U.S. Department
of Transportation
**National Highway
Traffic Safety
Administration**

NHTSA
www.nhtsa.gov

DOT HS 811 126 **March 2009**

Oxygen Consumption Rate in New and In-Service BFGoodrich P195/65R15 Tires

This document is available to the public from the National Technical Information Service, Springfield, Virginia 22161

DISCLAIMER

This publication is distributed by the U.S. Department of Transportation, National Highway Traffic Safety Administration, in the interest of information exchange. The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Department of Transportation or the National Highway Traffic Safety Administration. The United States Government assumes no liability for its contents or use thereof. If trade names, manufacturers' names, or specific products are mentioned, it is because they are considered essential to the object of the publication and should not be construed as an endorsement. The United States Government does not endorse products or manufacturers.

TECHNICAL REPORT DOCUMENTATION PAGE

1. Report No. DOT HS 811 126	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Oxygen Consumption Rate in New and In-Service BFGoodrich P195/65R15 Tires		5. Report Date March 2009 6. Performing Organization Code
7. Author(s) Edward R. Terrill, Ph.D., Mark Centea - Akron Rubber Development Laboratory, Inc.; James D. MacIsaac Jr. - National Highway Traffic Safety Administration		8. Performing Organization Report No.
9. Performing Organization Name and Address Akron Rubber Development Laboratory, Inc. 2887 Gilchrist Rd. Akron, Ohio 44305		10. Work Unit No. (TRAIS) 11. Contract or Grant No. DTNH22-03-D-08660
12. Sponsoring Agency Name and Address National Highway Traffic Safety Administration 1200 New Jersey Avenue SE Washington, DC 20590		13. Type of Report and Period Covered Final 14. Sponsoring Agency Code

15. Supplementary Notes

Project support, testing, and analysis services provided by the Akron Rubber Development Laboratory and Transportation Research Center, Inc.

16. Abstract

This report is the second in a series of scientific reports intended to provide an understanding of the chemical reactions responsible for the degradation of light vehicle tires during on-vehicle service. The report series was used to guide the agency's development of a laboratory-based accelerated service life test for light vehicle tires ("tire aging test"). This particular report examines the changes observed in the fixed oxygen level, elongation-to-break, and inter-belt peel adhesion of the belt-coat compound of an original equipment BFGoodrich tire model after varying lengths of service and accumulated mileages in Phoenix, Arizona. Since the degradation of the tire rubber compounds in passenger vehicle tires is known to be an oxidative process, samples of the belt-coat compound a new tire were repeatedly oven aged at different temperatures and oxygen partial pressures and compared to samples retrieved from in-service tires of the same model. Tensile elongation-to-break and ultra-sensitive oxygen consumption rate testing were used to assess the property decay kinetics of the belt-coat compound as a function of temperature and oxygen partial pressure (two primary variables in a tire aging test).

While the initial oxygen consumption rate of belt-coat compound in the new tire was about two to three times faster than those observed for in-service tires, it eventually approached the rate of in-service tires after many iterations of oven aging. The oxygen consumption rate was found to be more sensitive to the partial pressure of oxygen at low temperatures than higher temperatures. This has implications for the rate of material property evolution at ambient temperatures for tires that use higher inflation pressures (higher partial pressures of oxygen) in service, such as light truck tires. It may also lessen the influence of oxygen partial pressure at elevated temperatures such as those used for tire oven aging. The results were incorporated into the Diffusion Limited Oxidation computer model, which predicted that the belt-coat compound of this tire model would undergo about 60 percent of its aging while stationary (parked) and the other 40 percent while in rolling operation in Phoenix.

17. Key Words Tire, tire aging, rubber, tire safety, oxygen consumption, Phoenix, accelerated service life, belt-coat		18. Distribution Statement Report is posted at www.regulations.gov.	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 56	22. Price

Form DOT F 1700.7 (8-72) **Reproduction of completed page authorized**

TABLE OF CONTENTS

EXECUTIVE SUMMARY ..... **viii**
DEFINITIONS **1**
BACKGROUND **1**
EXPERIMENTAL TECHNIQUES **5**
Tire Dissection 5
Oven Aging 5
Tensile Properties 5
Oxygen Consumption Rates 5
RESULTS **7**
Tensile Elongation-to-Break Data 7
Oxygen Consumption Rate of the New Tire Belt-Coat Compound 10
Oxygen Consumption Rate of the In-Service Tires 19
Predicted Properties at Service Temperatures 29
Oxygen Consumption Rate as a Function of Oxygen Partial Pressure 30
Determination of Oxygen Consumption Rate in the Belt-Coat using the Diffusion Limited Oxidation Model 36
Shifted Tensile Data with the Effects of Oxygen Partial Pressure and In-Operation Time 39
SUMMARY **39**
REFERENCES **42**

LIST OF FIGURES

Figure 1. Fixed Oxygen in Belt-Coat Compound Versus Tire Age - NHTSA Phoenix Tire Study; Tire Type B 2
Figure 2. Tensile Elongation-to-Break of Belt-Coat Compound Versus Tire Age - NHTSA Phoenix Tire Study; Tire Type B 2
Figure 3. Average Inter-Belt Peel Adhesion, Belt-Coat Compound Versus Tire Age - NHTSA Phoenix Tire Study; Tire Type B 3
Figure 4. Average per Tire Tensile Elongation-to-Break Versus Average per Tire Percent Fixed Oxygen, Belt-Coat Compound - NHTSA Phoenix Tire Study; Tire Type B 4
Figure 5. Average Inter-Belt Peel Adhesion, Belt-Coat Compound Versus Average Ultimate Elongation - NHTSA Phoenix Tire Study; Tire Type B 4
Figure 6. Elongation-to-Break as a Function of Oven Aging Time for New Tire Belt-Coat Compound 8
Figure 7. Time-Temperature Superposition of Elongation-to-Break Data for New Tire Belt-Coat Compound 8
Figure 8. Elongation Shift Factors as a Function of Temperature for New Tire Belt-Coat Compound 9
Figure 9. Elongation-to-Break as a Function of Shifted Aging Time, Days at 65°C for New Tire Belt-Coat Compound 9
Figure 10. Elongation-to-Break as a Function of Shifted Aging Time, Days at 55°C for New Tire Belt-Coat Compound 10
Figure 11. Oxygen Consumption Rate of New Tire Belt-Coat Compound 11
Figure 12. Integrated Oxygen Consumption as a Function of Aging Time of the New Tire Belt-Coat Compound 11
Figure 13. Time-Temperature Superposition of Integrated Oxygen Consumption of the New Tire Belt-Coat Compound 12
Figure 14. Oxygen Consumption Shift Factors as a Function of Temperature of the New Tire Belt-Coat Compound 12
Figure 15. CO_2 Generation Rate of New Tire Belt-Coat Compound of the New Tire Belt-Coat Compound 13
Figure 16. Integrated CO_2 Generation as a Function of Aging Time of the New Tire Belt-Coat Compound 13
Figure 17. Time-Temperature Superposition of Integrated CO_2 Generation of the New Tire Belt-Coat Compound 14
Figure 18. CO_2 Generation Shift Factors as a Function of Temperature for the New Tire Belt-Coat Compound 14
Figure 19. CO Generation Rate of New Tire Belt-Coat Compound 15
Figure 20. Integrated CO Generation as a Function of Aging Time for New Tire Belt-Coat Compound 15
Figure 21. Time-Temperature Superposition of Integrated CO Generation for New Tire Belt-Coat Compound 16
Figure 22. CO Generation Shift Factors as a Function of Temperature of New Tire Belt-Coat Compound 16
Figure 23. Volatile Organic Generation Rate from New Tire Belt-Coat Compound 17
Figure 24. Integrated Volatile Organic Generation as a Function of Aging Time for New Tire Belt-Coat Compound 17

Figure 25. Time-Temperature Superposition of Integrated Volatile Organic Generation for New Tire Belt-Coat Compound 18
Figure 26. Volatile Organic Generation Shift Factors as a Function of Temperature for New Tire Belt-Coat compound 18
Figure 27. Summary of New Tire Shift Factors as a Function of Temperature for New Tire Belt-Coat Compound 19
Figure 28. Oxygen Consumption Rate of In-Service Tire Belt-Coat Compound 20
Figure 29. Integrated Oxygen Consumption as a Function of Aging Time for In-Service Tire Belt-Coat Compound 20
Figure 30. Time-Temperature Superposition of Integrated Volatile Organic Generation for In-Service Tire Belt-Coat Compound 21
Figure 31. Oxygen Consumption Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound 22
Figure 32. CO_2 Generation Rate of In-Service Tire Belt-Coat Compound for Tire Belt-Coat Compound 22
Figure 33. Integrated CO_2 Generation as a Function of Aging Time for In-Service Tire Belt-Coat Compound 23
Figure 34. Time-Temperature Superposition of Integrated CO_2 Generation for In-Service Tire Belt-Coat Compound 23
Figure 35. CO_2 Generation Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound 24
Figure 36. CO Generation Rate of In-Service Tire Belt-Coat Compound for In-Service Tire Belt-Coat Compound 24
Figure 37. Integrated CO Generation as a Function of Aging Time for In-Service Tire Belt-Coat Compound 25
Figure 38. Time-Temperature Superposition of Integrated CO Generation for In-Service Tire Belt-Coat Compound 25
Figure 39. CO Generation Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound 26
Figure 40. Volatile Organic Generation Rate of In-Service Tire Belt-Coat Compound for In-Service Tire Belt-Coat Compound 26
Figure 41. Integrated Volatile Organic Generation as a Function of Aging Time for In-service Tire Belt-Coat Compound 27
Figure 42. Time-Temperature Superposition of Integrated Volatile Organic Generation for In-Service Tire Belt-Coat Compound 27
Figure 43. Volatile Organic Generation Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound 28
Figure 44. Summary of In-Service Tire Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound 28
Figure 45. Elongation-to-Break as a Function of Shifted Aging Time, Years at 20°C 29
Figure 46. Comparison of Predicted Elongation-to-Break Results to In-Service Tire Elongation-to-Break Data 30
Figure 47. Effect of Oxygen Partial Pressure on Oxygen Consumption Rate for the New Tire .. 31
Figure 48. Effect of Oxygen Partial Pressure on Oxygen Consumption Rate for the In-Service Tire 32

Figure 49. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the New Tire at 20°C 32
Figure 50. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the New Tire at 55°C 33
Figure 51. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the New Tire at 65°C 33
Figure 52. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for In-Service Tire at 20°C 34
Figure 53. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the In-Service Tire at 55°C 34
Figure 54. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the In-Service Tire at 65°C 35
Figure 55. Beta as a Function of Temperature 35
Figure 56. Dynamic Shoulder Component Temperatures 37
Figure 57. DLO Model Prediction for the Oxygen Consumption Rates in an inflated, stationary tire in Phoenix, AZ 38
Figure 58. DLO Model Prediction for the Oxygen Consumption Rates in running tire 38
Figure 59. Comparison of Predicted Elongation-to-Break Results to In-Service Tire Elongation-to-Break Data 39

LIST OF TABLES

Table 1. List of Tires used in Oxidation Kinetics with Tensile Testing 5
Table 2. Roadwheel Test Conditions 36
Table 3. Shoulder Component Steady-State Running Temperatures Used in DLO Simulation .. 37

EXECUTIVE SUMMARY

As a result of the TREAD Act of 2000, NHTSA initiated an effort to develop a laboratory-based accelerated service life test for light vehicle tires (herein referred to as a "tire aging test"). In view of the fact that the rate of degradation in tire rubber components increases with temperature, NHTSA expected that the "worst case" in-service tires in the US would be found in the hottest states and therefore chose Phoenix, Arizona as the collection site. Part of the test development project included examining how an original equipment BFGoodrich Touring T/A SR4 P-metric P195/65R15 89S tire model changed during service by measuring its material properties after varying lengths of service and accumulated mileages in Phoenix. Significant changes in the fixed oxygen level and elongation-to-break of the belt-coat compound, as well as the inter-belt peel adhesion were observed with increasing durations of service. Since the degradation of the tire rubber compounds in passenger vehicle tires is known to be an oxidative process, a better understanding of the decay process and decay rate was desired as well as its effects on physical properties.

This report is the second in a series of scientific reports intended to provide an understanding of the chemical reactions responsible for the degradation of light vehicle tires during on-vehicle service. A primary goal of this report was to determine if the property decay rate at service life temperatures can be predicted from the combination of ultra-sensitive oxygen consumption rate data and physical property testing. Samples of the belt-coat compound of one new and four in-service tires of the same BFGoodrich model were subjected to tensile elongation to break and ultra-sensitive oxygen consumption rate testing to assess the property decay kinetics of the belt-coat compound. Additional samples from the new tire of were repeatedly oven-aged at different temperatures and oxygen partial pressures and compared to samples retrieved from in-service tires. One key question was to determine the reason for rapid decay in belt-coat properties of in-service tires during the first few years of service that eventually levels off with longer periods of service.

The kinetic study results were analyzed using time-temperature superposition to provide details about the aging kinetics and mechanism in tire belt-coat compounds. Combining the oxidation kinetics with tensile elongation-to-break aging studies provided a way to predict property decay in tires at service temperatures. The new tire belt-coat compound differed from samples retrieved from an in-service tire in its initial oxygen uptake rate. The new tire belt-coat compound oxidation rate was about two to three times faster than the in-service tire belt-coat compound. This may explain the rapid property decay observed in some in-service tires during their initial years (1-3 years) of service. The new tire compound oxidation rate eventually approached the rate of in-service tires after many iterations of oven aging. The oxygen consumption rate was found to be more sensitive to the partial pressure of oxygen at low temperatures than higher temperatures. Therefore, the partial pressure of oxygen is an important factor governing tire aging (oxidation rate) at ambient temperatures. This has implications for the rate of material property evolution at ambient temperatures for tires that use higher inflation pressures (higher partial pressures of oxygen) in service, such as light truck tires. It may also lessen the influence of oxygen partial pressure at elevated temperatures such as those used for tire oven aging.

The empirical shift factors were an exponential function of inverse temperature, from which the activation energy was determined to be 23 kilocalories/mole based on the combined oxygen consumption, CO2 generation, CO generation, and tensile time-temperature kinetic analysis. This agrees with the literature value for activation energy of oxidation of organic compounds. All four data sets had similar activation energies (22-23 kcal/mole); however, the activation energy of volatile organic generation in the new tire belt-coat compound (30 kcal/mole) was higher than this value. This suggests that the sources of volatile organics generated by the new tire belt-coat compound cannot be attributed solely to oxidation. On the other hand, the activation energy for volatile organic generation from the in-service tire belt-coat compounds was 25 kcal/mole. Therefore, the volatile organic generation of an in-service tire belt-coat compound can be attributed solely to oxidation after some initial period of service. The activation energy for the in-service tire belt-coat compound was 24 kcal/mole based on oxygen consumption, CO2 generation, CO generation, and volatile organic generation time-temperature kinetic analysis. All four data sets had similar activation energies (23-26 kcal/mole).

The predicted belt-coat compound elongation-to-break as a function of time at ambient temperature (decay curve) was obtained using the oxygen consumption rate shift factors. The predicted property decay curve incorporated factors experienced by the belt-coat compound while in service, which affected the aging (decay curve). One key effect was oxygen partial pressure. An in-service tire inflated with air has higher oxygen partial pressure than the atmospheric oxygen partial pressure due to the increased total pressure inside the tire. To correctly predict the belt-coat property decay, the data was corrected for oxygen partial pressure. Another factor important in modeling the decay curve was the effect of oxygen partial pressure on oxygen consumption rate (beta). The experimentally determined effects of oxygen partial pressure on oxygen consumption rate (beta) as a function of temperature were incorporated. Tire geometry and oxygen diffusion are a couple of additional factors that affect belt-coat aging kinetics. The Diffusion Limited Oxidation (DLO) model was used to predict the effect of these factors (tire geometry and oxygen diffusion rate) on the oxygen consumption rate in the belt-coat compound during service. The effects of inflation pressure loss and oxygen partial pressure loss during service were incorporated. The effect of in-operation (rolling tire) was included. The in-service tire was estimated to be stationary (parked) for 96 percent of its service time and in-use (running) for 4 percent of its service time. These effects were included in the predicted decay curve (for belt-coat tensile elongation-to-break as a function of service time at ambient temperature). The agreement between predicted and actual in-service tire belt-coat elongation-to-break data was very good. Therefore, the physical property decay observed in the in-service tire can be attributed to oxidation.

The tire DLO model was used to predict belt-coat compound oxygen consumption while the tire is parked (stationary) and while in operation. The computer model was used to calculate the relative importance of the two conditions. Although it was assumed that a tire mounted on a vehicle axle is stationary (parked) for 96 percent of its service life, and in operation for the other 4 percent, the model predicted that the belt-coat compound of the BFGoodrich tire studied would undergo about 60 percent of its aging while stationary (parked) and the other 40 percent while in-operation in Phoenix. This is attributed to the higher tire temperatures experienced during rolling operation.

DEFINITIONS

- In-Service tires: Also referred to as "field" tires, are used tires retrieved from on-vehicle service in Phoenix, Arizona by U.S. DOT/NHTSA and subsequently analyzed. New versions of each tire type were purchased for comparison.
- Belt-coat compound: Also referred to as "skim," "skimcoat," or "wirecoat" compound, is the rubber compound applied to the steel belts before the belts are placed in the tire during building. When multiple belts are laid on top of each other during the build process, the resulting skim coat thickness determines the spacing between the two adjacent belts.
- Fixed oxygen level: The amount of oxygen that is chemically combined to the rubber compound.
- Oxygen consumption rate: The rate at which oxygen combines with a rubber compound at a specified condition.

BACKGROUND

One goal of this report was to determine if the property decay rate at service life temperatures could be predicted from the combination of ultra-sensitive oxygen consumption rate data and physical property testing. This approach was utilized herein to assess property decay kinetics of the belt-coat compound in an original equipment BFGoodrich tire model. One key question was to determine the reason for rapid decay in belt-coat properties of in-service tires during the first few years of service that eventually levels off with longer periods of service.[1]

Tires of the same model used in this paper were collected from on-vehicle service in Phoenix, Arizona and analyzed by NHTSA ("Tire Type B") during development of an accelerated tire durability test.[1] Since the most significant safety issue for light vehicle radial tires has been shown to be separation of the tire in the belt edge region, the basic properties of the belt-coat (wirecoat) rubber compound were analyzed to examine changes during on-vehicle service. One chemical property measured was the level of fixed oxygen in the tire belt-coat compound, which was plotted against the age of the tire at retrieval in Figure 1. During service, the level of oxygen in the belt-coat compound was observed to increase with increasing tire age. Another physical property measured was ultimate elongation to break of the tire belt-coat compound, which is determined from a tensile test. The ultimate elongation in percent was plotted against the age of the tire at retrieval in Figure 2. During service, the ultimate elongation of the belt-coat compound was observed to decrease with increasing tire age. Finally, the peel adhesion of the belt-coat compound between the top and bottom steel belts is plotted against the age of the tire at retrieval in Figure 3. As seen in the figure, the average peel adhesion between the two steel belts in the belt package region was observed to decrease with increasing tire age.

Figure 1. Fixed Oxygen in Belt-Coat Compound Versus Tire Age - NHTSA Phoenix Tire Study; Tire Type B

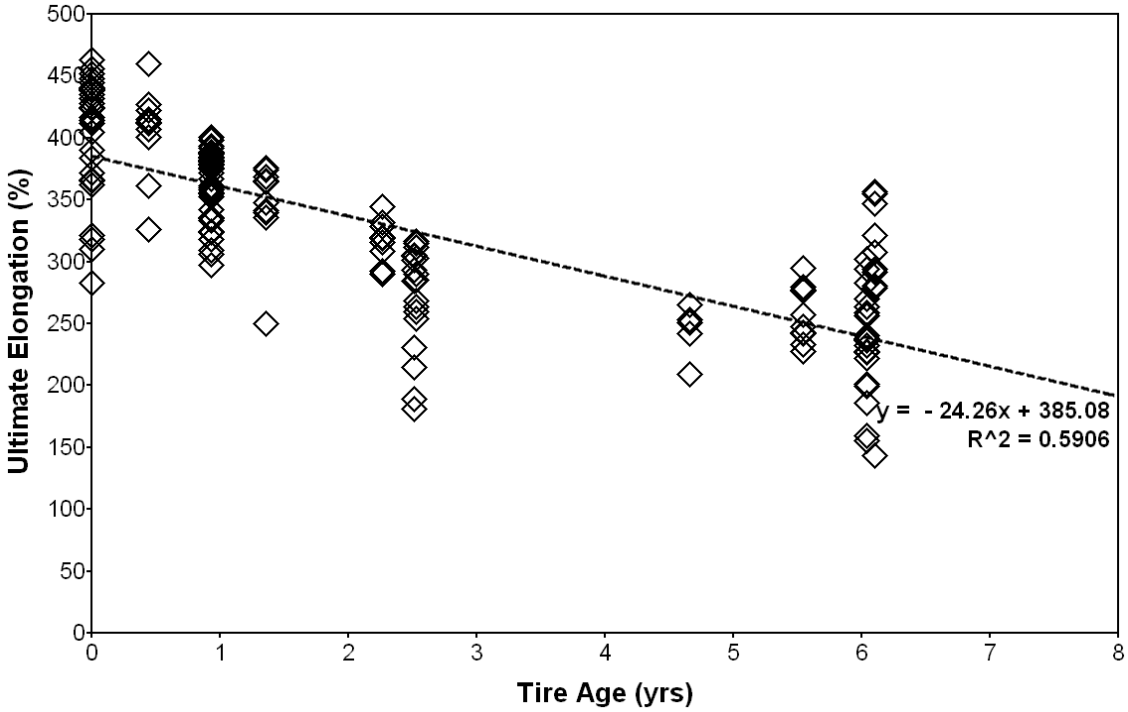


Figure 2. Tensile Elongation-to-Break of Belt-Coat Compound Versus Tire Age - NHTSA Phoenix Tire Study; Tire Type B

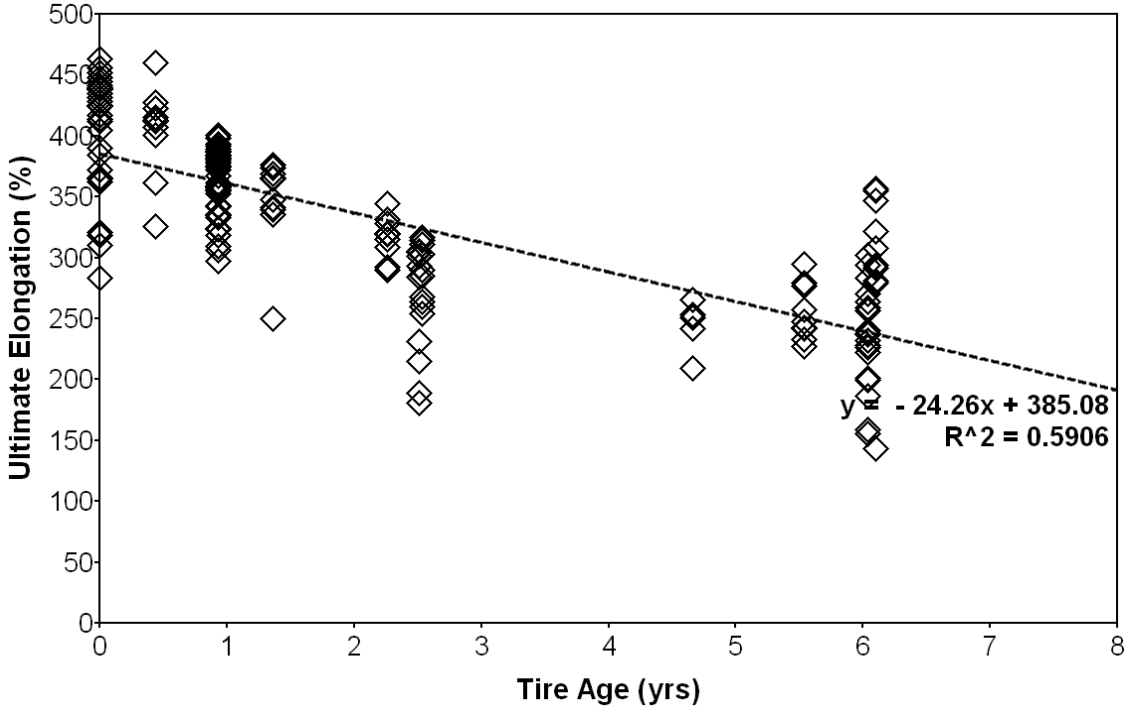
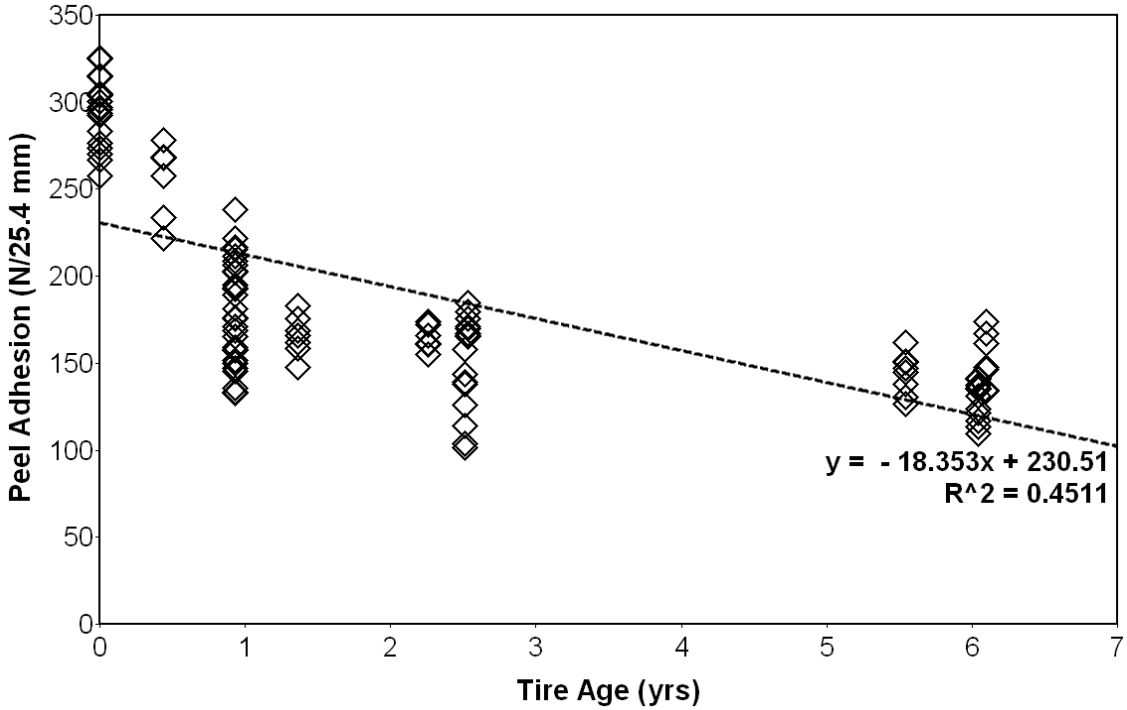


Figure 3. Average Inter-Belt Peel Adhesion, Belt-Coat Compound Versus Tire Age - NHTSA Phoenix Tire Study; Tire Type B



When the ultimate elongation data for each tire's belt-coat compound were averaged and plotted against the average fixed oxygen level for each tire's belt-coat compound, a correlation coefficient (R^2) of 0.8755 was observed (Figure 4). When the inter-belt peel adhesion data for each tire were averaged and plotted against the average ultimate elongation data, a weaker yet illustrative relationship (R^2 of 0.7472) was exhibited between the two measures (Figure 5). Therefore, the oxygen uptake of the tire belt-coat rubber compound appears to be linked to changes in the tensile properties of the compound, which in turn appear to factor into the composite properties of this region such as peel adhesion. Since the degradation of the tire rubber compounds in passenger vehicle tires is known to be an oxidative process 1), a better understanding of the decay process and decay rate was desired as well as its effects on physical properties. The ultra-sensitive oxygen consumption technique has been shown to be able to determine the oxidation aging kinetics at service temperatures 2). From the oxidation rate data, the property decay at service life temperatures can be determined when combined with physical property testing. This approach was utilized herein to assess property decay kinetics of a BFGoodrich tire belt-coat compound.

Figure 4. Average per Tire Tensile Elongation-to-Break Versus Average per Tire Percent Fixed Oxygen, Belt-Coat Compound - NHTSA Phoenix Tire Study; Tire Type B

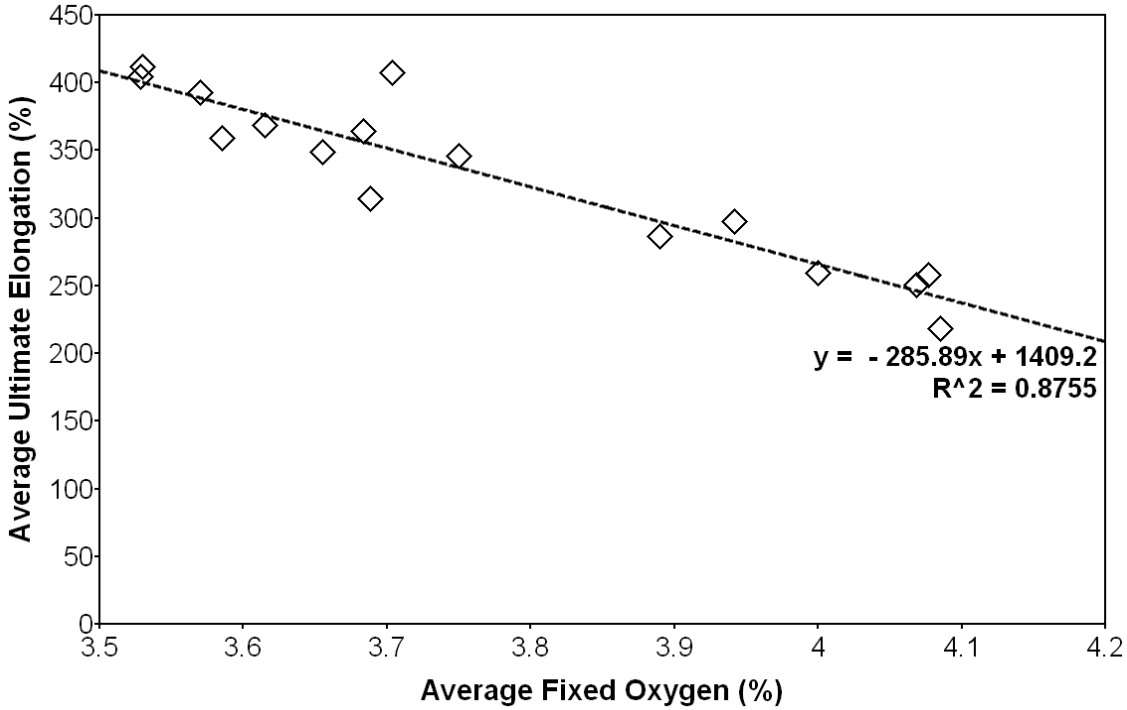
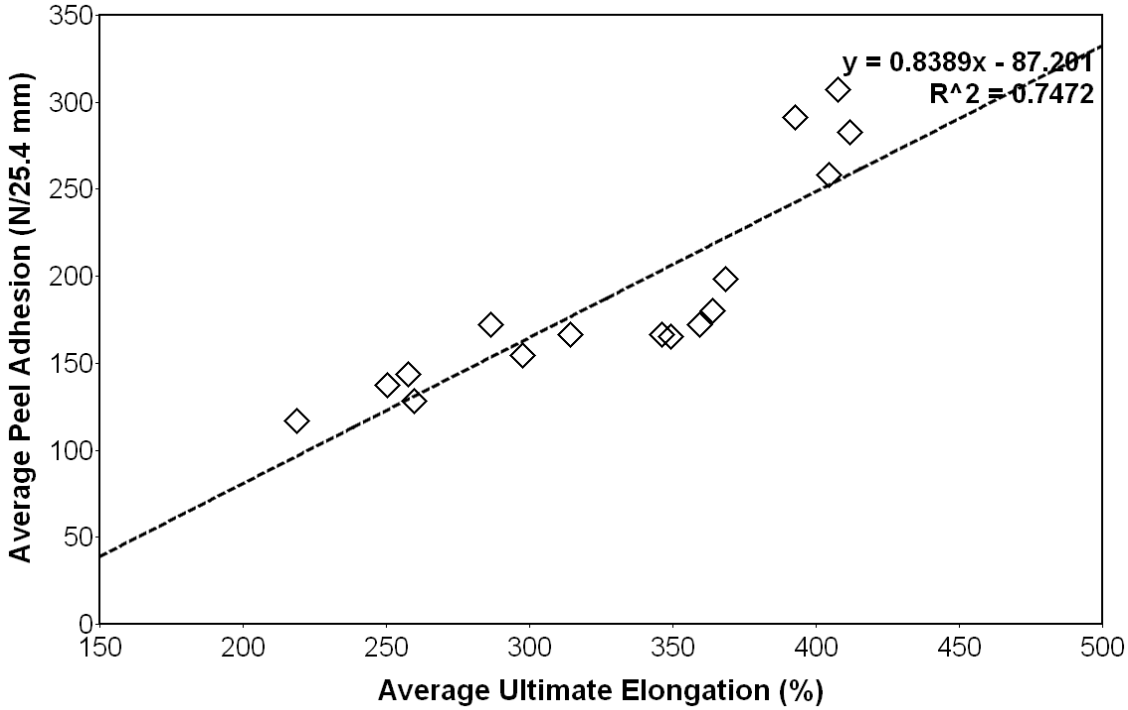


Figure 5. Average Inter-Belt Peel Adhesion, Belt-Coat Compound Versus Average Ultimate Elongation - NHTSA Phoenix Tire Study; Tire Type B



EXPERIMENTAL TECHNIQUES

Tire Dissection

The tires were dissected to remove the belt-coat (skim) compound for testing. The belt-coat compound was taken from between the belts, excluding the wedge compound (i.e. the rubber was not taken from the flared region near the edge of belt #2). The BFGoodrich Touring T/A SR4 P-metric P195/65R15 89S tire was used (Table 1). A new tire of the same model and construction was not available from the Ardmore, OK plant (code *"AP"*). Therefore, a new tire was obtained from the *"K4"* plant in Queretaro, Mexico. Belt-coat compounds have been optimized by a manufacturer for adhesion to the brass-coated wire belts and, unlike many tire components, seldom change over time or between plants.

Table 1. List of Tires used in Oxidation Kinetics with Tensile Testing

ARDL NB #	NHTSA Tire #	Description	DOT Code	DOT Mid Week Date	DOT Age (yrs)	Mileage (km)
ERTNB2-59-5	-	New Tire	**K4**C6BB510803*	2/22/2003	0	0
ERTNB2-59-1	N0064	In-Service, OE Tire	**AP**C6BB11455**	11/8/1995	7.3	71,431
ERTNB2-59-2	N0068	In-Service, OE Tire	**AP**C6BB21077**	2/19/1997	6.1	39,286
ERTNB2-59-3	N0026	In-Service, OE Tire	**AP**C6BB1117**	3/19/1997	6.0	82,707
ERTNB2-59-4	N0023	In-Service, Repl. Tire	**AP**C6BB21077**	2/19/1997	6.1***	N/A

* K4 Plant = AutoPartes Internacional (Groupe Michelin), Queretaro, Mexico
** AP Plant = Groupe Michelin (Uniroyal-Goodrich), Ardmore, OK
*** Tire N0023 had mixed service: 4.59 years of service in TX, 1.5 years of service in AZ. The three other tires were on vehicles registered in AZ their entire service lives.

Oven Aging

The extracted (dissected) belt-coat compound was subjected to oven aging at four temperatures (55°C, 65°C, 80°C, and 95°C). Oven aging was done in an air oven at atmospheric pressure in Akron, Ohio.

Tensile Properties

Tensile and elongation properties were measured according to ASTM method D 412.

Oxygen Consumption Rates

The oxygen consumption rates were measured according to methodology described in prior publications.[2,4] Oxygen consumption rates were measured by sealing (using knife-edge flanges and copper gaskets) known amounts of the elastomer under investigation with known amounts of

oxygen gas (O_2) in stainless steel reactors of known volume, typically about 30 cc. The dissolved gases had been removed from the elastomer by placing the sample under vacuum for three days. Oxygen starting pressures at the temperature of the aging experiment were about 3.5 psi. The reactors were allowed to equilibrate (come to O_2 solubility equilibrium) for two or more days. Additional O_2 was added as necessary to restore the O_2 pressure to the desired starting pressure. The reactors were then placed in ovens to thermally age the elastomer for time periods chosen to consume about 20 percent of the O_2 (to make the average partial pressure during aging approximately equal to ambient conditions in Akron [partial pressure of O_2 about 3.1 psi]. After aging the residual gas composition in the reactors were measured directly using a Perkin Elmer AutoSystem XL ARNEL gas chromatograph (gc) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), which were quantified using a calibration standard for oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), and carbon monoxide (CO). Separation was performed using a series/bypass scheme based on a six-port valve and a ten-port valve. The first column was Hayesep and the second column was composed of molecular sieves. The columns were at 60°C. The TCD and FID detectors were at 200°C. The TCD output quantified the O_2, N_2, CO, and CO_2 gases and FID output provided the volatile organic levels. Each aging condition was run in duplicate and the results averaged. Oxygen consumption rate (φ) values were calculated as using Equation. 1:

$$\varphi = \frac{d[O2]}{dt} = \frac{-\Delta n}{m\Delta t}$$

Equation. 1

Where Δn, the change in number of moles of O_2, was calculated as

$$\Delta n = \frac{p_f V_{free}}{RT_f} - \frac{p_o V_{free}}{RT_o}$$

Equation. 2

Using the ideal gas law, V_{free} is the free (gas) volume of the reactor, p_o is the oxygen partial pressure measured at room temperature T_o at the beginning of the aging interval, p_t is the oxygen partial pressure measured at room temperature T_f after aging. Production rates of CO and CO_2 were calculated analogously. Gas concentrations were measured by two methods- 1) direct measurement of gas concentrations with the gas chromatograph (gc) and 2) partial pressure contributions to the total pressure in the reactors at the end of an aging experiment. Total gas pressure in the reactors at the end of each aging cycle was measured directly with a Validyne model CD379 pressure transducer. To avoid diffusion limited oxidation the published criterion of sample thickness[5] was followed.

To measure the effect of oxygen partial pressure on oxygen consumption rate, the O_2 backfill pressures were varied over the range of interest (3 to 30 psi O_2 partial pressure). The

measurement methodology was the same as the atmospheric O_2 partial pressure experiments in all other aspects.

RESULTS

Tensile Elongation-to-Break Data

Figure 6 shows the elongation-to-break data as a function of oven aging time at 55°C, 65°C, 80°C or 95°C. For an identical amount of time in the oven in the 55-95°C range, the higher the oven aging temperature, the greater the decrease observed in the elongation-to-break of the belt-coat compound. Superposition of that data (Figure 7) generates a master curve of property decay kinetics. For most chemical reactions, the rate of the reaction is dependent on the temperature of the reaction. Time temperature superposition is based on the principles first introduced by J. H. van't Hoff in 1884 and explained by Svante Arrhenius in 1889. The rate of a chemical reaction depends on the activation energy and the absolute temperature (in Kelvin) of the reaction. If a reaction is studied over time at different temperatures and the curves are parallel, then the conclusion is that the same reaction is taking place at each temperature but at a different rate. A shift factor then is used to shift the curve onto a master curve, which models the reaction rate dependence on time and temperature. Superposition can be used to model the temperature-variance of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions. Ferry[6] expanded the principle to apply to many chemical and viscoelastic properties of polymers above the glass transition temperature. According to Ferry[6], it holds for polymers when matching shapes of the adjacent curves is obtained, and the shift factor is a reasonable function (Arrhenius, Williams-Landel-Ferry, etc.). Subsequently, the empirical shift factors (Figure 8) can be used to generate a decay curve at 65°C (Figure 9) and 55°C (Figure 10). To shift the property decay onto time at service temperatures, the ultra-sensitive oxygen consumption rate technique was employed. Elongation-to-break in combination with oxygen consumption rate measurements were needed to correctly predict material property changes at service temperatures.

Figure 6. Elongation-to-Break as a Function of Oven Aging Time for New Tire Belt-Coat Compound

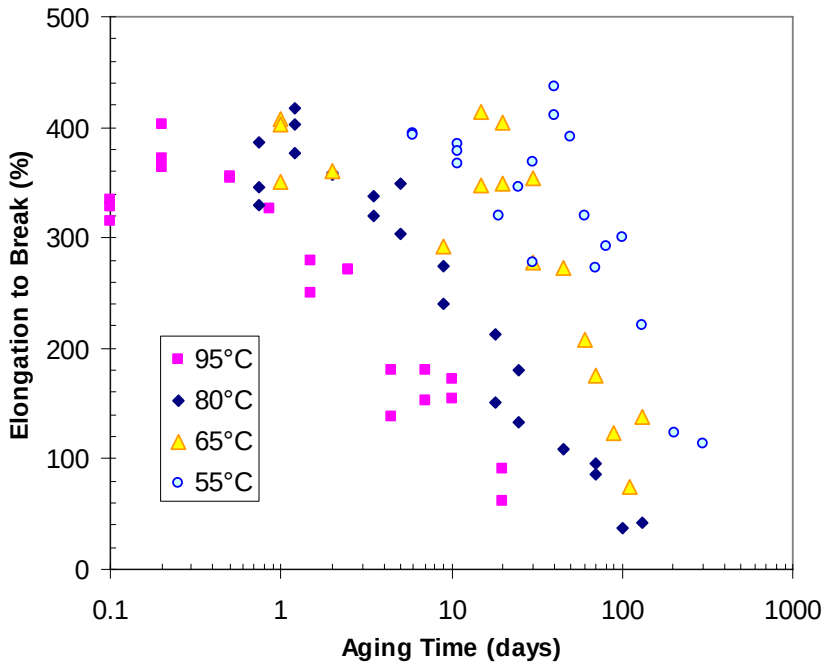


Figure 7. Time-Temperature Superposition of Elongation-to-Break Data for New Tire Belt-Coat Compound

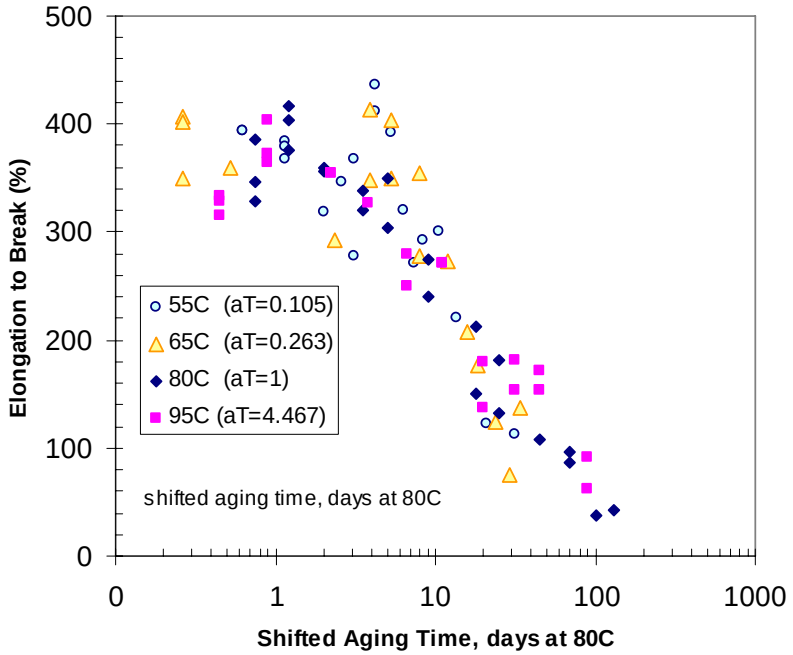


Figure 8. Elongation Shift Factors as a Function of Temperature for New Tire Belt-Coat Compound

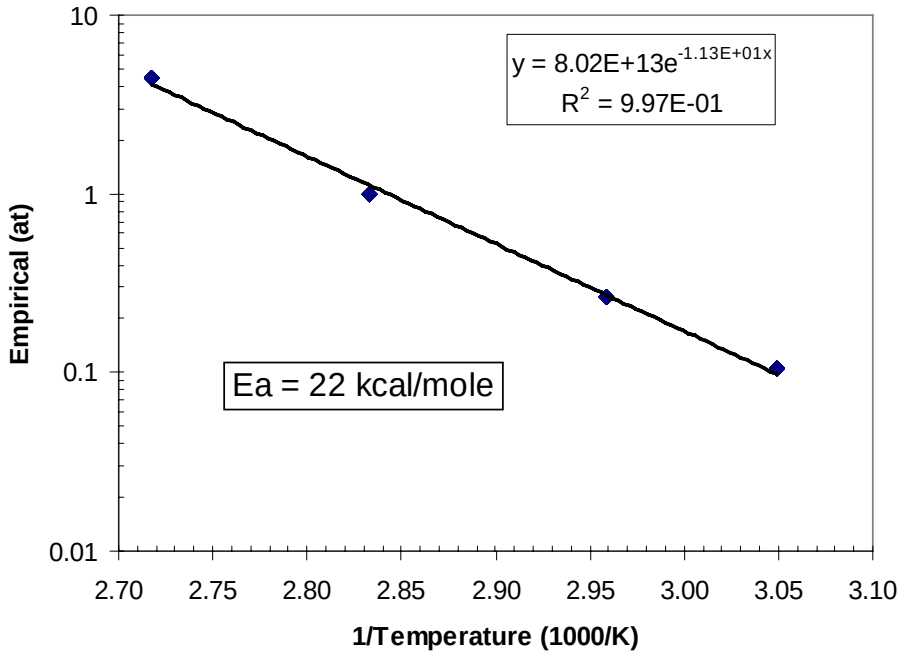


Figure 9. Elongation-to-Break as a Function of Shifted Aging Time, Days at 65°C for New Tire Belt-Coat Compound

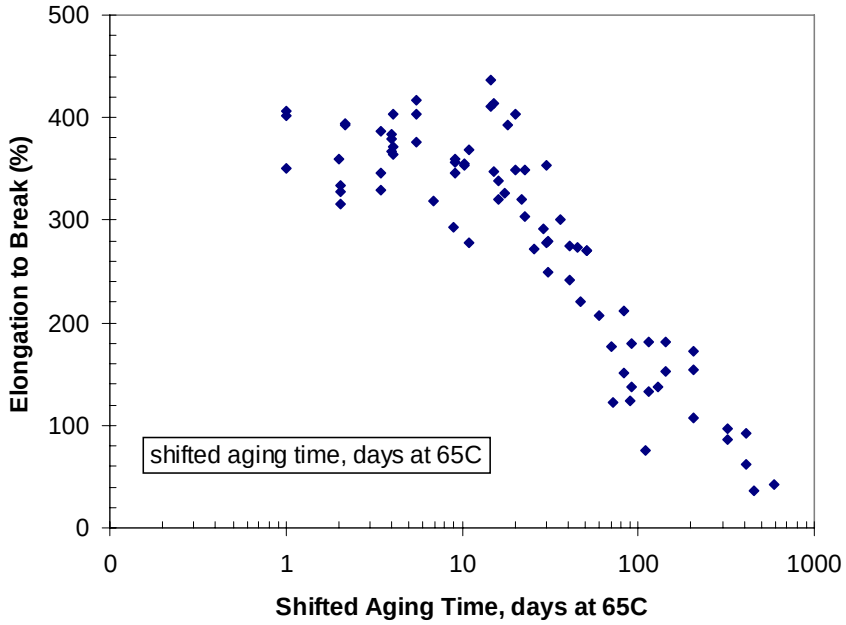
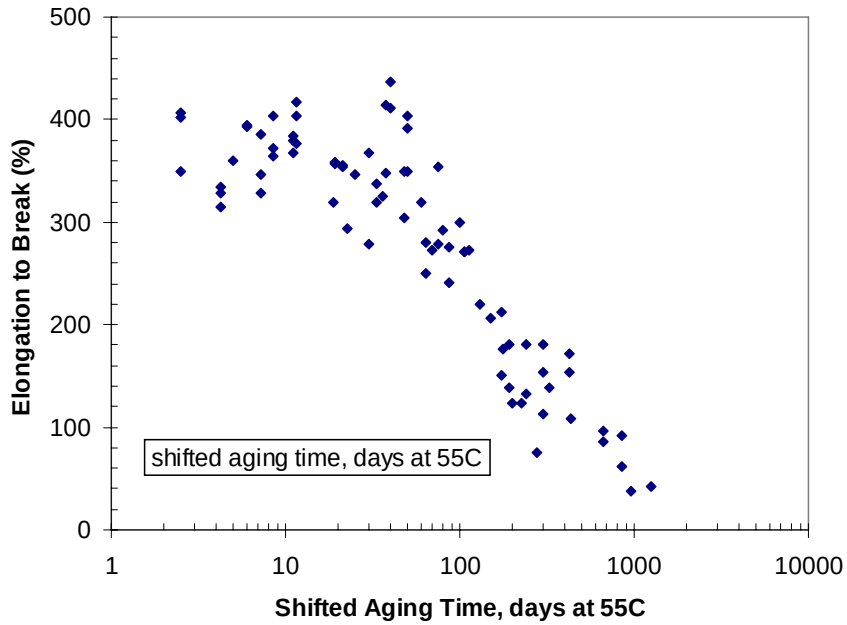


Figure 10. Elongation-to-Break as a Function of Shifted Aging Time, Days at 55°C for New Tire Belt-Coat Compound



Oxygen Consumption Rate of the New Tire Belt-Coat Compound

To determine the shift factors at lower temperatures, oxygen consumption rates for new belt-coat rubber were measured at one of six temperatures, and then the test was repeated at that temperature up to 7 times (Figure 11). The overall oxygen consumption rate at an elevated temperature such as 65 deg C was found to be 100 percent greater than at room temperature (20 deg C). A key observation is that the initial oxygen consumption rate measurements (on fresh material) were two to three times faster than the repeatedly aged material (5th and 6th repeat measurements on the same material). This may, in part, explain the rapid property decay observed in some in-service tires during the initial years of service (Figure 2 & Figure 3) that eventually levels off with longer periods of service.

Integrated oxygen uptake as a function of aging time allows superposition (Figure 12). The shift factors, which are the relative rates, were a linear function of inverse temperature in an Arrhenius plot with activation energy of 22 kcal/mole (Figure 13 & Figure 14). CO_2 and CO generation kinetics were likewise analyzed (Figure 15-Figure 22). In each case, the behavior was linear in an Arrhenius plot with activation energies of about 23 kcal/mole. The volatile organic material generation kinetics (Figure 23-Figure 27) yielded an activation energy of 30 kcal/mole. This suggested that some of the volatile organics are not attributed to oxidation.

Figure 11. Oxygen Consumption Rate of New Tire Belt-Coat Compound

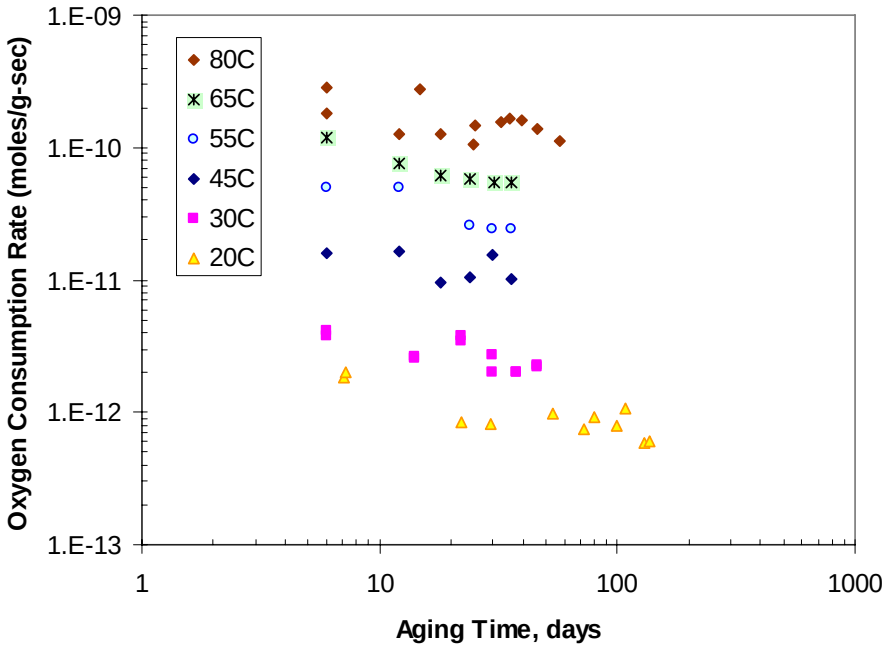


Figure 12. Integrated Oxygen Consumption as a Function of Aging Time of the New Tire Belt-Coat Compound

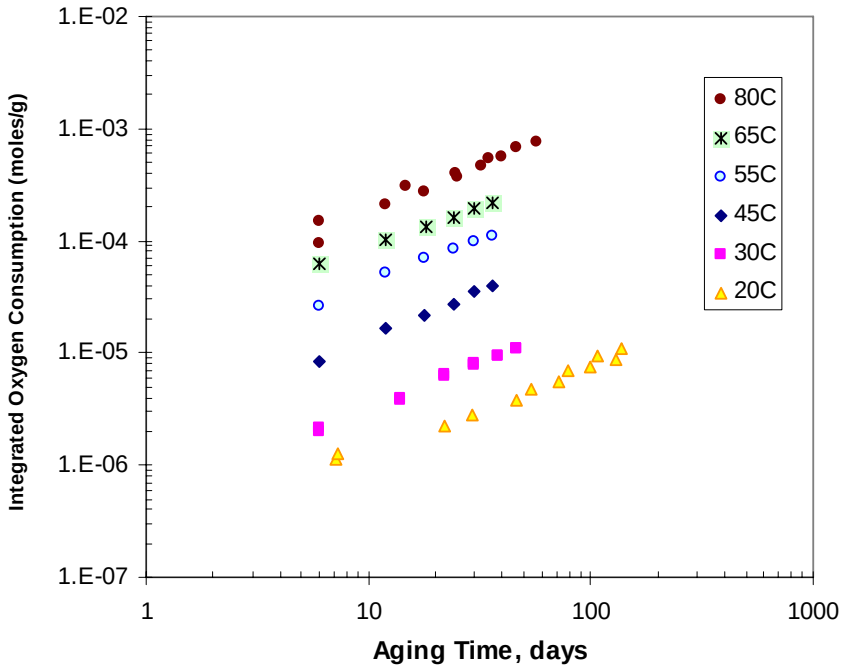


Figure 13. Time-Temperature Superposition of Integrated Oxygen Consumption of the New Tire Belt-Coat Compound

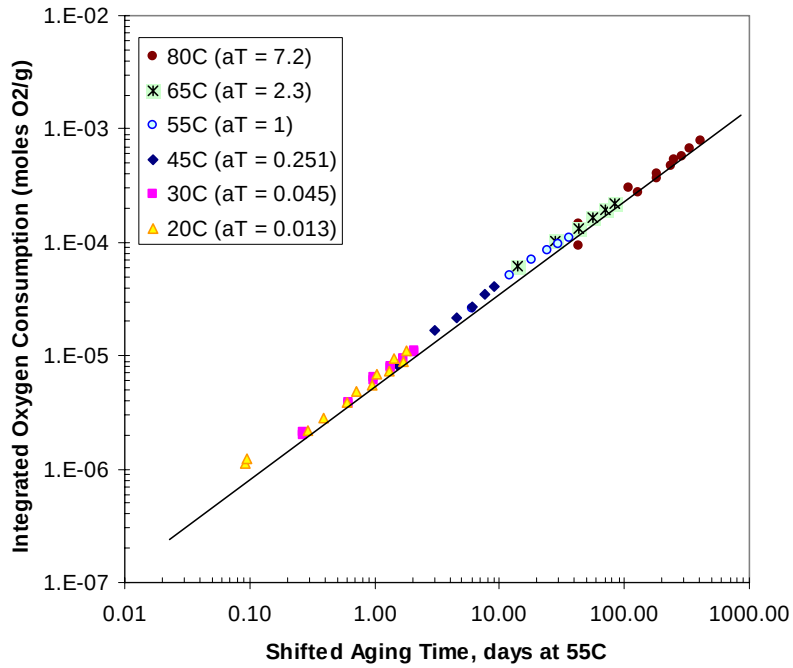


Figure 14. Oxygen Consumption Shift Factors as a Function of Temperature of the New Tire Belt-Coat Compound

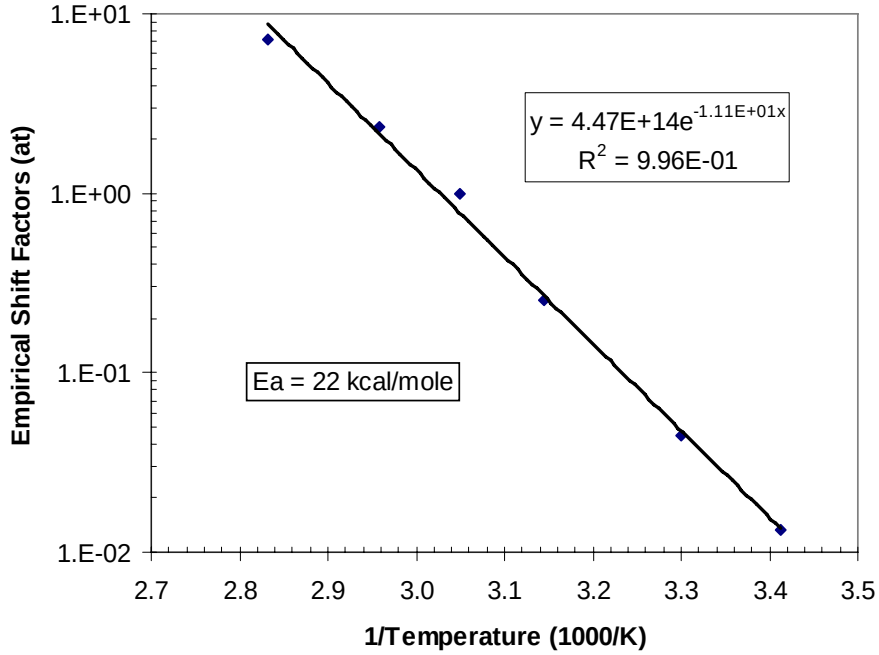


Figure 15. CO_2 Generation Rate of New Tire Belt-Coat Compound of the New Tire Belt-Coat Compound

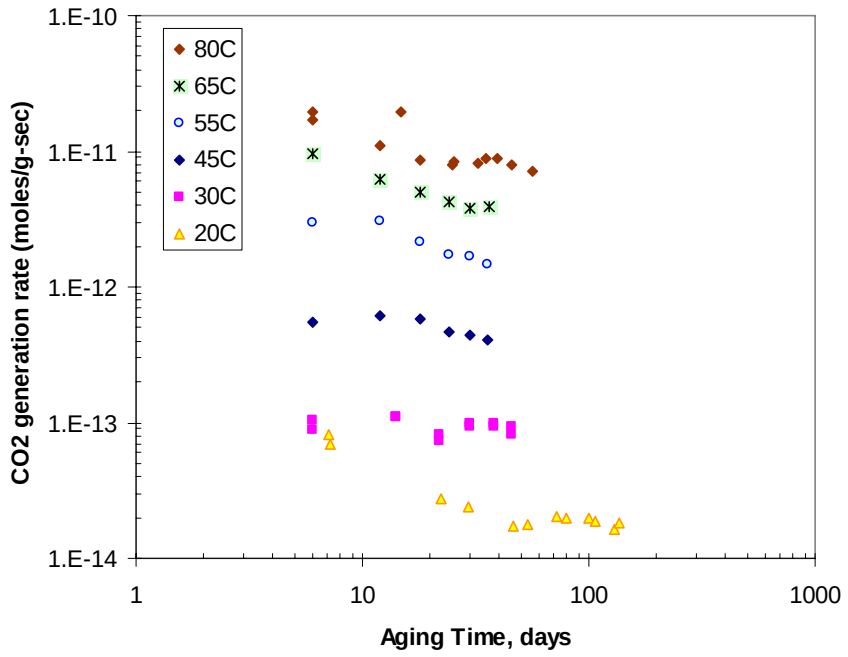


Figure 16. Integrated CO_2 Generation as a Function of Aging Time of the New Tire Belt-Coat Compound

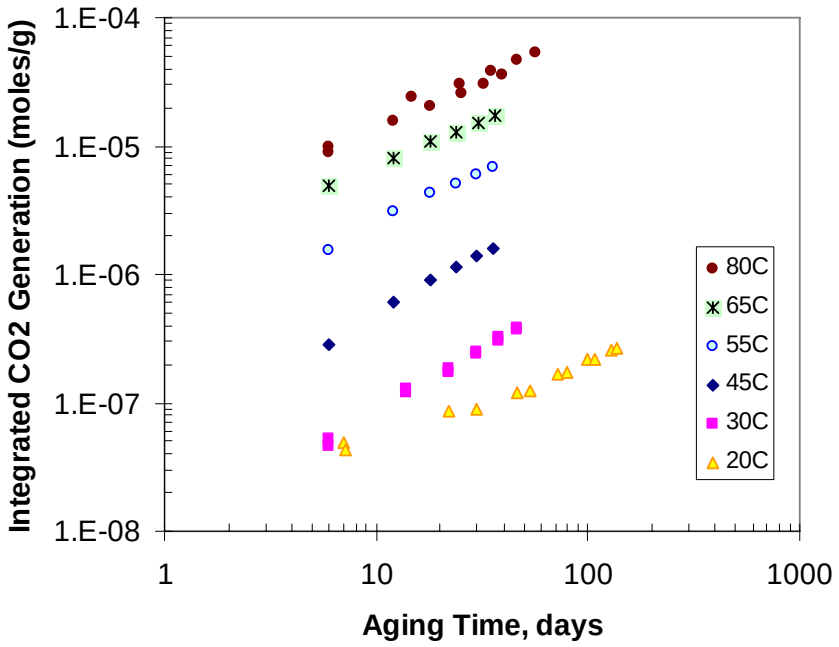


Figure 17. Time-Temperature Superposition of Integrated CO_2 Generation of the New Tire Belt-Coat Compound

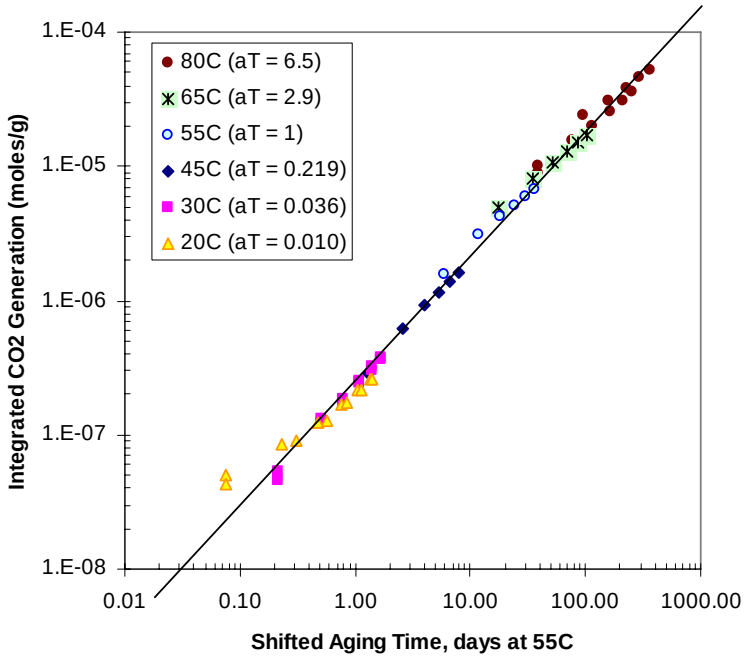


Figure 18. CO_2 Generation Shift Factors as a Function of Temperature for the New Tire Belt-Coat Compound

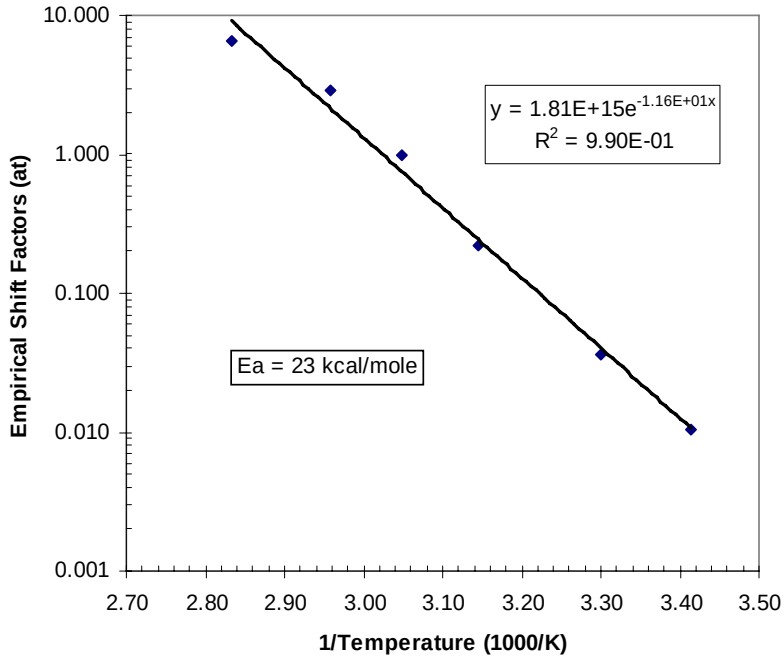


Figure 19. CO Generation Rate of New Tire Belt-Coat Compound

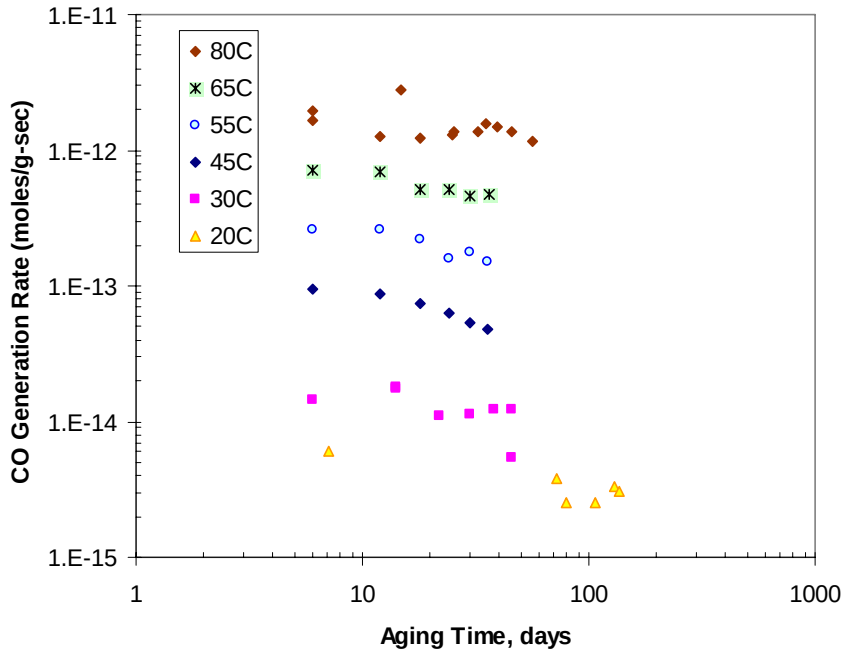


Figure 20. Integrated CO Generation as a Function of Aging Time for New Tire Belt-Coat Compound

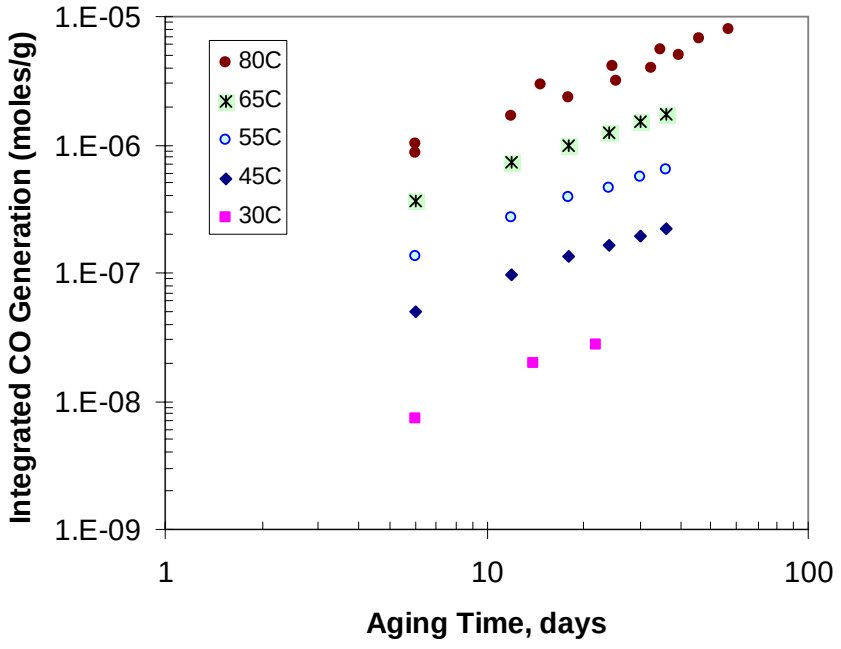


Figure 21. Time-Temperature Superposition of Integrated CO Generation for New Tire Belt-Coat Compound

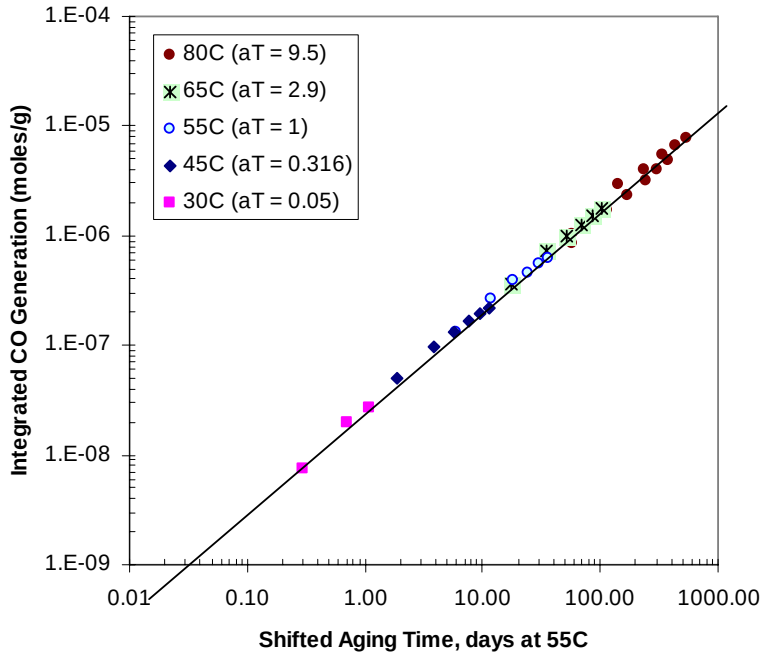


Figure 22. CO Generation Shift Factors as a Function of Temperature of New Tire Belt-Coat Compound

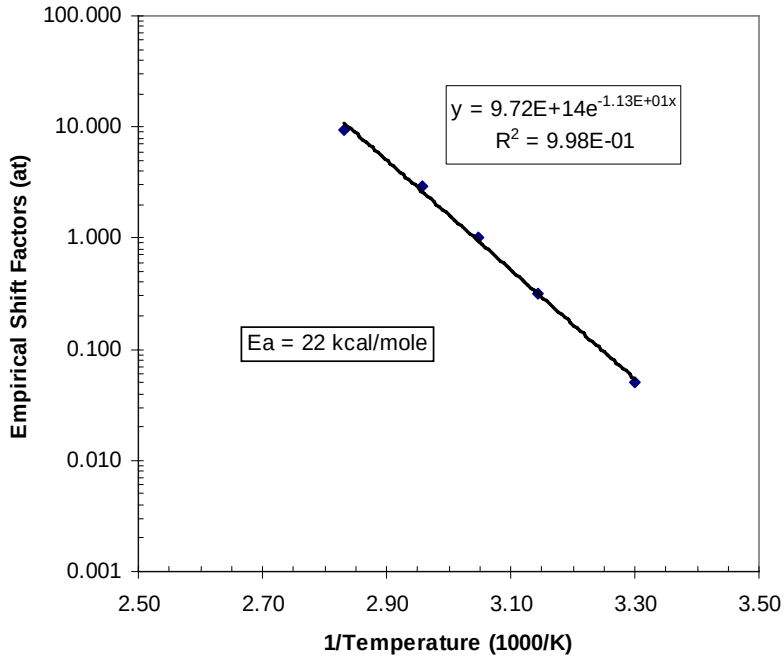


Figure 23. Volatile Organic Generation Rate from New Tire Belt-Coat Compound

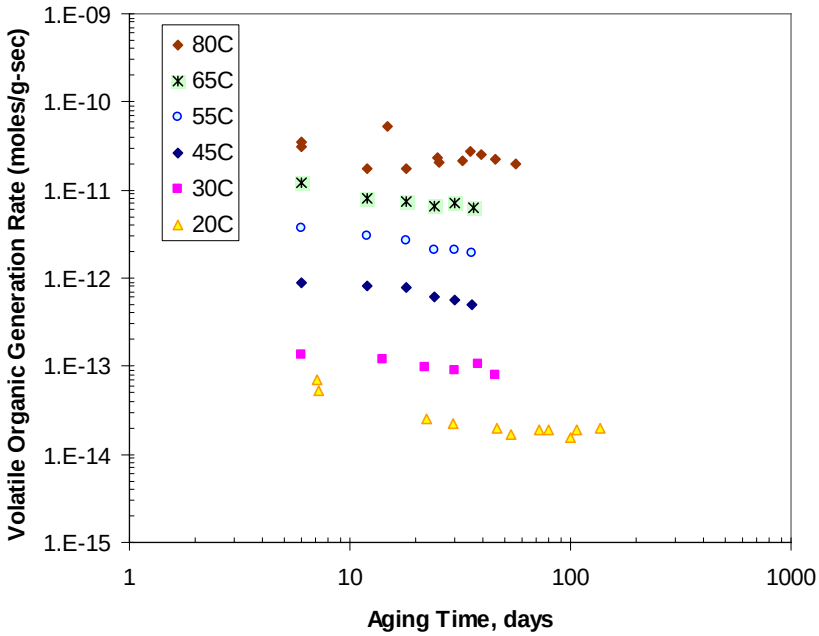


Figure 24. Integrated Volatile Organic Generation as a Function of Aging Time for New Tire Belt-Coat Compound

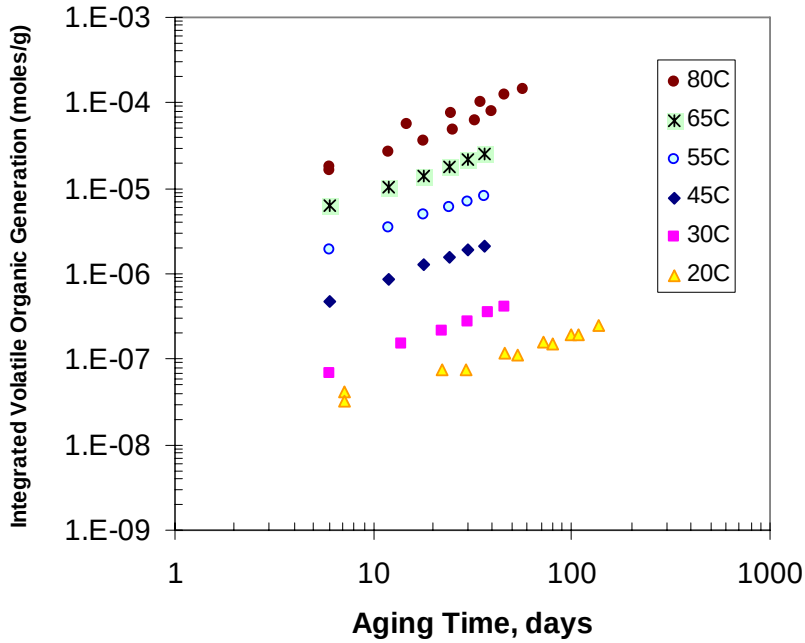
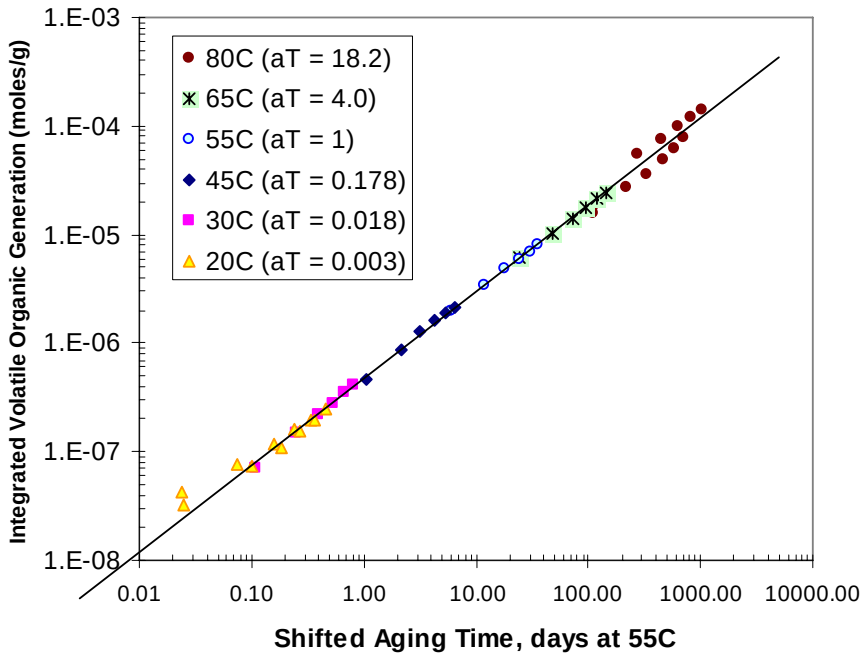


Figure 25. Time-Temperature Superposition of Integrated Volatile Organic Generation for



New Tire Belt-Coat Compound

Figure 26. Volatile Organic Generation Shift Factors as a Function of Temperature for New Tire Belt-Coat compound

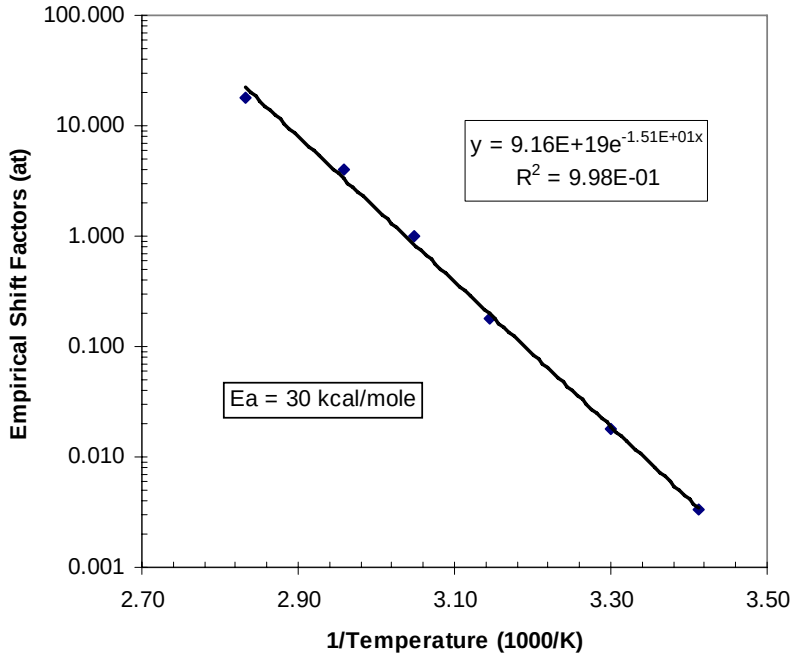
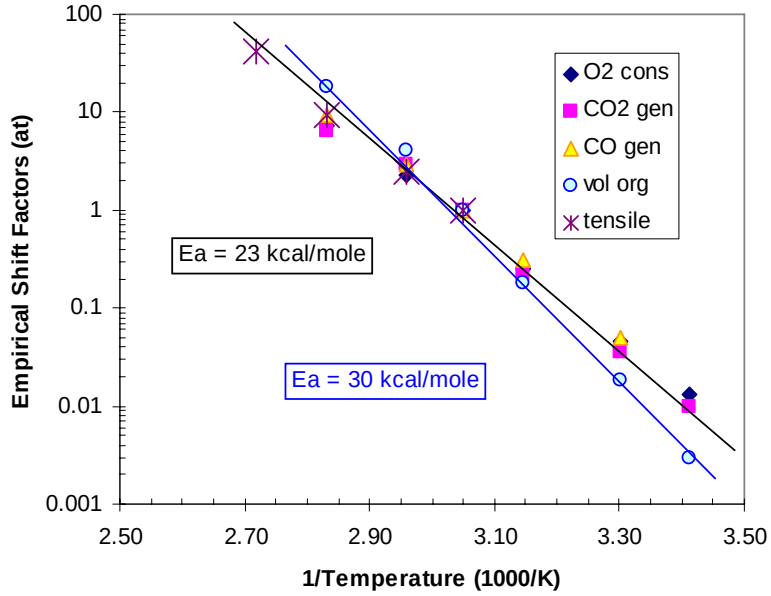


Figure 27. Summary of New Tire Shift Factors as a Function of Temperature for New Tire Belt-Coat Compound



Oxygen Consumption Rate of the In-Service Tires

Subsequently, the oxygen consumption rates from an in-service BFGoodrich tire belt-coat were measured. The oxygen consumption rates for tires removed from service were very similar to the values from the new tire belt-coat compound after repeated measurements (Figure 28). Time-temperature superposition (Figure 29-Figure 31) yielded constant activation energies in an Arrhenius plot over the temperature range.

The CO_2, CO, and volatile organic generation kinetics were found to follow the same activation energy (Figure 32-Figure 44). The in-service tire volatile organic generation activation energy matched the activation energies of oxygen consumption, CO_2, and CO generation, suggesting all of the volatile organic can be attributed to oxidation.

Figure 28. Oxygen Consumption Rate of In-Service Tire Belt-Coat Compound

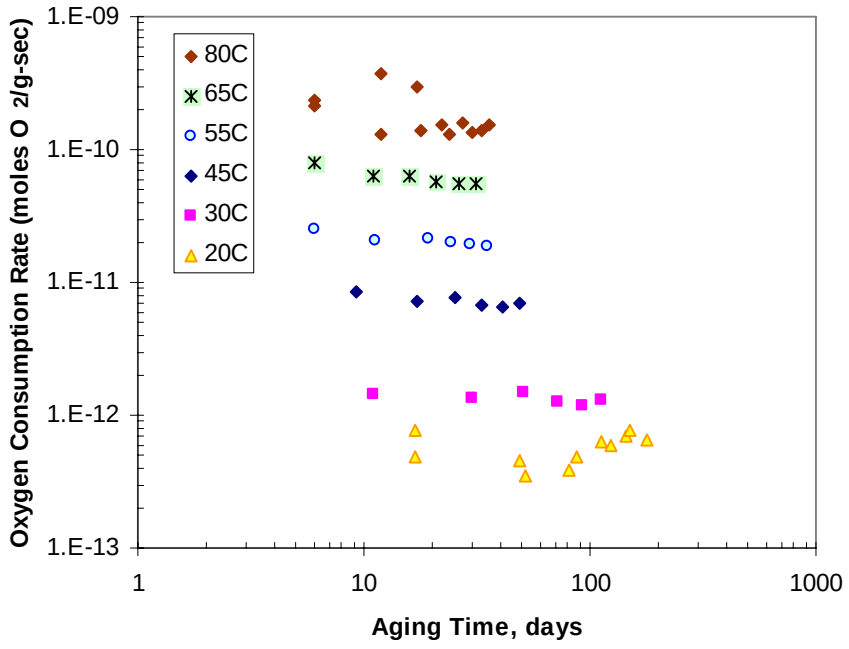


Figure 29. Integrated Oxygen Consumption as a Function of Aging Time for In-Service Tire Belt-Coat Compound

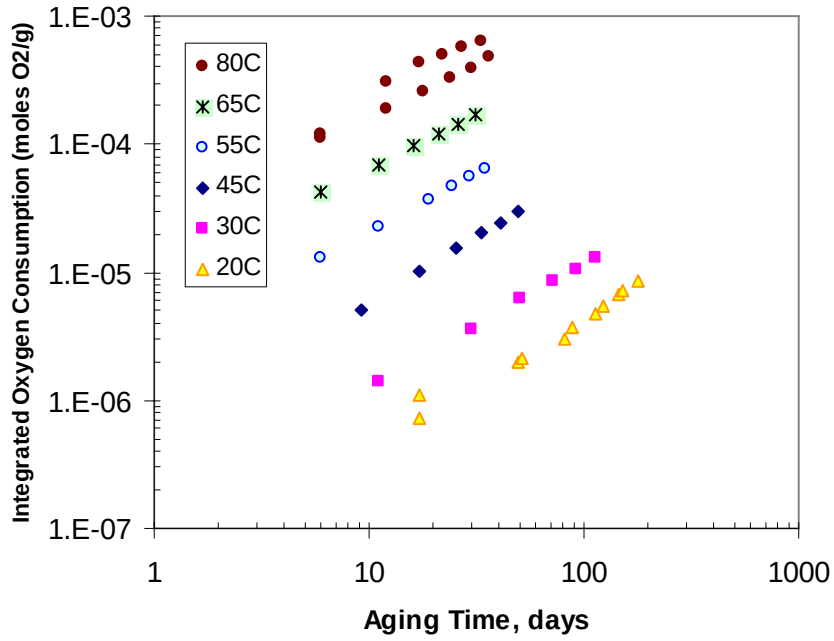


Figure 30. Time-Temperature Superposition of Integrated Volatile Organic Generation for In-Service Tire Belt-Coat Compound

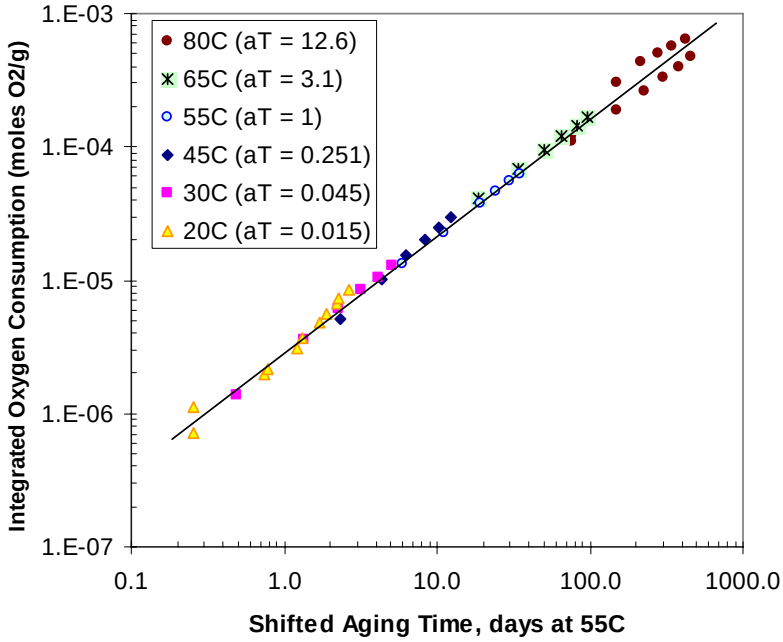


Figure 31. Oxygen Consumption Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound

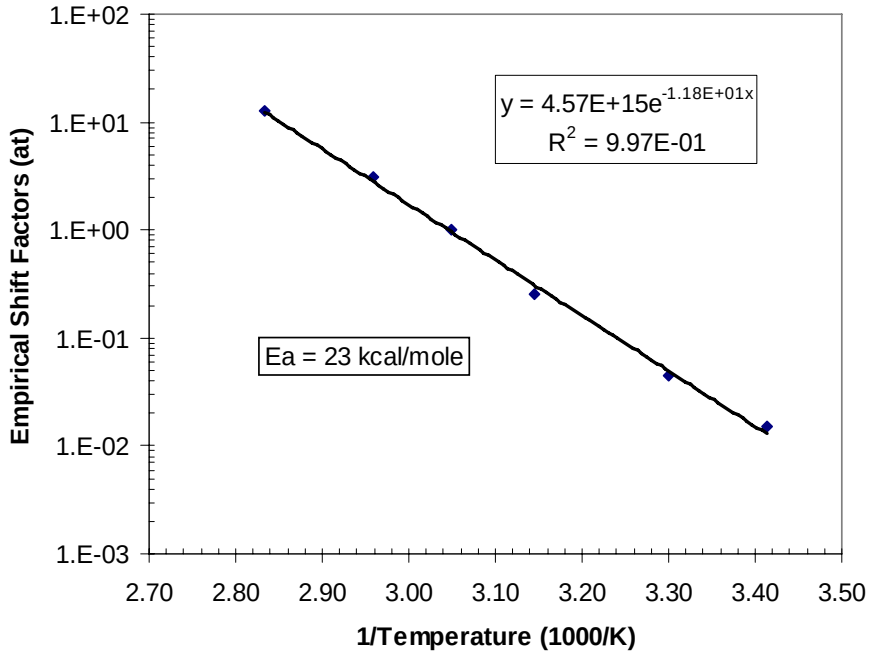


Figure 32. CO_2 Generation Rate of In-Service Tire Belt-Coat Compound for In-Service Tire Belt-Coat Compound

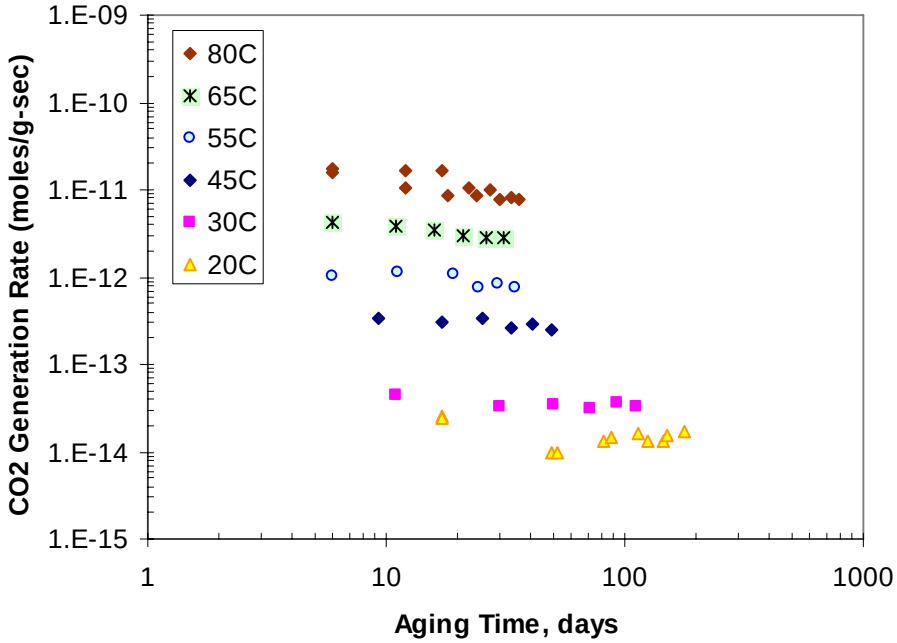


Figure 33. Integrated CO_2 Generation as a Function of Aging Time for In-Service Tire Belt-Coat Compound

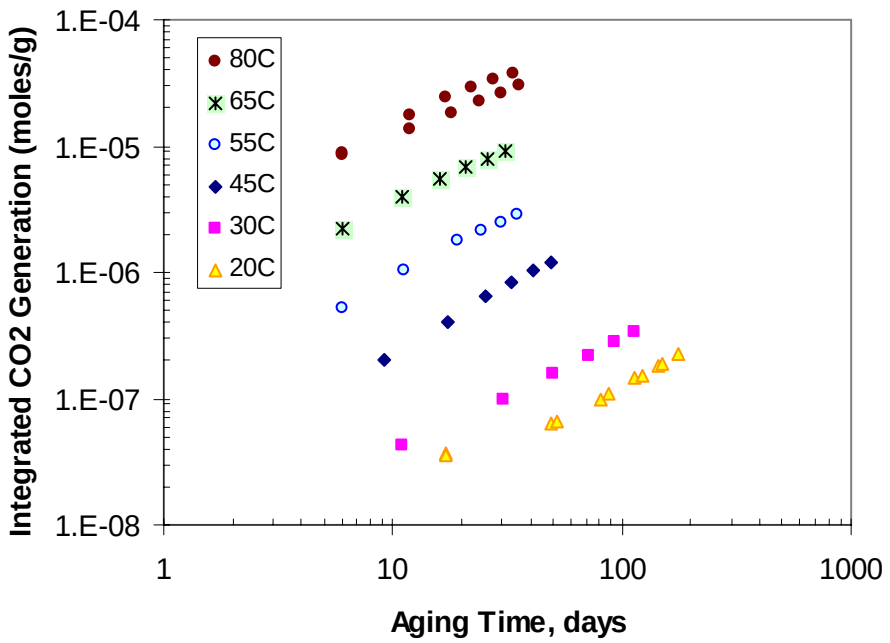


Figure 34. Time-Temperature Superposition of Integrated CO_2 Generation for In-Service Tire Belt-Coat Compound

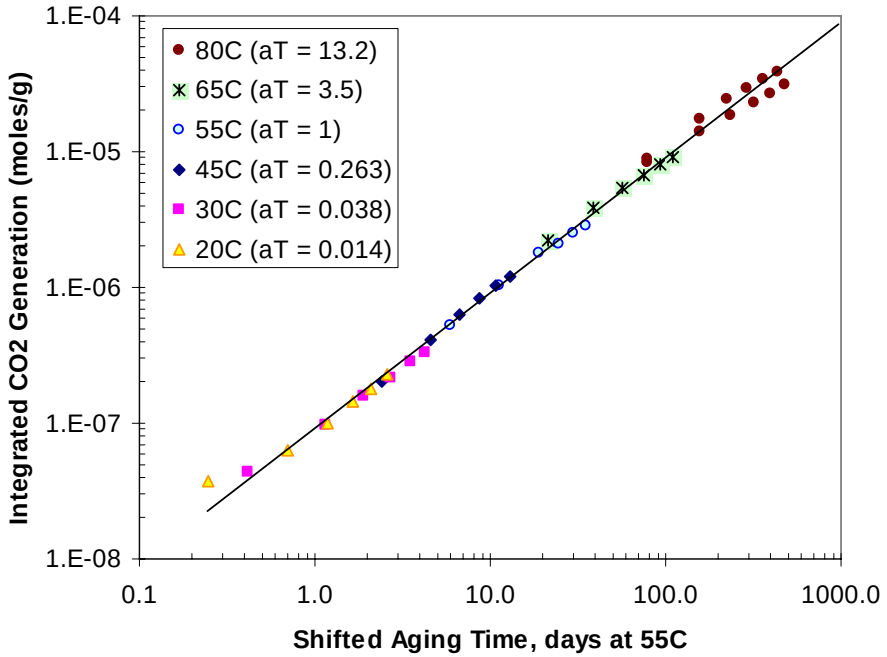


Figure 35. CO_2 Generation Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound

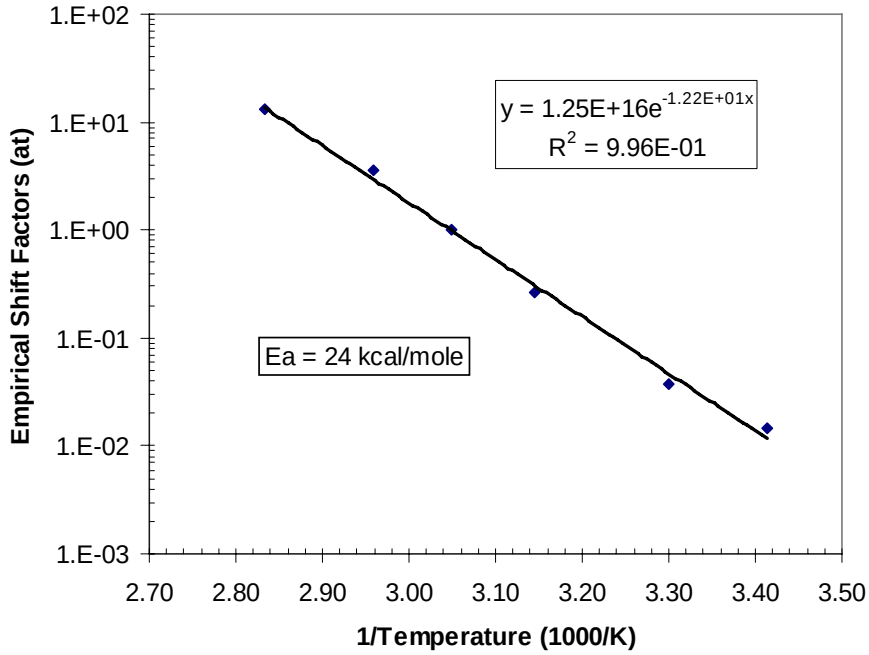


Figure 36. CO Generation Rate of In-Service Tire Belt-Coat Compound for In-Service Tire Belt-Coat Compound

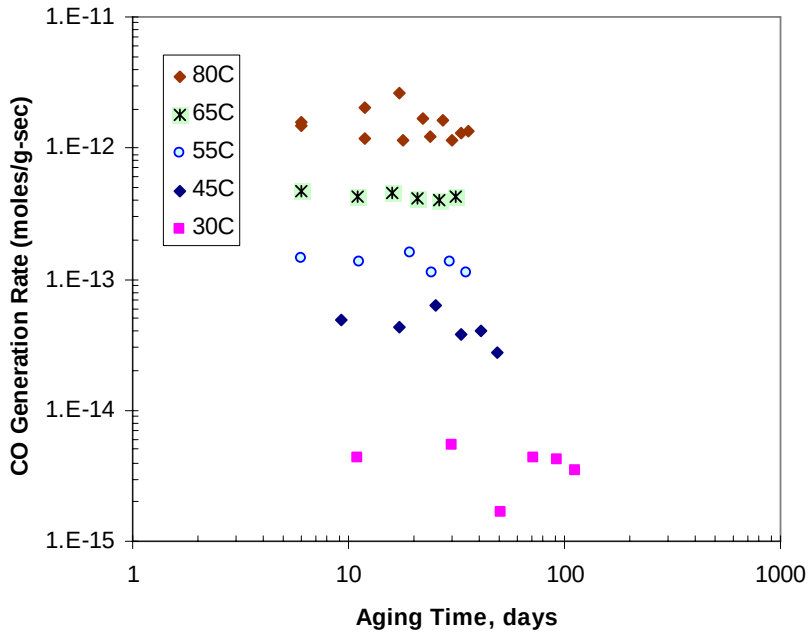


Figure 37. Integrated CO Generation as a Function of Aging Time for In-Service Tire Belt-Coat Compound

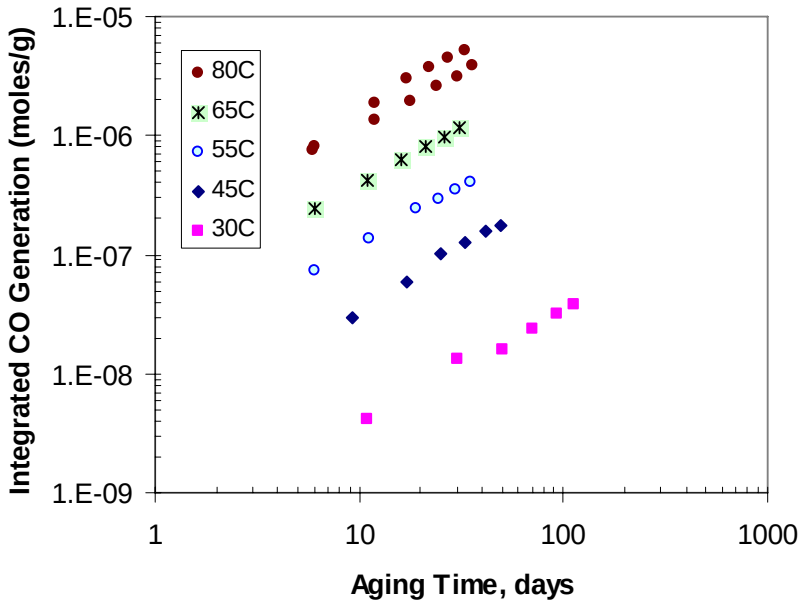


Figure 38. Time-Temperature Superposition of Integrated CO Generation for In-Service Tire Belt-Coat Compound

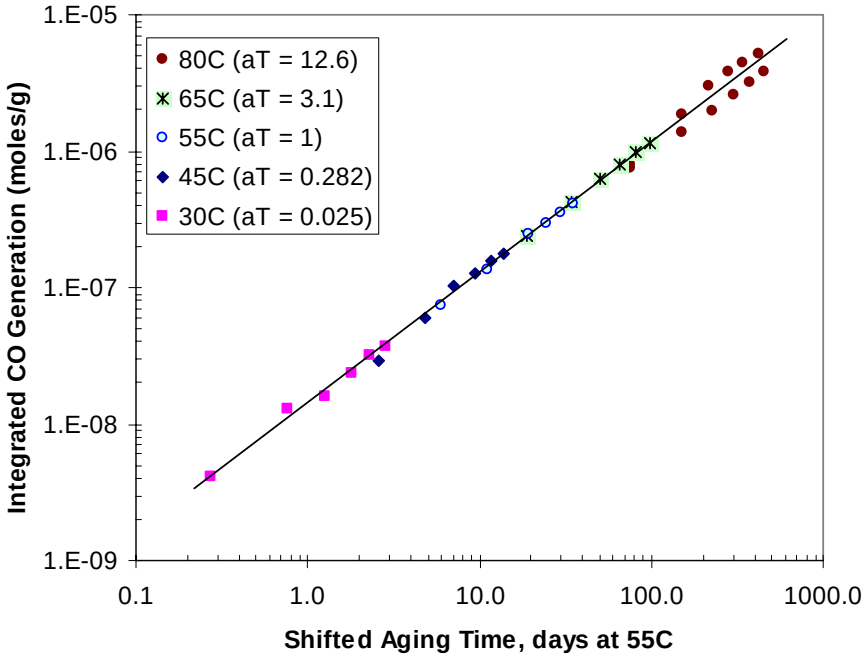


Figure 39. CO Generation Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound

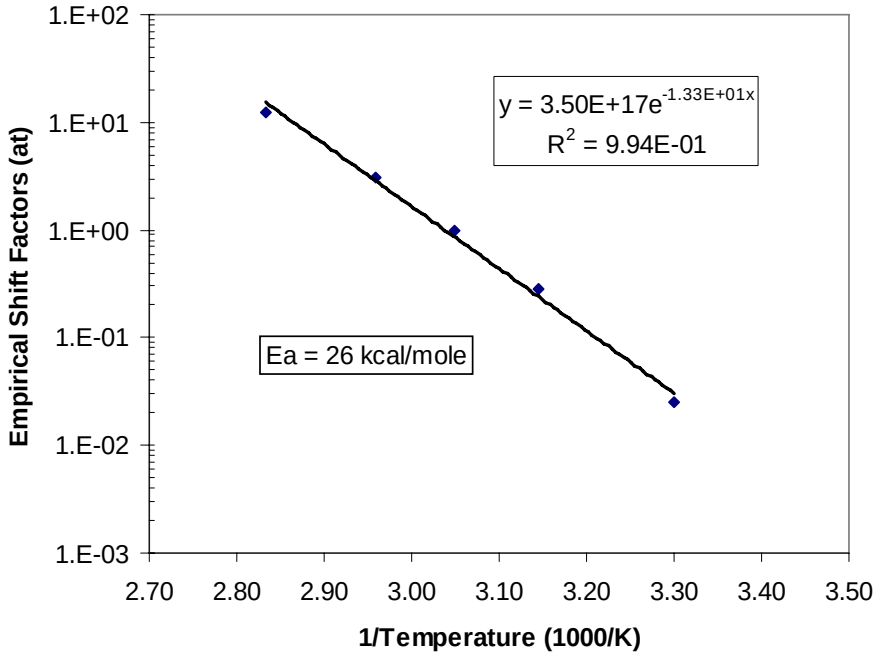


Figure 40. Volatile Organic Generation Rate of In-Service Tire Belt-Coat Compound for In-Service Tire Belt-Coat Compound

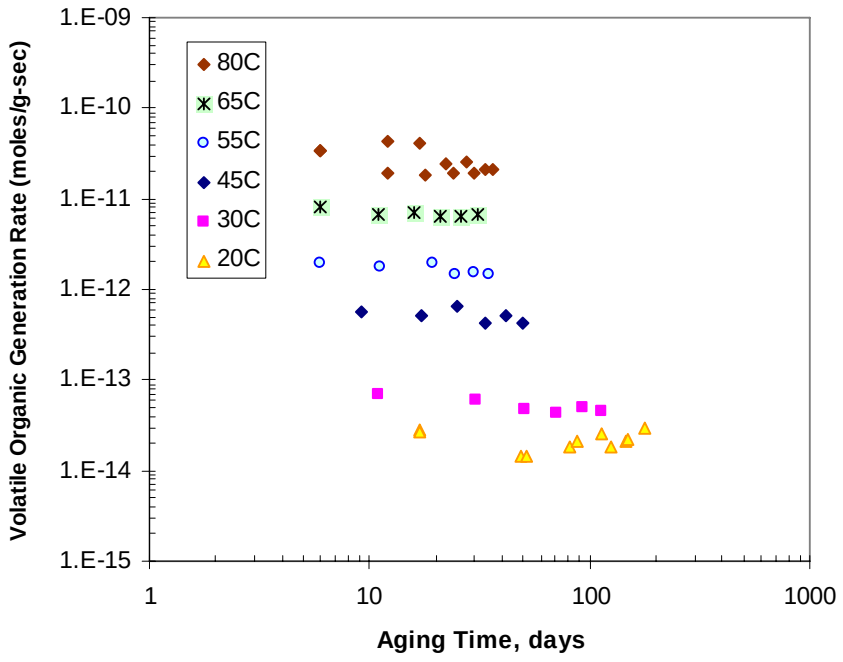


Figure 41. Integrated Volatile Organic Generation as a Function of Aging Time for In-service Tire Belt-Coat Compound

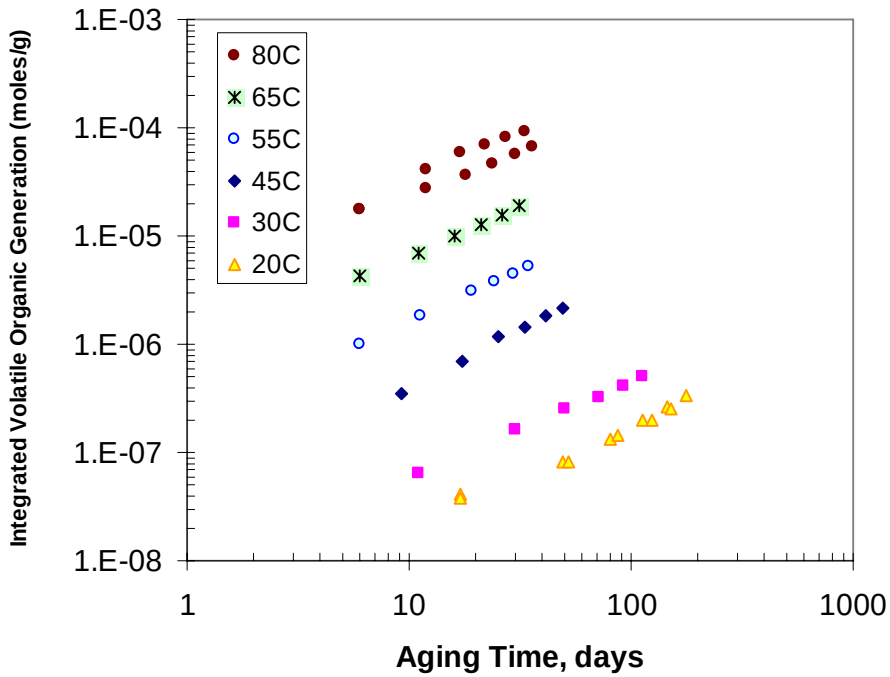
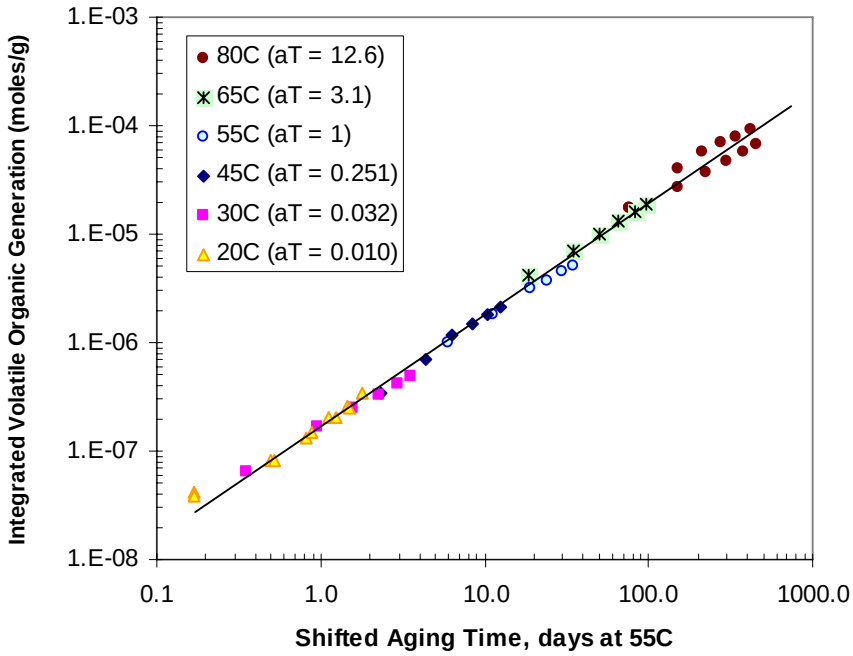


Figure 42. Time-Temperature Superposition of Integrated Volatile Organic Generation for



In-Service Tire Belt-Coat Compound

Figure 43. Volatile Organic Generation Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound

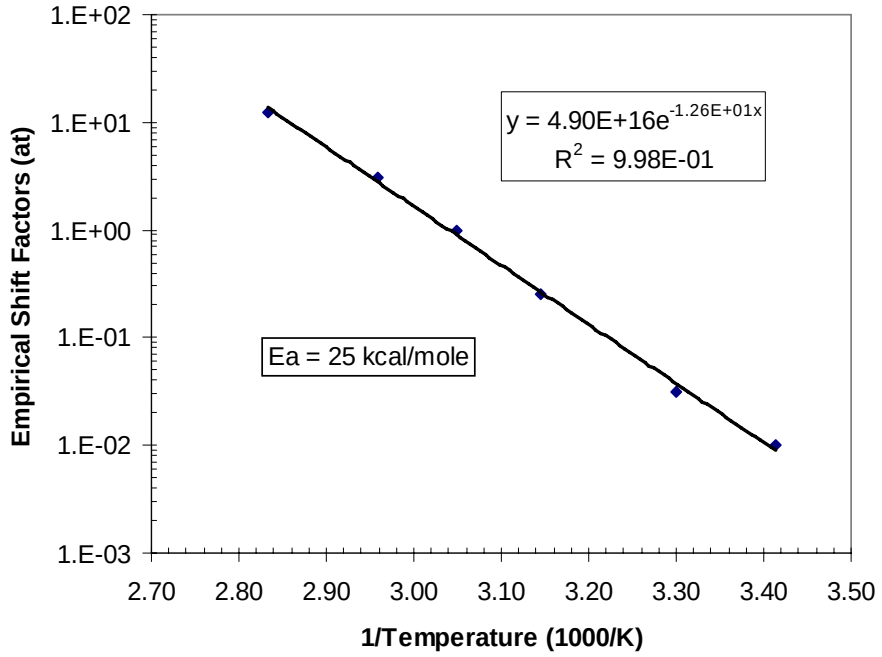
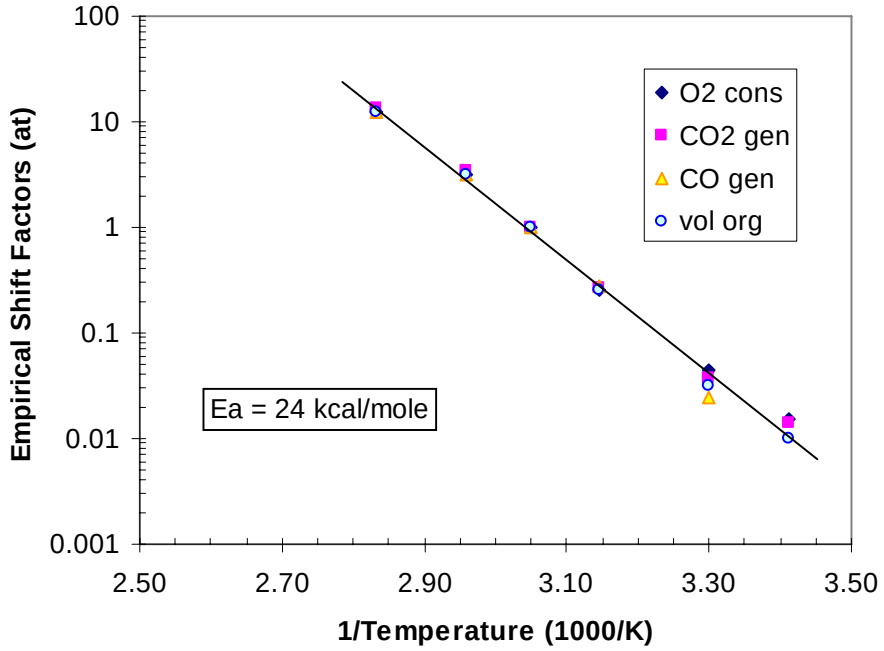


Figure 44. Summary of In-Service Tire Shift Factors as a Function of Temperature for In-Service Tire Belt-Coat Compound



Predicted Properties at Service Temperatures

Once the shift factors were known for this material in the range from 20°C to 95°C, the elongation-to-break data was shifted onto service temperatures. For example, Figure 45 shows the ambient temperature (20°C) predicted elongation-to-break decay curve for the belt-coat compound from the new BFGoodrich tire.

Figure 45. Elongation-to-Break as a Function of Shifted Aging Time, Years at 20°C

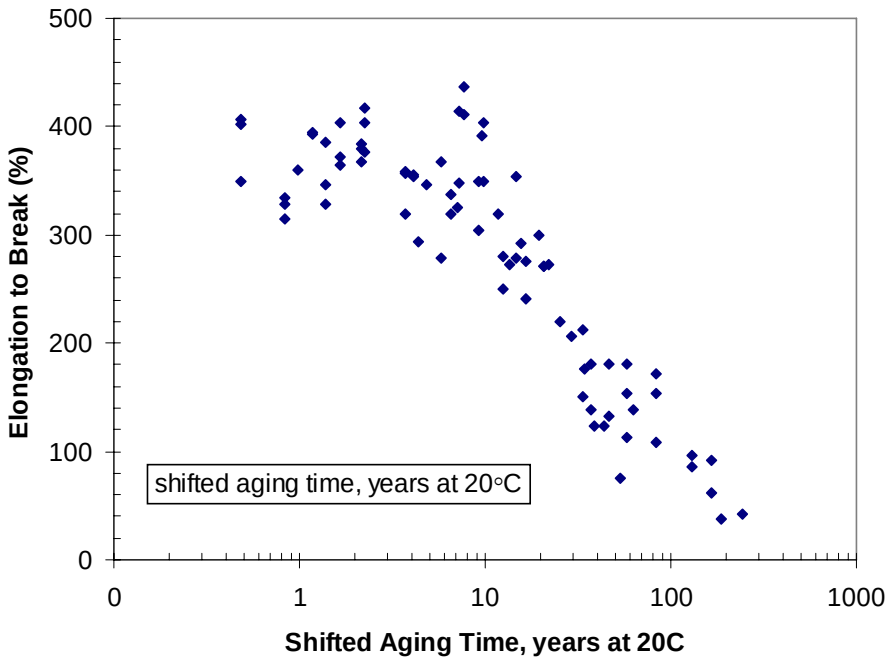
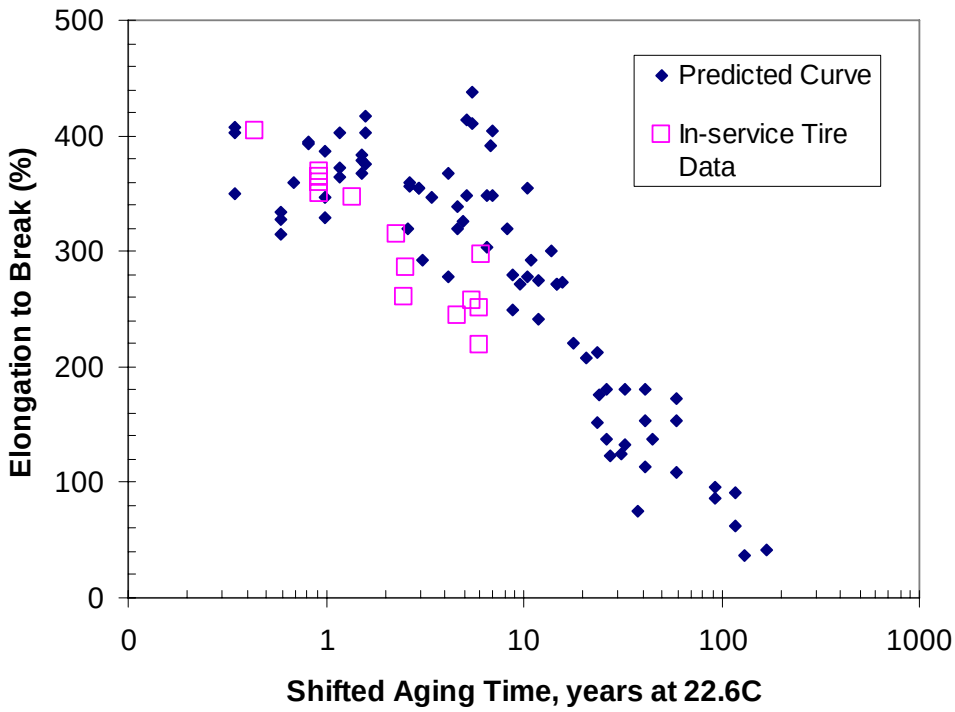


Figure 46 is an overlay plot of BFGoodrich in-service tire belt-coat data with predicted data for ambient temperature aging in thin rubber sheets. The difference between the predicted elongation-to-break data and the measured elongation-to-break data is due to differences in oxygen partial pressure. The predicted results are based on atmospheric oxygen partial pressure. The belt-coat of a tire is subject to higher oxygen partial pressure than is provided by atmospheric oxygen pressure. Actual tire property decay would be expected to be more rapid because inflation pressures would increase the oxygen partial pressure in the belt-coat compound. Secondly, the effect of oxygen partial pressure on oxygen consumption rate is not known for this material. The elevated oxygen partial pressure may be accelerating oxidation. Thirdly, an in-service tire spends a portion of its time at running temperatures. For this work we assumed that an average tire is running 4 percent of the time while in service and parked 96 percent of the time.

Figure 46. Comparison of Predicted Elongation-to-Break Results to In-Service Tire Elongation-to-Break Data



Oxygen Consumption Rate as a Function of Oxygen Partial Pressure

An in-service tire has higher oxygen partial pressure, due to the tire inflation pressure, than atmospheric oxygen partial pressure. To correctly predict the belt-coat property decay, the effect of oxygen partial pressure on oxygen consumption rate was measured. The effect of oxygen partial pressure on oxygen consumption rate is an asymptotic curve. The dependence of oxygen consumption rate on oxygen partial pressure has been described mathematically by a term called beta (β).[2] The equation is shown below, where phi (φ) is oxygen consumption rate and p is oxygen partial pressure. The term p_{air} refers to atmospheric oxygen partial pressure in Akron, Ohio.

$$\varphi_p/\varphi_{air} = \frac{1 + \beta}{(p_{air}/p) + \beta}$$

Equation. 3

The curves were experimentally determined at three temperatures (ambient, 55°C, and 65°C) for new and in-service BFGoodrich belt-coat compounds (Figure 47 - Figure 54). The beta values were determined from the plots of φ_p/φ_{air} as a function of p/p_{air} (Figure 49– Figure 54). From

that data, the predicted properties could be corrected for the oxygen partial pressure in the belt-coat compound of the in-service tire. To the authors' knowledge, this is the first time the effect of temperature on beta has been reported for this type of material. The oxygen consumption rate was more sensitive to oxygen partial pressure at low temperatures (lower beta) than higher temperatures (Figure 55). That means oxygen consumption rate (beta) increased with temperature. This means partial pressure is an important factor governing tire aging (oxidation rate) at ambient temperatures. These effects were incorporated into the Diffusion Limited Oxidation (DLO) computer model to predict the oxygen consumption rate of the belt-coat rubber of an in-service tire.

Figure 47. Effect of Oxygen Partial Pressure on Oxygen Consumption Rate for the New Tire

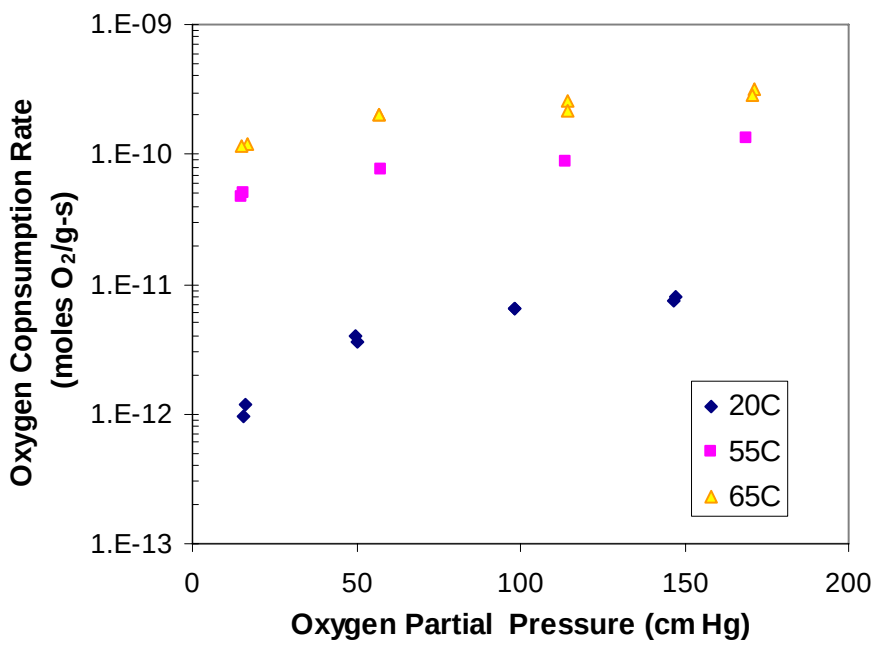


Figure 48. Effect of Oxygen Partial Pressure on Oxygen Consumption Rate for the In-Service Tire

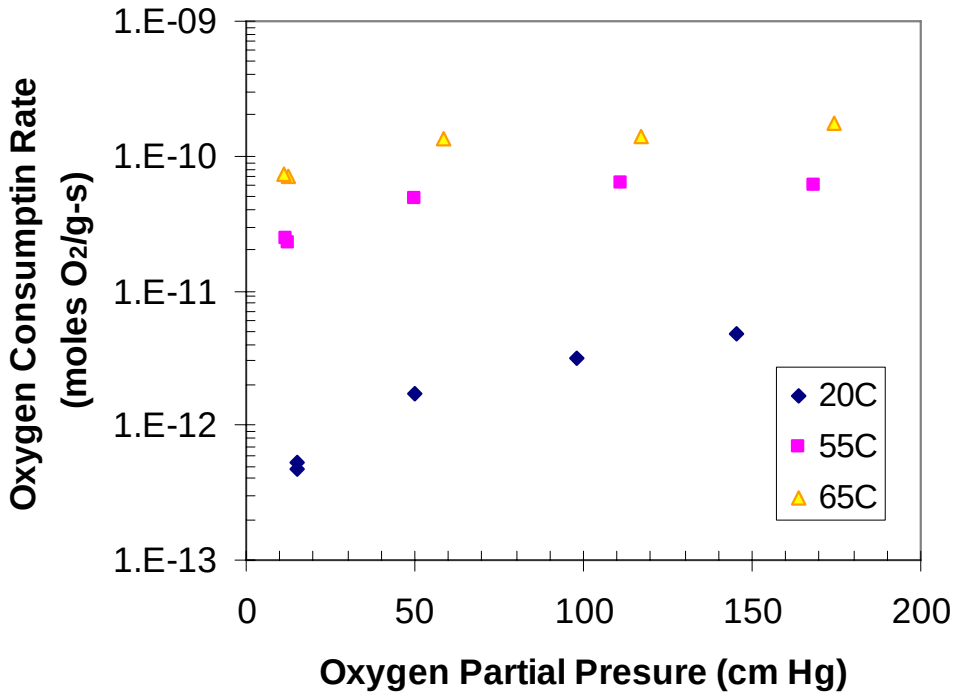


Figure 49. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the New Tire at 20°C

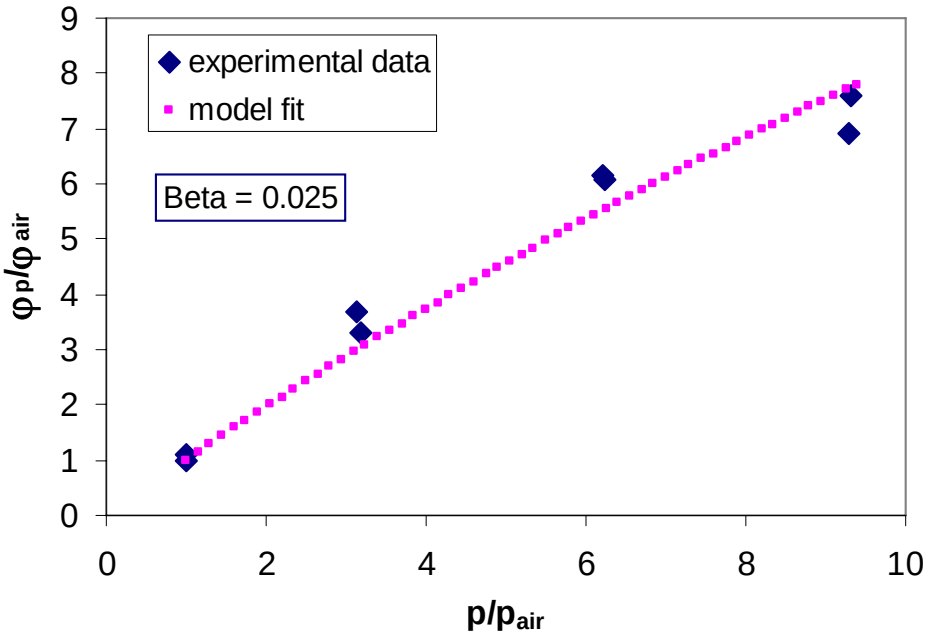


Figure 50. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the New Tire at 55°C

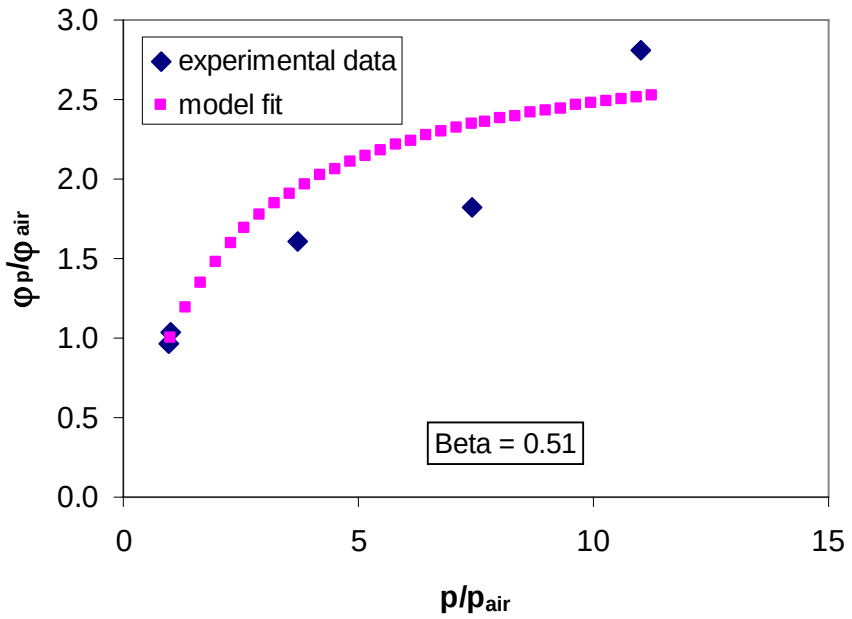


Figure 51. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the New Tire at 65°C

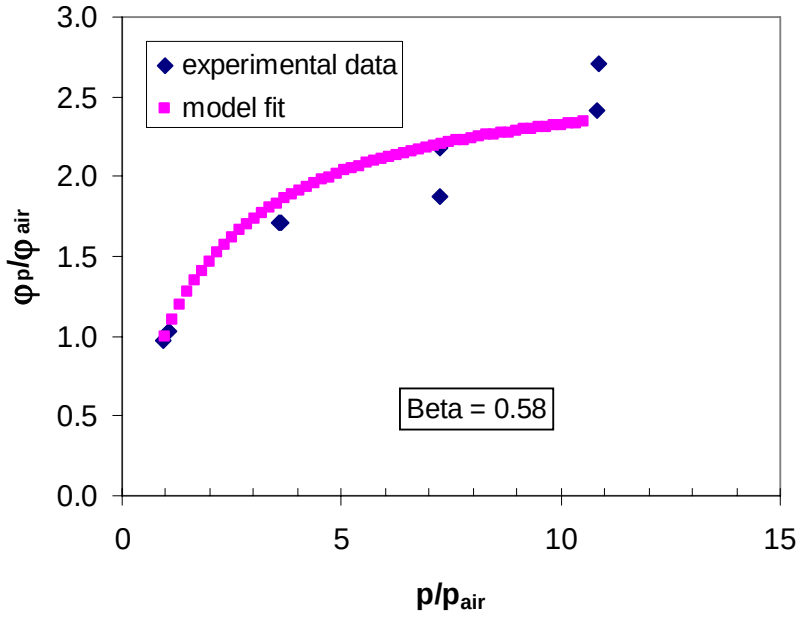


Figure 52. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for In-Service Tire at 20°C

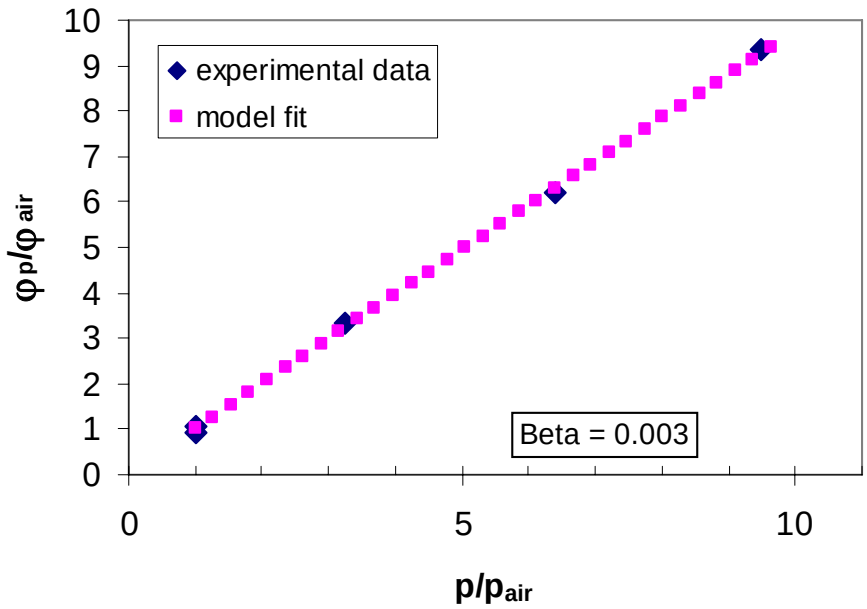


Figure 53. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the In-Service Tire at 55°C

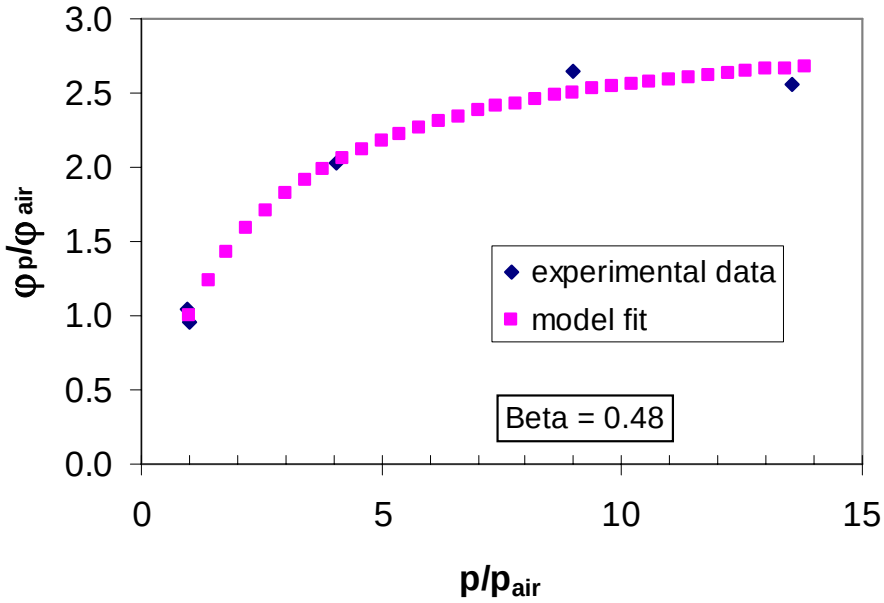


Figure 54. Relative Oxygen Consumption Rate as a Function of Relative Oxygen Partial Pressure for the In-Service Tire at 65°C

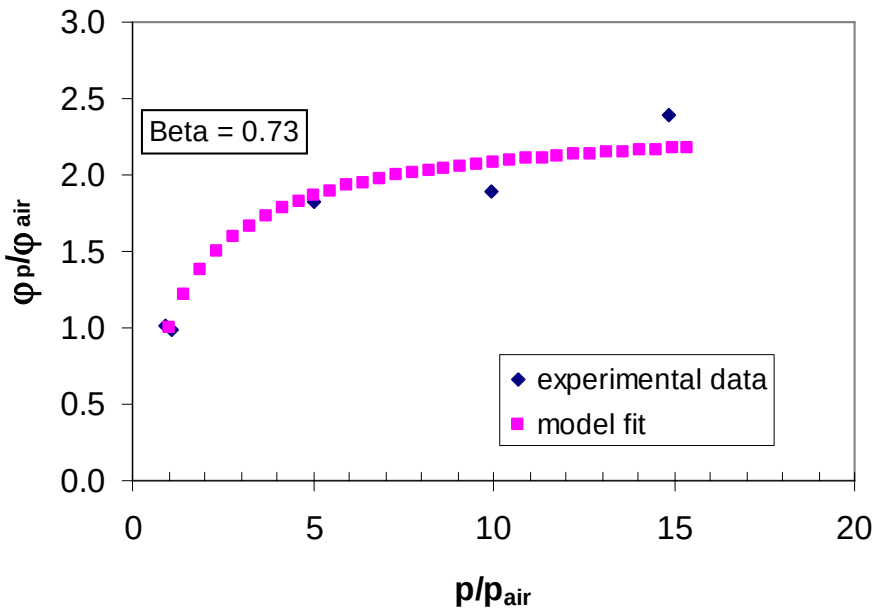
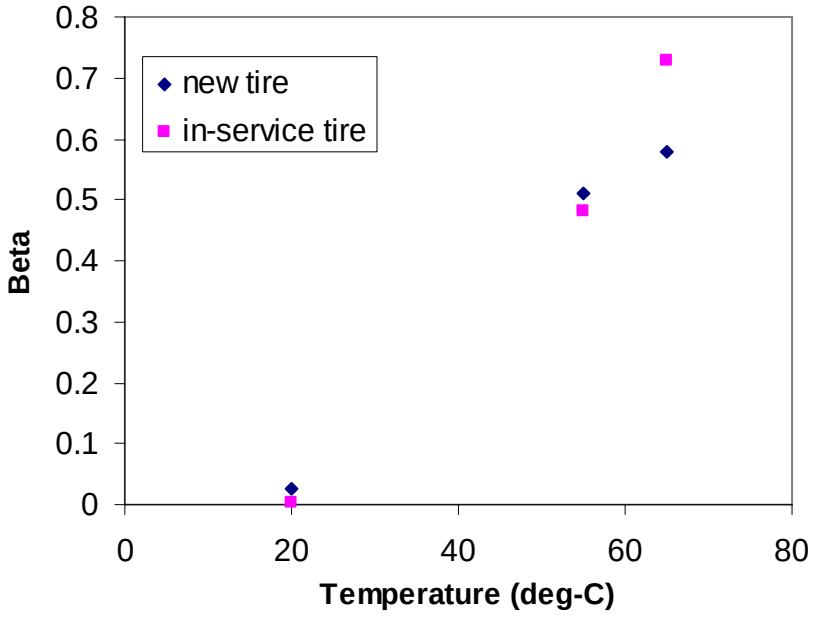


Figure 55. Beta as a Function of Temperature



Determination of Oxygen Consumption Rate in the Belt-Coat using the Diffusion Limited Oxidation Model

The component running temperatures in the shoulder region were measured in a BFGoodrich tire on a roadwheel for the conditions listed in Table 2 (locations of the thermocouples were confirmed by x-ray). The steady-state temperatures (Figure 56) for the innerliner, plycoat, belt package, tread base, and tread are listed in Table 3. These temperatures were used as estimates of the internal component temperatures of the tire during daytime service in Phoenix. The experimentally determined effects of oxygen partial pressure on oxygen consumption rate (beta) as a function of temperature were incorporated into the Diffusion Limited Oxidation (DLO) Model to predict the oxygen consumption rate in the belt-coat compound of the BFGoodrich tire.[7,8] The model used the Phoenix, AZ annual average temperature and literature values for oxygen solubility and oxygen permeability as a function of temperature.[9-14] The effects of inflation pressure loss and oxygen partial pressure loss during service were incorporated. The in-service tire oxygen consumption rate at relative positions across the tire profile, from *0* at the inner surface, to *100* at the outer tread surface, was predicted for a stationary (parked) tire (Figure 57). The oxygen consumption rate was also predicted for an in-use (running) tire (Figure 58). The in-service tire was estimated to be stationary (parked) for 96 percent of its service time and in-use (running) for 4 percent of its service time. The average oxygen consumption rate of the belt-coat compound during normal service was calculated from the DLO model. This provided the shift factor to predict belt-coat property (elongation-to-break) decay for the BFGoodrich tire.

Table 2. Roadwheel Test Conditions

Test Equipment	Test Pressure	Test Load	Speed	Ambient Temperature
1.707-m (67.23-in) road wheel dynamometer	100% Sidewall Maximum (240 kPa [35 psi])	100% Sidewall Maximum (580 kg [1279 lbs])	96.6 km/h (60 mph)	38 deg C +/- 3 deg C

Figure 56. Dynamic Shoulder Component Temperatures

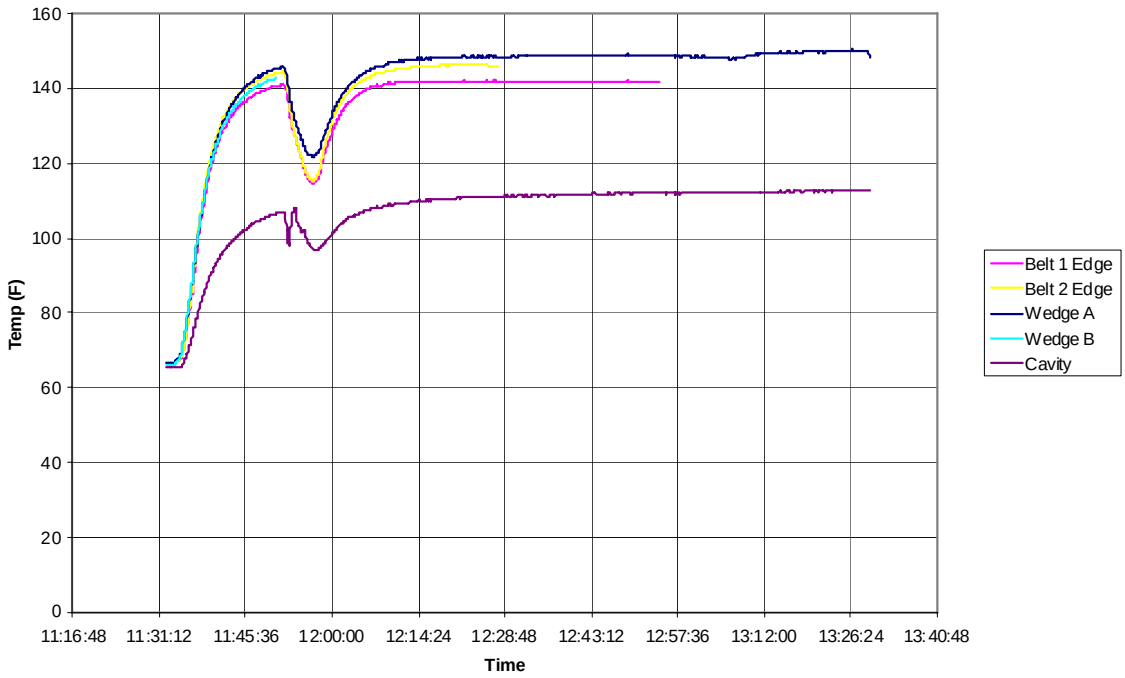


Table 3. Shoulder Component Steady-State Running Temperatures Used in DLO Simulation				
Innerliner	**Plycoat**	**Belt Package**	**Tread Base**	**Tread**
44°C (111°F)	50°C (122°F)	63°C (145°F)	63°C (145°F)	60°C (140°F)

The tire model was used to predict belt-coat compound oxygen consumption while the tire is parked (stationary) and while in operation. The computer model was used to calculate the relative influence of the two conditions on oxygen consumption rates. Even though the in-service tire is assumed to be stationary (parked) for 96 percent of the time, and to be in operation for the other 4 percent, the model predicted the BFGoodrich tire belt-coat did about 60 percent of its aging while stationary (parked) and the other 40 percent while in operation in Phoenix. This is attributed to the higher tire temperatures experienced during rolling operation.

Figure 57. DLO Model Prediction for the Oxygen Consumption Rates in an inflated, stationary tire in Phoenix, AZ

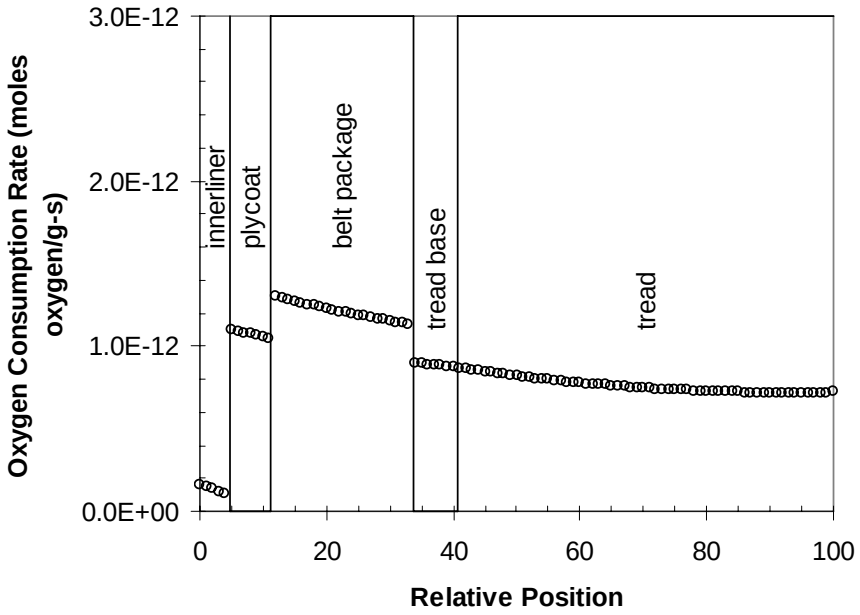
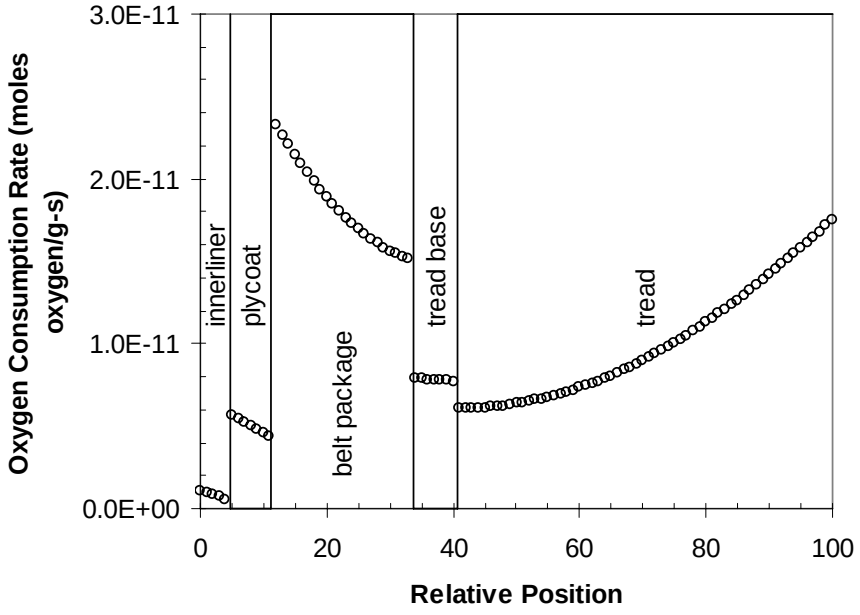


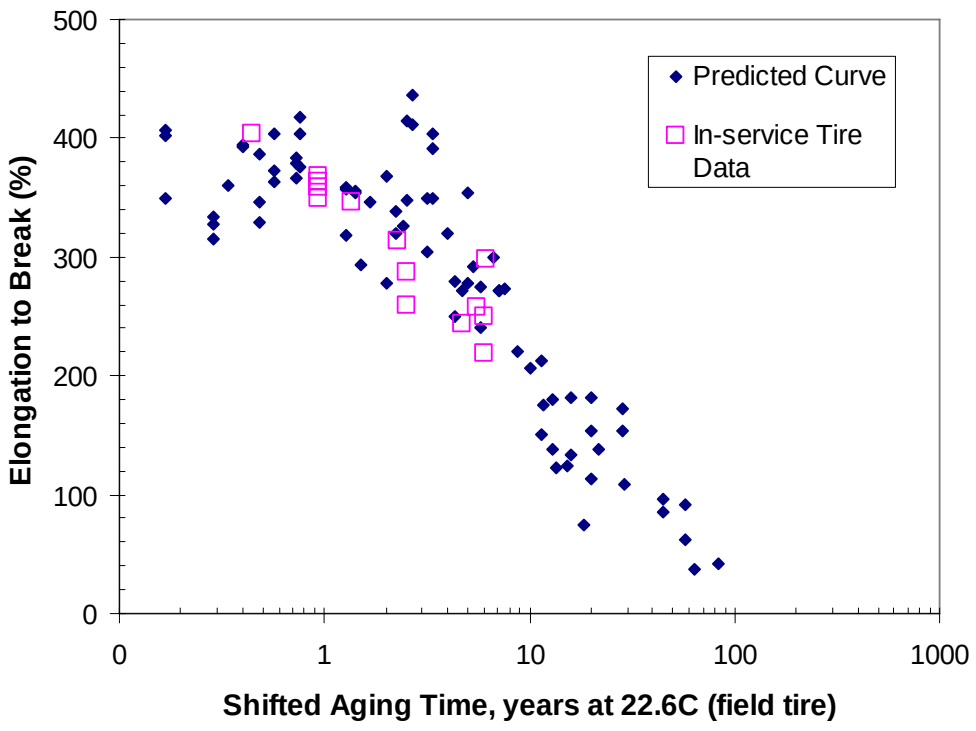
Figure 58. DLO Model Prediction for the Oxygen Consumption Rates in running tire



Shifted Tensile Data with the Effects of Oxygen Partial Pressure and In-Operation Time

The predicted average oxygen consumption rate for an in-service tire was significantly higher than that of a static tire because of the effects from beta, inflated tire oxygen partial pressure, and higher belt edge temperatures in a running tire. The predicted belt-coat oxygen consumption rate from the tire model was then used to calculate the shift factor for the elongation-to-break data. The most significant factor was the contribution from the in-operation (running) time of a tire. This provided a predictive model for belt-coat property (elongation-to-break) decay for the BFGoodrich tire. Good agreement between predicted and measured in-service tire belt-coat elongation-to-break data was observed (Figure 59).

Figure 59. Comparison of Predicted Elongation-to-Break Results to In-Service Tire Elongation-to-Break Data



SUMMARY

Oxygen consumption rate measurements were performed on belt-coat compound extracted from new and in-service BFGoodrich T/A SR4 P-metric P195/65R15 89S tires using the ultra-sensitive oxygen consumption technique. The kinetic study results were analyzed using time-temperature superposition to provide details about the aging kinetics and mechanism in tire belt-coat compounds. Combining the oxidation kinetics with tensile elongation-to-break aging studies provided a way to predict property decay in tires at service temperatures. The new tire

differed from an in service tire in its initial oxygen uptake rate. The new tire belt-coat compound oxidation rate was about two to three times faster than the in service tire belt-coat compound. This may, in part, explain the rapid property decay observed in some in-service tires during their initial years (1-3 years) of service that eventually levels off with longer periods of service. The new tire compound oxidation rate approaches the in-service tire oxidation rate after many iterations of oven aging (5th and 6th repeat tests on the same material). The oxygen consumption rate was found to be more sensitive to the partial pressure of oxygen at low temperatures than higher temperatures. Therefore, the partial pressure of oxygen is an important factor governing tire aging (oxidation rate) at ambient temperatures. This has implications for the rate of material property evolution at ambient temperatures for tires that use higher inflation pressures (higher partial pressures of oxygen) in service, such as light truck tires. It may also lessen the influence of oxygen partial pressure at elevated temperatures, such as those used for tire oven aging.

The empirical shift factors were an exponential function of inverse temperature, from which the activation energy was determined to be 23 kilocalories/mole based on the combined oxygen consumption, CO_2 generation, CO generation, and tensile time-temperature kinetic analysis. All four data sets had similar activation energies (22-23 kcal/mole); however, the new tire belt-coat compound volatile organic generation activation energy (30 kcal/mole) was significantly higher than this value. This suggests that the sources of volatile organics generated by the new tire belt-coat compound cannot be attributed solely to oxidation. On the other hand, the activation energy for volatile organic generation from the in-service tire belt-coat compounds was 25 kcal/mole. Therefore, the volatile organic generation of an in-service tire belt-coat compound can be attributed solely to oxidation after some initial period of service. The activation energy for the in-service tire belt-coat compound was 24 kcal/mole based on oxygen consumption, CO_2 generation, CO generation, and volatile organic generation time-temperature kinetic analysis. All four data sets had similar activation energies (23-26 kcal/mole).

The predicted belt-coat compound elongation-to-break decay curve based on Phoenix, Arizona average ambient temperature (22.6°C) was obtained using the oxygen consumption rate shift factors. An in-service tire has higher oxygen partial pressure than atmospheric oxygen partial pressure (air inflation pressure). To correctly predict the belt-coat property decay, the data was corrected for oxygen partial pressure. The effect of oxygen partial pressure on oxygen consumption rate was experimentally determined at three temperatures. The experimentally determined effects of oxygen partial pressure on oxygen consumption rate (beta) as a function of temperature were incorporated into the Diffusion Limited Oxidation Model to predict the oxygen consumption rate in the belt-coat compound in a tire. The model used the Phoenix, AZ annual average temperature and literature values for oxygen solubility and oxygen permeability as a function of temperature. The effects of inflation pressure loss and oxygen partial pressure loss during service were incorporated. The in-service tire was estimated to be stationary (parked) for 96 percent of its service time and in-use (running) for 4 percent of its service time. From Diffusion Limited Oxidation modeling, the oxygen consumption rate was predicted for the belt-coat compound in this tire during normal service. The predicted belt-coat oxygen consumption rate from the tire model was then used to calculate the shift factor for the tensile elongation-to-break data. This technique (including experimental measurements, DLO modeling, and time temperature superposition) provided a predictive model for belt-coat property (elongation-to-

break) decay for the BFGoodrich tire. Therefore, the physical property decay observed in the in-service tire can be attributed to oxidation.

Additionally, a method for predicting belt-coat compound property decay during tire service has been developed. The tire model was used to predict belt-coat compound oxygen consumption while the tire is parked (stationary) and while in-operation. The computer model was used to calculate the relative importance the two conditions. Assuming the in-service tire to be stationary (parked) for 96 percent of the time that it is in service, and to be in rolling operation for the other 4 percent, the model predicted that the belt-coat compound of the BFGoodrich tire will undergo about 60 percent of its aging while stationary (parked) and the other 40 percent while in rolling operation. This is attributed to the higher tire temperatures experienced during rolling operation.

REFERENCES

1. Phoenix Tire Dataset Version 4.0 (2006). Available at website http://www-nrd.nhtsa.dot.gov/vrtc/ca/tires.htm.
2. Ahagon, A., Kida, M., & Kaidou, H. (1990). Rubb. Chem. Technol., 63, 683.
3. Wise, J., Gillen, K. T., & Clough, R. L. (1955). *Polymer Deg. Stab*. **49**, 403.
4. Terrill, E. R., Pannikottu, A., & Lewis, J. T. (May, 2005). Paper No. 24 at a meeting of the Rubber Division, American Chemical Society in San Antonio, TX.
5. Wise, J., Gillen, K.T., & Clough, R. L. (1997). *Polymer* **38 (8)** 1929.
6. Ferry, J. D. (1980). Viscoelastic Properties of Polymers, Wiley, New York.
7. Gillen, K. T., Clough, R. L. (1992). *Polymer* **33(20)**, 4358.
8. Causa, A. G., Terrill, E. R. (2001). *Tire Technology International, Annual Review* **46**.
9. K T Gillen, M Celina, and M Keenan, *Rubber Chemistry and Technology* **73(2)**, 265 (2000).
10. Brandrup, J., Immergut, E. H., & Grulke, E. A. (Eds.). (1999). Polymer Handbook, Fourth Edition, John Wiley & Sons Inc., New York.
11. Van Amerongen, G. J. (1964). *Rubber Chemistry and Technology* **37(5)**, 1065.
12. Van Krevelen, D. W. (1990). Properties of Polymers: Their Correlation and Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions. Third Edition, Elsevier Science Publishers, Amsterdam, The Netherlands.
13. Morgan, L. B., Naunton, W. J. S. (1939). *Rubber Chemistry and Technology* **12(2)**, 235.
14. Van Amerongen, G. J. (1946). *Journal Applied Physics* **17**, 972.

DOT HS 811 126
March 2009

U.S. Department
of Transportation
**National Highway
Traffic Safety
Administration**

NHTSA
www.nhtsa.gov