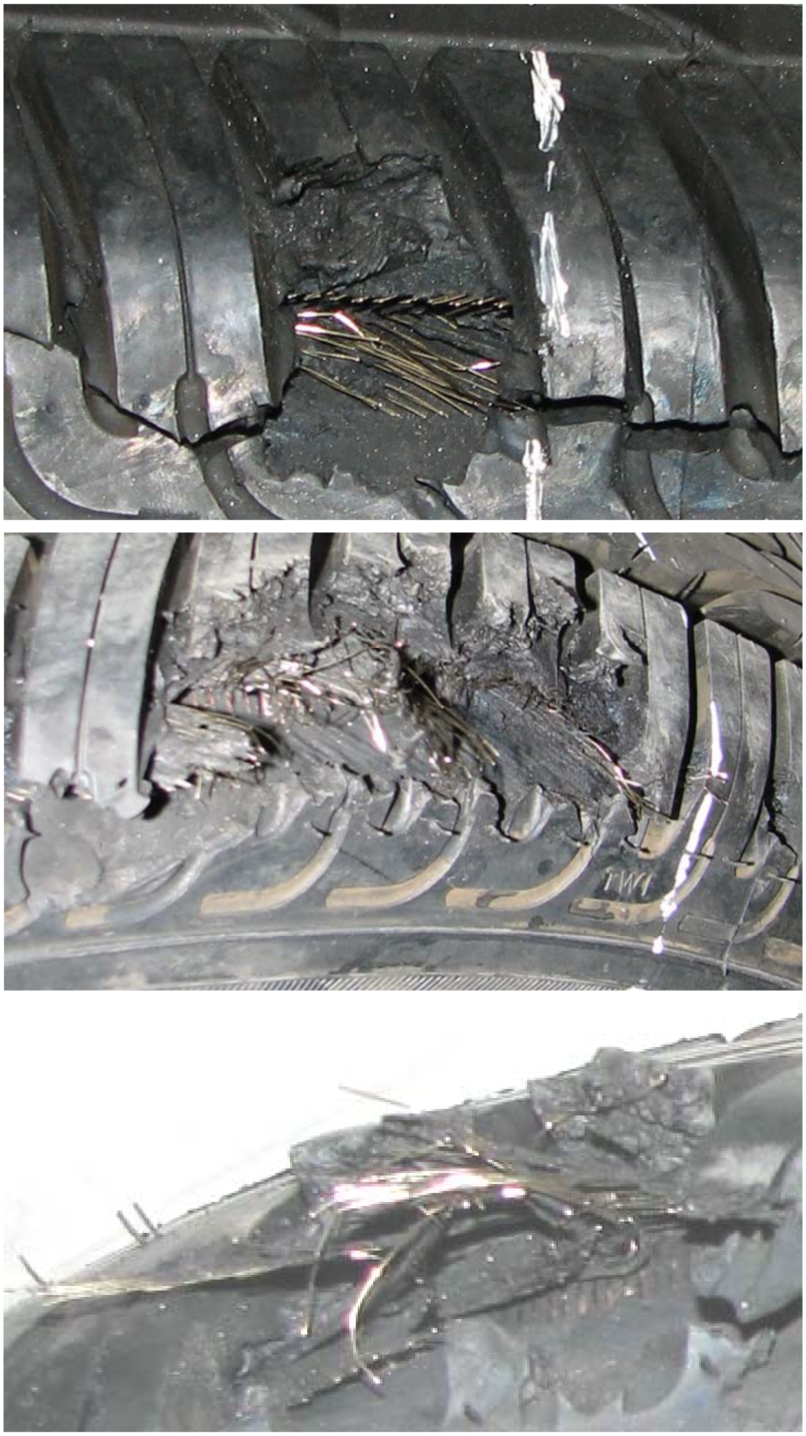

Figure 10. Total Shearography Crack Areas (mm^2) for the Oven-aged and Roadwheel-tested P205/60 SR15 Tires as a Function of Roadwheel Run Times.

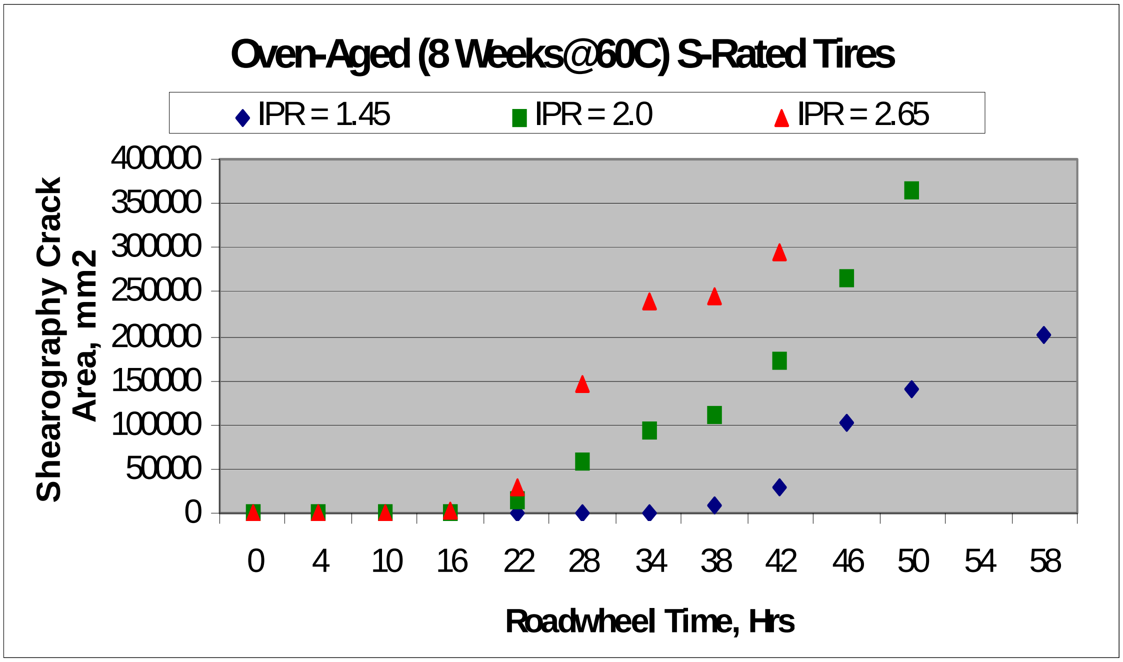

Figure 11. Correlation of Tire IPR Loss Rate Values (%/month) to Total Shearography Crack Areas (mm^2) for the Oven-aged and Roadwheel-tested P205/60 SR15 Tires after 34 (top graph), 38 (middle), and 42 Hours (bottom) of Total Running Time.

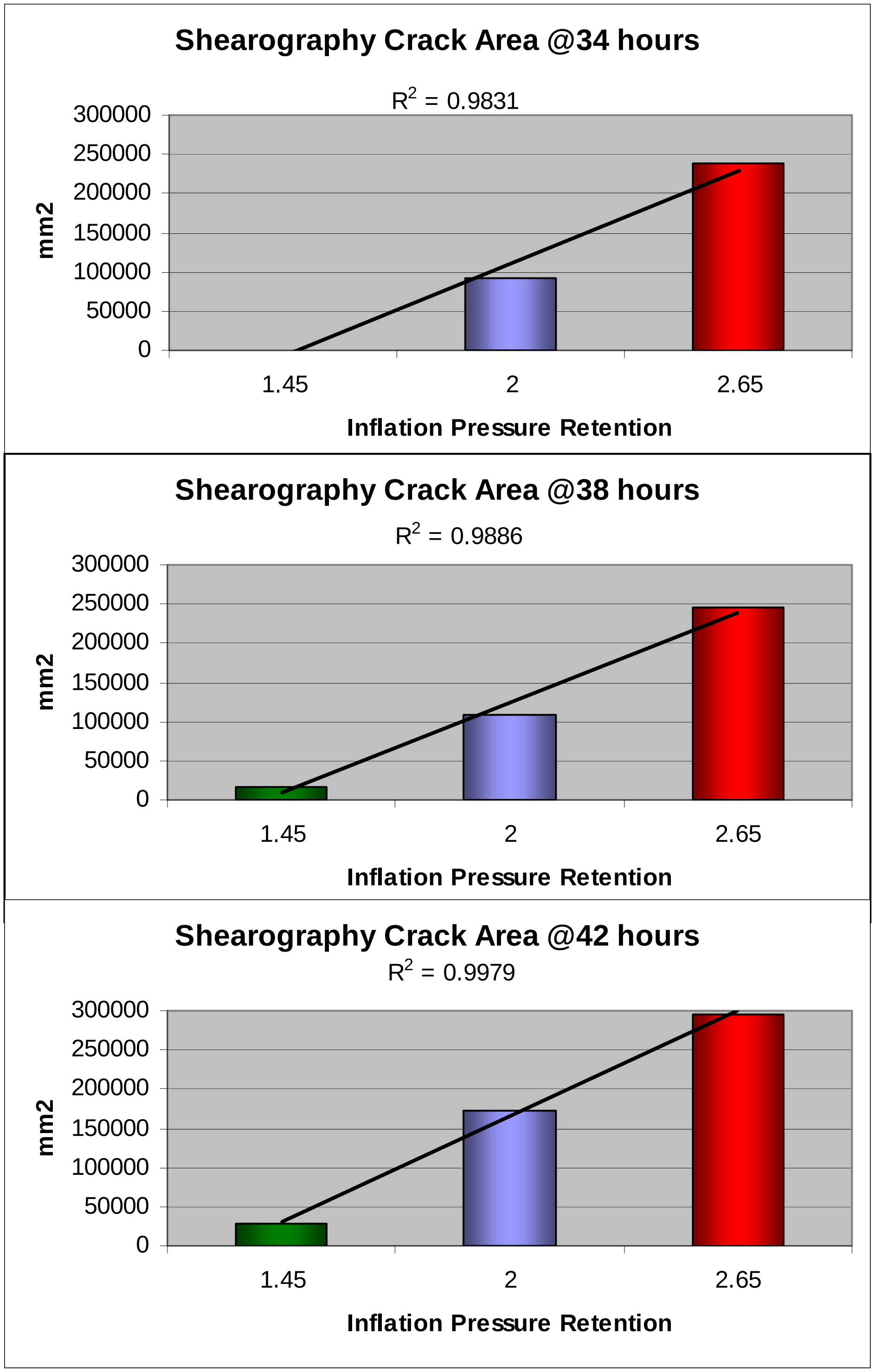

Figure 12. Correlation of Tire IPR Loss Rate Values (%/month) to Total Hours to Failure on the Laboratory Roadwheel for oven-aged P205/60 SR15 Tires.