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EFFECT OF NITROGEN PURITY ON THE OXIDATION OF BELT COAT COMPOUND

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Abstract

Nitrogen filling in tires has been carried out to reduce pressure loss and moisture in tires as well as to reduce the oxidative component aging process in tires. This study aims to develop the understanding of the effect of nitrogen purity on tire component oxidation using an efficient design of experiment technique. Traditional tensile/elongation testing technique has been carried out on steel belt coat compounds in tire reactors to study the relative effect of nitrogen purity compared to time, temperature, and antioxidant levels.

Introduction

Nitrogen tire inflation has been widely used as a fill gas for race tires. Air is typically used as a fill gas for most other applications such as the ubiquitous passenger, light and medium truck automotive population.

Until recently, a safe, viable technology and infrastructure that could economically supply high purity nitrogen tire fill gas to the general public was not available. With the advent of properly constructed generators with cost effective diffusion separation membranes, a high purity nitrogen inflation infrastructure is being developed. Air is a mixture of 3 important components that affect the tire performance, approximately 80% nitrogen, 20% oxygen and highly variable moisture levels. The oxygen component of the fill gas is the active component that determines the oxidative weakening of the tire component. The oxidative deterioration of elastomers used in tires has been described in the literature and accepted by the scientific community.

Tire pressure monitoring systems will soon be mandatory on all vehicles. Contamination or degradation of these systems would be minimized by high purity nitrogen inflation. Nitrogen molecules migrate through rubber more slowly than oxygen resulting in better retention of inflation pressure. Moisture inside a tire causes inflation pressure anomalies and possible deterioration of the wheels and reinforcing textiles. Oil from the air compressor is also undesirable.

This study focuses on how changes in the nitrogen/oxygen ratio of the fill gas affects the aging characteristics of a typical belt coat rubber compound. Purity of nitrogen in the tire is a function of the initial generator purity, target pressure of the tire and the number and method of refills of the cavity gas. For a tire with a target pressure of 32 psig, filling with a nitrogen generator of 98 percent nitrogen purity output will generate a final nitrogen purity of 92, 96 and 97 percent with each successive complete refill. Similarly, for a nitrogen generator of 95 percent purity output, we achieve 90, 94, and 95 percent target purity with each successive complete refill. It has been shown that property changes with greater than 95% purity in a tire are within the error limits inherent in tire cure variations.

The research presented in this paper will concentrate on providing data on rubber degradation and extent of oxidative aging in relation to the purity of the nitrogen. This information is applicable to tire belt edge compounds as well as to rubber products used in an oxidative environment such as gas powered machine tools. The relative importance of oxygen partial pressure, antioxidant level, time and temperature will be evaluated using a novel design of experiments. The correlation between crack growth at belt edge, oxidation and whole tire durability will be established in a subsequent paper utilizing the tire reactors from this statistical design of experiments. Effect of nitrogen purity on whole tire crack development at belt edge and tire durability will be studied in a future paper.

Experimental

Design of Experiments

A statistical design of experiments was setup using JMP Statistical Discovery Software Release: 5.0.1.2. Four inputs were studied, temperature, time, partial pressure of oxygen, antioxidant level. A full factorial 2x2x2x2 design of experiments was setup with a single center point. The data from the experiments is plugged into the same JMP program to handle and model the inputs with the output generated and illustrate the influence of the effects on the output.

The compounded slabs were aged in the inner cavity of the tire. This allows for the accurate measurement and monitoring of the partial pressure of the oxygen in the vicinity of the samples as well as accurate aging of the tire reactors in calibrated ovens for different times. The partial pressure was maintained within 5 percent of the original set value. Tire were flushed and refilled to adjust to the original partial pressure of oxygen value. This compensates for the loss of the cavity gas due to whole tire permeation. The design box encompasses real world conditions. If a tire is filled to 80psi the resulting partial pressure of oxygen is 19.79 psia.

The Design of experiment conditions of inputs are maintained using calculated pressures and adjusted based on temperatures to maintain the same level of partial pressure of oxygen levels at all the design points.

This novel design of experiment provides us with two studies with a minimal usage of materials and time. The first study is the effect of the 4 inputs on the compounded slabs aging inside the tire reactors. The second study is the effect of time, temperature, and partial pressure of oxygen on the tires used as reactors.

Materials

Compounded Materials

3 types of compounds were formulated based on typical belt coat compounds used in tires. The three compounds are designated by letters A, B and C differentiating the level of antioxidants used 0.5, 1.25 and 2 phr. The formula is shown in Table I. All slabs are compression molded to a uniform thickness of 40 thousands of an inch

Tire Reactors

5 tire reactors were used. All 5 tire reactors were of one size and DOT code, a Hankook LT245/75R16 load range E, rated load of 3042 lbs at 80psi Cold with 2 steel, 2 polyester and 2 nylon plies in the tread.
Two types of materials were evaluated. A design of experiment was setup to illustrate the effect of the 4 inputs on two types of materials.
The design of experiments setup resulted in two superimposed studies. The first is the effect of time, temperature, partial pressure of oxygen, and antioxidant level on compounded material properties aged in tire reactors. The second is the effect of time, temperature, and partial pressure of oxygen on the tire manufactured with an unchanged chemical formulation. For the first study, compounded rubber slabs are aged in specially marked polyethylene bags inside the tire reactors. Tensile specimens are punched out and 3 samples are aged for each design of experiment condition. Additionally intact rubber slabs are aged to avoid severe diffusion limited oxidation conditions.

Fill Gas

Nitrogen and oxygen fill gas tanks are obtained from Praxair. The gasses obtained are dry and contain less than 10ppm of moisture. The gas is mixed to achieve the required percent oxygen in the tire reactors based on the design of experiments.

Physical Properties

Oxygen Content

Oxygen content of the tire reactors was measured using a Balston ® 72-730 Oxygen Analyzer from Parker Hannifin Corporation. The Balston 72-730 Oxygen Analyzer is designed to monitor the oxygen concentration in a process stream, display this concentration in digital form. The Balston oxygen analyzer has been certified to IEC 1010 Standards (CSA 22.2 No.1010.1-92) and bears the CSA safety marking on the product label. The sensing device designed into the Balston 72-730 and 72-O2730NA Oxygen Analyzers is a galvanic cell. The Oxygen Analyzer has an internal temperature compensation circuit to provide accurate readings within a specified temperature range, with an accuracy of ±1% of the calibration gas concentration. The oxygen concentration LED display shows oxygen concentration, in percent, to the nearest 0.1%. The calibration controls are located to the left of the oxygen concentration display. The zero potentiometer is used to zero the instrument when a zero gas (containing no oxygen) is introduced.

Tire Pressure
Tire pressure measurement is done using as digital pressure gauge with a range of 0-100 psig with pressure resolution of 0.5 psig. The tire pressure gauge is calibrated traceable to a NIST calibration certificate.

Temperature Humidity Measurements
Oven aging is calibrated with a NIST traceable Humidity Temperature Meter from Omega with add-on K type Thermocouple.

Tensile Testing
Dumbbell specimens were die cut using an ASTM D 638 Type V dumbbell die and tested per ASTM D 412. Samples were tested at 2.0 inches per minute (50.08 cm/minute). Testing was done in a controlled environmental space maintained at 50% relative humidity and at 70 degrees F. Test output includes elongation to break, stress at break, modulus at 25%, 50%, 100%, 200%, 300% and 400% elongation.

Results and Discussions

As stated in the introduction natural rubber belt coat compound ages in the presence of oxygen. Higher the purity of the nitrogen the lesser is the oxidative effect on the belt coat compound.

Fig.1 shows the correlations using a 2x2x2x2x full factorial model with one center point to construct a formulation between time, temperature, antioxidant level, and partial pressure of oxygen. All four input effects are significant in the elongation to break model. The data and correlations indicate that the partial pressure of oxygen is a significant factor in the degradation of the rubber.

Fig 2 indicates the use of a prediction profiler used to maximize the output variable, in this case elongation to break. The JMP program indicates that the significant controlling inputs are temperature, time, and partial pressure of oxygen followed by antioxidant level. It is important to note this conclusion for compound and tire designers. Tire design can significantly affect running temperatures. A lower belt temperature can cause less degradation of the rubber compared to a better compounded belt coat compound in the limits of our study variables. Inclusion of modulus at 100% elongation in the model illustrates that the DLO conditions have affected the model input of modulus.

Fig 3 indicates the Ahagon chart analysis method for the tensile test data. This chart shows the plot of the log of the elongation ratio at break on the y axis and log of the modulus at 100% strain for tensile dumbbells punched out and aged in tire reactors according to the design of experiments. The design of experiments was constructed to illustrate the effect the four input variable on the rubber properties. We observe a negative 6 slope for the compounds aged at high temperature and high partial pressure of oxygen irrespective of the quality of the compound. It is important to note that literature reveals a -0.75 slope for samples aged at a much lower window of partial pressure of oxygen designated by Type I oxidative reactions. However, in our study we aged tensile dumbbells. This affects the data points at high temperature and high partial pressure. A condition of high modulus at the surface due to diffusion limited oxidation exists. Preliminary testing on the Modulus Profiler indicates a worst case condition with a factor of 3 modulus increase between the surface and the inner regions on the slab for the compound with lowest antioxidant aged for the longest time at the highest temperature. This would cause the data point to slide to the right of the chart falling on the -0.75 slope Type I oxidative curve. It is important to note that the lower purity nitrogen data points would lie further down this degradation slope. As the surface modulus controls the elongation to break, our model is not affected. It is important to note that we need to understand better the changes in compounded slab studies as we see this effect in slabs that are only 40 thousands of an inch in thickness.

Fig 4 shows the same chart with data showing tensile dumbbells punched out after the slabs of rubber were aged. This data is different because of the effects of diffusion limited oxidation are different. The slabs aging behaves differently because it acts as a non continuous sandwich of high modulus surfaces with oxygen starved central region. We observe the antioxidant effect as well. The antioxidant migrates to the surface and creates an artificial diffusion limited conditions. The low antioxidant samples shift to the left on the slabs compared to the dumbbells on the Ahagon chart because the samples have a higher diffusion limited oxidation effect.

Conclusions

The overall conclusion of this study is as follows

- Cavity gas partial pressure of oxygen is a significant factor influencing the rate of degradation of belt coat compound.
- Higher temperatures and higher partial pressure of oxygen induce severe property degradation rates on belt coat compounds.
- Purity of the nitrogen plays a very significant role in the aging of rubber compounds.
- A tire filled with nitrogen will degrade but at a significantly slower rate than tires filled with air.
- Further study of the diffusion limited effects in tires and the influence of nitrogen purity on failure pathways, belt edge crack growth in tires and tire durability will be evaluated in a follow up paper.

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TABLE I: Formulation of compound used in the study

Ingredient	Supplier Code	Description	phr
Non-productive mix			
Natural Rubber			100
Carbon Black N326			65
Aromatic Oil			3
ZnO			5
Stearic Acid			2
Cobalt Naphthenate	Manobond 680C		0.5
TMQ			1
Productive mix			
ZnO			3
6PPD			formula A = .5 formula B = 1.25 formula C= 2
Santogard PVI			0.1
Insoluble sulfur	crystex sulfur	80% sulfur	5.6
DCBS			0.7
Total			**formula A = 185.50** **formula B = 186.25** **formula C= 187.00**

FIGURE 1: Statistical Design of experiments and Model Fit

2x2x2x2 Factorial

2x2x2x2 Factorial
Design 2x2x2x2 Factorial
Model

Columns (6/0)
Pattern
Temp. (Celcius)
Part. Press. O2 (psia)
Antioxidant level (phr)
Time (days)
Elongation to break (percent)

Rows

All Rows	17
Selected	0
Excluded	0
Hidden	0
Labelled	0

	Pattern	Temp. (Celcius)	Part. Press. O2 (psia)	Antioxidant level (phr)	Time (days)	Elongation to break (percent)
1	----	50	1	0.5	7	550.26
2	+++-	70	21	2	7	490.16
3	++-+	70	21	0.5	49	157.22
4	+-+-	70	1	2	7	516.66
5	+-++	70	1	2	49	339.11
6	++++	70	21	2	49	179.27
7	---+	50	1	0.5	49	556.3
8	-+++	50	21	2	49	526.9
9	--++	50	1	2	49	573.36
10	-+--	50	21	0.5	7	541.47
11	+--+	70	1	0.5	49	323.1
12	++--	70	21	0.5	7	456.56
13	+---	70	1	0.5	7	481.36
14	-++-	50	21	2	7	561.68
15	0000	60	11	1.25	28	481.1
16	--+-	50	1	2	7	590.42
17	-+-+	50	21	0.5	49	496.06

FIGURE 2: Prediction profiler and Desirability Function

Response D-Elongation to break (percent)

Parameter Estimates

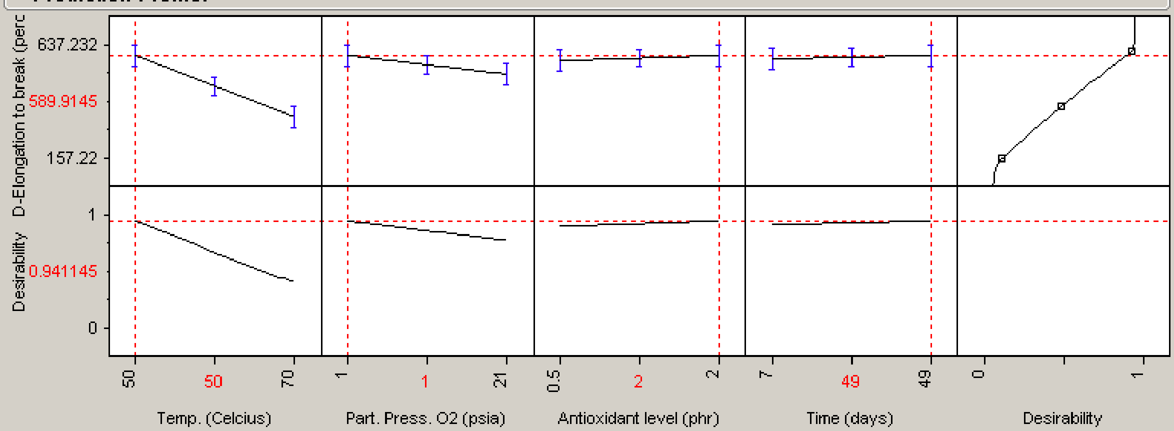
Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Temp. (Celcius)(50,70)	1	1	131952.38	241.2955	<.0001
Part. Press. O2 (psia)(1,21)	1	1	16981.35	31.0530	0.0014
Antioxidant level (phr)(0.5,2)	1	1	2895.25	5.2944	0.0610
Time (days)(7,49)	1	1	67242.97	122.9643	<.0001
Temp. (Celcius)(50,70)*Part. Press. O2 (psia)(1,21)	1	1	3386.95	6.1936	0.0472
Temp. (Celcius)(50,70)*Antioxidant level (phr)(0.5,2)	1	1	0.11	0.0002	0.9893
Part. Press. O2 (psia)(1,21)*Antioxidant level (phr)(0.5,2)	1	1	0.21	0.0004	0.9850
Temp. (Celcius)(50,70)*Time (days)(7,49)	1	1	45670.90	83.5164	<.0001
Part. Press. O2 (psia)(1,21)*Time (days)(7,49)	1	1	7378.38	13.4925	0.0104
Antioxidant level (phr)(0.5,2)*Time (days)(7,49)	1	1	117.23	0.2144	0.6597

Effect Details

Scaled Estimates

Prediction Profiler



Least Squares Fit

Response D-Elongation to break (percent)

Response D-Modulus 100% (psi)

Prediction Profiler

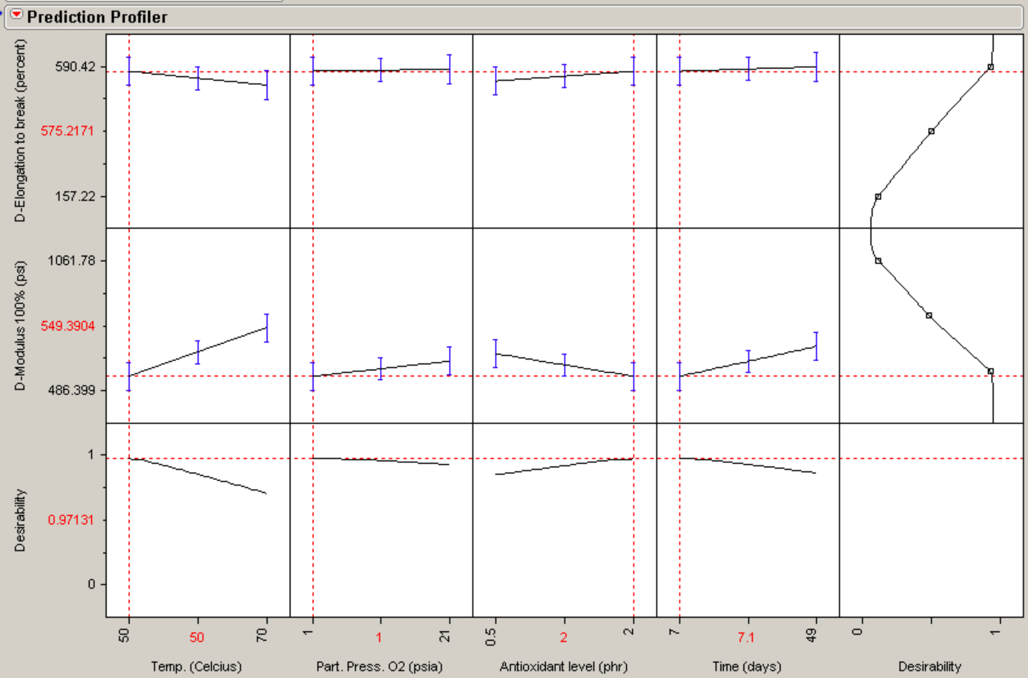


FIGURE 3: Ahagon Chart for belt coat compound tensile dumbbells

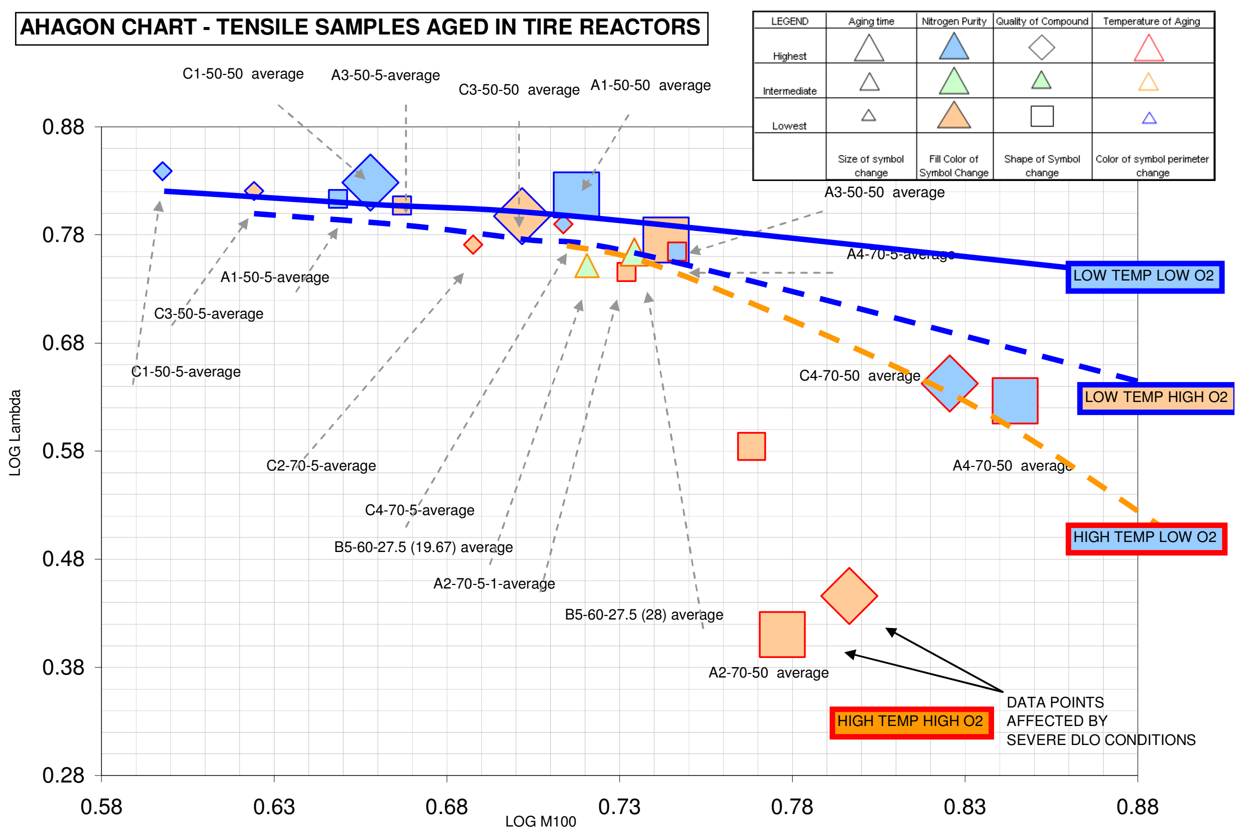


FIGURE 4: Ahagon Chart for belt coat compound slabs.