



Paper No 5

Study on Crosslink Network in Tire Belt-Coat Compounds

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Abstract

Aerobic aging of tire belt-coat compounds led to increased crosslink densities. Their crosslink distribution changes were tracked using wet chemistry (thiol cleavage agents). By this technique the new crosslinks formed would appear to be either polysulfidic type or monosulfidic type. The results of the wet chemistry initially indicated that the crosslinks formed in the field tire were mostly "polysulfidic", while in oven-aged tires they were mostly "monosulfidic". However, from ^{13}C NMR spectroscopic analysis, no evidence was found for formation of more purely sulfur-based crosslinks in the field or oven-aged belt-coat compounds. By IR spectroscopy, the linkages formed during aerobic aging appear to be oxygenated species (sulfoxide, ether, epoxide, or peroxide). The triphenylphosphine results of the extractable sulfur in the network suggested that the original sulfur network stayed in-tact during both of these aging conditions (no evidence of thermal reversion). However, the sulfur linkages are probably participating in the formation of crosslinks in the form of sulfoxide linkages. At higher temperature (e.g. oven aging) the oxygenated linkages rearrange to carbon-carbon linkages with the evolution of CO_2 , CO , and SO_2 .

The effect of aged crosslink structure on physical properties was studied. Compounds differing in crosslink types with the same crosslink density were not significantly different in physical properties. The mechanism of property decay during aerobic aging was considered by examining crystallization kinetics before and after aging. The crystallization kinetic data suggested that oxidation of natural rubber compound is associated with loss of crystallizability on stretching.

Background

What is the structure of the chemical crosslinks formed during oxidative aging in tire wirecoat compounds? What is the effect of aging conditions on the structure of the new crosslinks? Changes in cis to trans isomers and the disappearance of carbon-sulfur linkages during aging has been reported. The appearance of oxygenated species (hydroxyl and carbonyl) had been found¹⁻⁴; however there was a need for more information on the chemical structures of the new crosslinks formed during aerobic aging and their affects on physical properties.

Strategy for Determining What Happens to the Chemical Network in a Wirecoat Compound

To try to answer these questions about the chemical network changes in beltcoat compounds during aerobic aging, the beltcoat compounds from four tires were examined (Table 1).

Table 1 Beltcoat Compounds							
Tire Manufacturer	Tire Model	Tire Size	Load Range	Speed Rating	DOT	Max IP kPa	Description
BF Goodrich	T/A SR4	P195/65R15	89	S	APC6BB113803	240	New
BF Goodrich	T/A SR4	P195/65R15	89	S	APC6BB11455	240	Field – 7.38 yrs / 44,385 miles of service in Phoenix, Arizona
BF Goodrich	T/A SR4	P195/65R15	89	S	APC6BB113803	240	Oven aged at 60°C for 6 weeks, max sidewall pressure, 42% O ₂ inflation gas, capped
BF Goodrich	T/A SR4	P195/65R15	89	S	APC6BB113803	240	Wheel tested for 168 hrs
Model Compounds							
Source	Polymer		Cure System		Filler Loading		Aging
Lab Mix	Natural Rubber		Conventional		Unfilled		Un-aged
Lab Mix	Natural Rubber		Efficient		Unfilled		Un-aged

A combination of methods was used to characterize the network structures. This work included crosslink density by solvent swelling, free induction decay by pulsed proton NMR, crosslink distribution by thio cleavage agents, C¹³ NMR, extractable sulfur with triphenylphosphine, soluble polymer, free sulfur, and Infrared spectroscopy. Physical properties were studied by tensile stress/strain, miniDeMattia crack growth, thermal mechanical analysis, and crystallization kinetics.

Experimental

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. The rubber was not taken from the flared region near the edge of belt #2.

Field Tire: The BF Goodrich tire was a 7.38 year old tire with 44,385 miles of service in Phoenix, Arizona.

Oven Aged Tire: The BF Goodrich tire was aged for six weeks at 60°C at maximum sidewall pressure (capped - not adjusted throughout the duration) and 42% oxygen concentration fill gas.

Wheel-tested Tire: The BF Goodrich tire was subjected to a confidential tire industry supplied roadwheel aging/durability test for 168 hours in total. No visible defects were detected at test end.

Crosslink Density by Solvent Swelling: Crosslink densities were measured using the technique published by Campbell and Saville⁵.

Crosslink Distribution by Cleavage Agents: Crosslink distributions were measured using the technique published by Campbell and Saville⁵.

Pulsed Proton NMR Measurements: A Bruker 20MHz minispec model mq20 was used for pulsed proton NMR measurements of the NMR Relaxation Time. The solid state NMR pulsed proton instrument is used for measuring the transversal relaxation decay curves to probe the changes in the chemical structure. The free induction decay curves were normalized by signal intensity and sample weight. The relaxation time was taken as the time to 0.8 of the initial normalized signal.

Triphenylphosphine Determination of Polysulfidics: Triphenylphosphine extractable sulfur levels were determined as a measure of polysulfidic content using the reported technique⁵⁻⁹.

¹³C NMR Crosslink Structure Analysis: ¹³C NMR Crosslink Structure Analysis was completed in Professor Jack Koenig's lab at Case Western Reserve University using the technique published by Koenig^{2,3}.

Infrared Spectroscopy: Attenuated Total Reflectance (ATR) mode was used on an infrared spectrometer.

Tensile Properties: Tensile properties were measured according to ASTM D412-98a using ASTM D 638-02a Type V die.

Crack Growth Resistance: Crack growth resistance was measured using the mini-DeMattia technique published by B Matthies¹⁰.

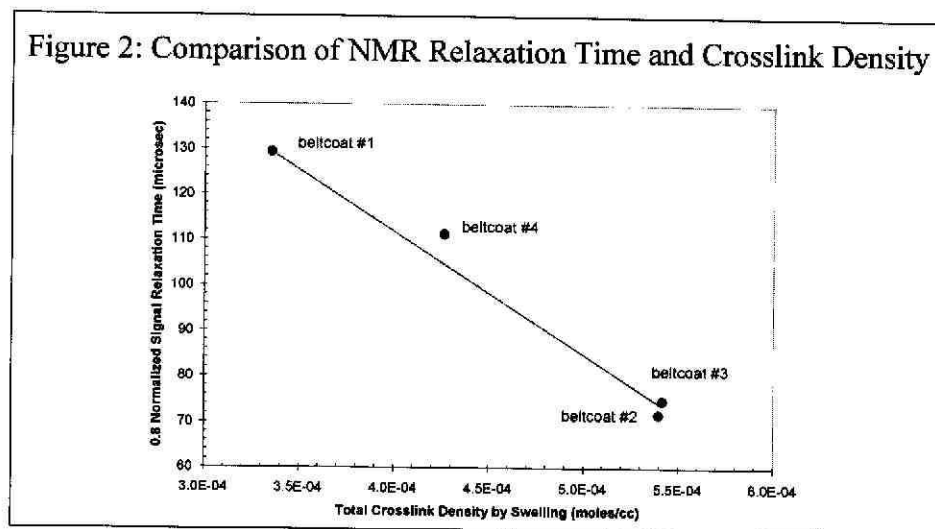
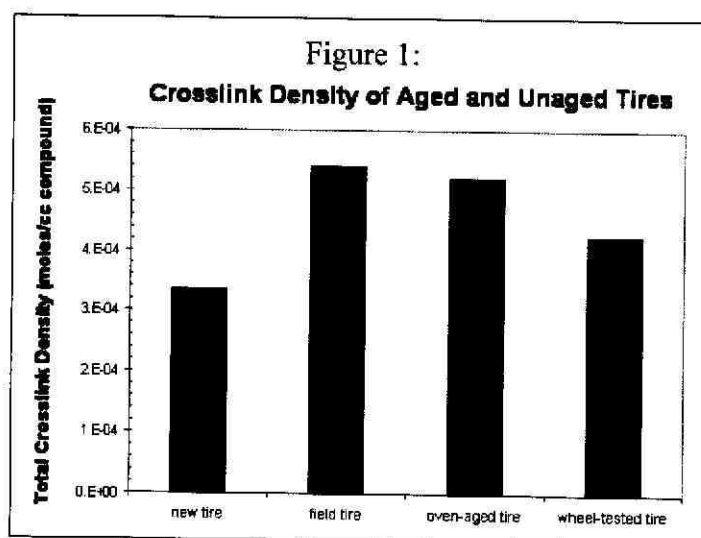
Crystallization Kinetics: Crystallization kinetics was measured using the technique published by Gent¹⁸. The melting point was obtained by slowly warming the stretched and crystallized sample at the conclusion of the crystallization kinetic experiment.

Thermomechanical Analysis ASTM E 1545-00: The specimens were tested using a Perkin-Elmer Series 7 DMA/TMA, scanning from -100°C to 20°C at 3°C/min. The static stress was 30 mN in the expansion mode.

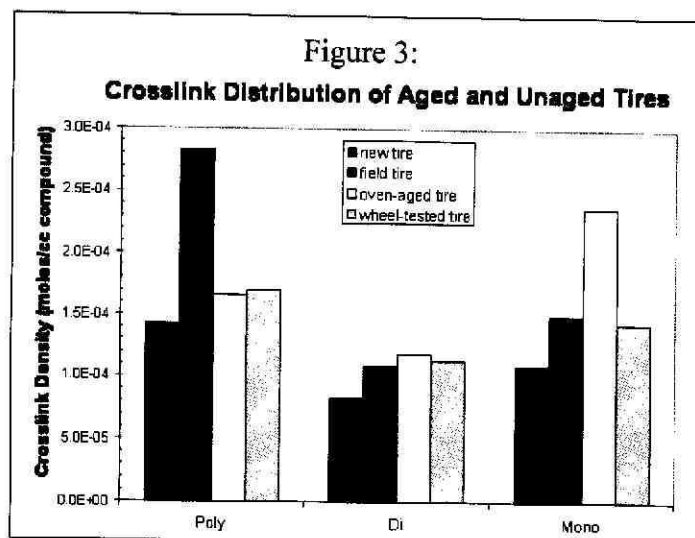
Results and Discussion

Chemical Analysis (Crosslink Density, Pulsed Proton NMR, Crosslink Distribution, ¹³C NMR, TPP Extractable Sulfur, and Infrared Spectroscopy)

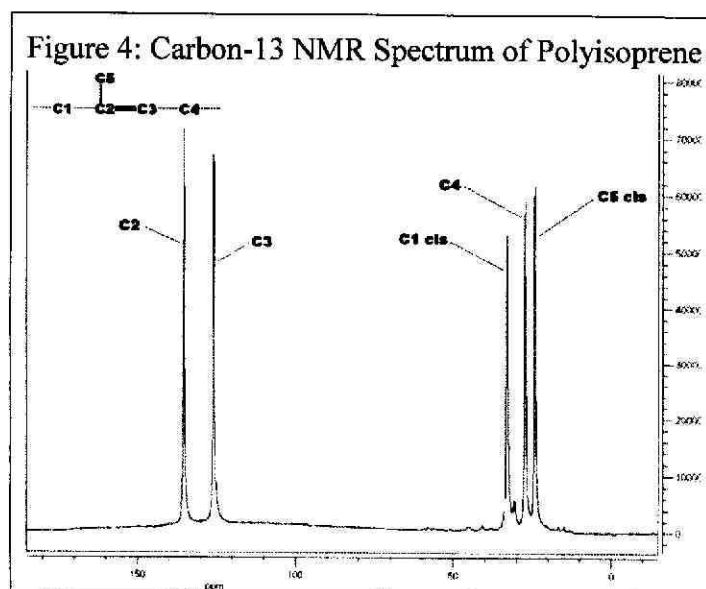
Crosslink density was determined by solvent swelling in toluene (Figure 1) and pulsed proton NMR relaxation time (Figure 2). The results show that the oven aging conditions more readily achieved the crosslink density observed in the beltcoat compound of field tires than the wheel aging conditions. Pulsed proton NMR substantiate the crosslink density ranking of these compounds.

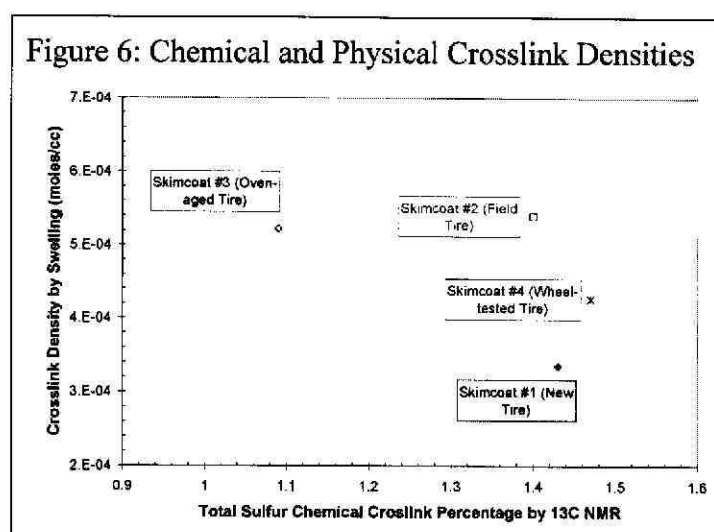
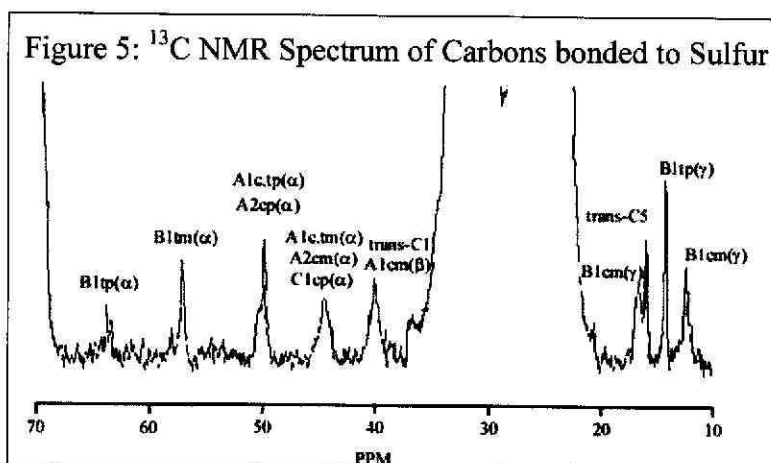


The belt-coat compounds' crosslink distribution changes were tracked using wet chemistry (thiol cleavage agents)⁵. By this technique the new crosslinks formed may appear to be either polysulfidic type, disulfidic type, or monosulfidic type. The results of the wet chemistry initially indicated that the crosslinks formed in the tire (retrieved from service in Phoenix, Arizona) were mostly "polysulfidic", while for over aged tiresa they were mostly "monosulfidic" (Figure 3). The increase in polysulfidic crosslinks was unexpected. This paper tries to explain this result.



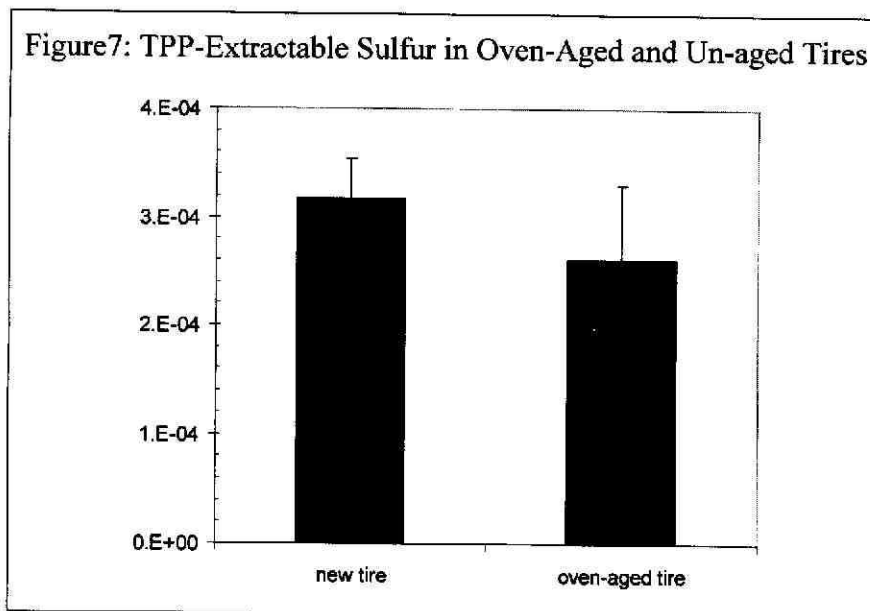
Determination of sulfur crosslink structures in belt-coat compounds by solid state ^{13}C NMR spectroscopy was performed on aged and un-aged tire belt-coat compounds and lab compounds. The work was performed by Regan Silvestre and Professor Jack Koenig at Case Western Reserve University. A typical spectrum of cured natural rubber shows the five carbon atoms in the monomer repeat unit (Figure 4). In addition, there are many small peaks which have been assigned to carbon atoms which are bonded to sulfur (Figure 5). The percentages of sulfur crosslink structures are reported as absolute percentages of the sample total (total of all the ^{13}C peaks). From ^{13}C NMR spectroscopic analysis, no evidence was found for the formation of more purely sulfur-based crosslinks in the field or oven-aged belt-coat compounds (Figure 6).





Extractable sulfur by triphenylphosphine (TPP) has been used by several authors for the network structure elucidation in vulcanized elastomers⁵⁻⁷. These earlier authors used triphenylphosphine to probe the network structure as a function of cure agents and cure temperature. In contrast to those earlier authors, this work used triphenylphosphine as a selective cleavage agent to probe the network and provide insight into the crosslink types formed during oxidation. In the methodology used for this work, the triphenylphosphine was shown to remove a repeatable amount of sulfur from the sample. The sample was initially extracted to remove soluble sulfur, and subsequently exposed to triphenylphosphine. The reaction was found to be complete in about 30 minutes. The sulfur was removed primarily from the polysulfidic crosslinks. Therefore, if polysulfidic crosslinks were lost by thermal reversion, the TPP extractable sulfur would have decreased significantly. Since TPP extractable sulfur did not change significantly, thermal reversion could not be the mechanism. Soluble polymer and free sulfur are also sensitive (good indicators) to thermal reversion. Soluble polymer and free sulfur showed no evidence of thermal reversion. The triphenylphosphine extractable sulfur results suggest that the original sulfur network stays intact during both of these aging conditions (not thermally reverted). Low levels of sulfur may be lost during oven aging. This is

probably associated with oxidation. During oxidation, sulfur bonds form oxygenated sulfur crosslinks that rearrange to carbon-carbon crosslinks with the evolution of CO₂, CO, and SO₂.



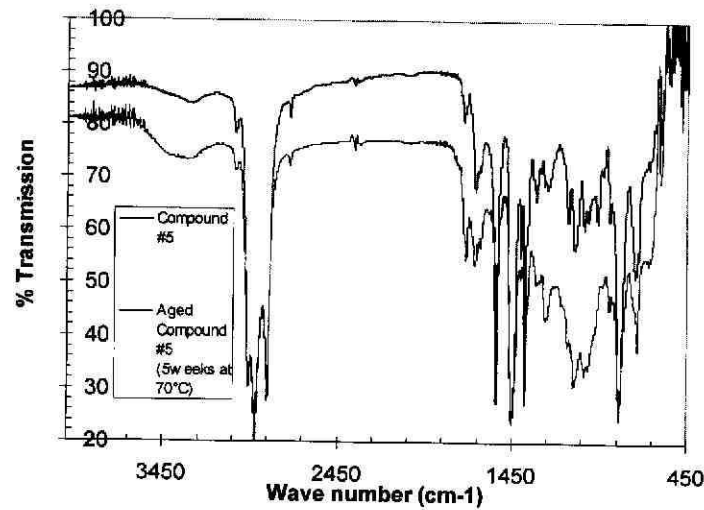
Infrared Spectroscopy (IR) was used to look for chemical structure changes associated with oxidative aging^{11, 12}. An unfilled, natural rubber based compound with high sulfur was used as a model wirecoat compound for Infrared spectroscopy because carbon black scattered the light and destroyed the spectrum quality. This compound was carbon black free, yielding clean IR spectra. Presumably, pendant side-groups form by the reaction of oxygen with the rubber and/or the sulfur network. Also, cis to trans rearrangements might occur associated with the reaction³. The following peaks were followed as a function of aging. The peak at 1010 wavenumber associated with the formation of peroxide, ether, epoxide and sulfoxide linkages. The peak at 1710 associated with the formation of the carbonyl group. The peak at 3400 wavenumber associated with the formation of hydroxyl groups. In each case, the peak absorbance increased with aging (Table 2 and Figure 8). The following peaks were followed as a measure of cis alkene disappearance (1673, 836, and 3035 wavenumber). The results in Table 11 indicate that the model compound (conventional cure, unfilled, un-aged, high polysulfidic content) exhibited the formation of new chemical structures (peroxide, ether, sulfoxide, carbonyl, and hydroxyl) bonds and pendant groups. The model compound was aged 5 weeks at 70°C. The distribution of chemical structures (carbonyl and hydroxyl structures) formed in the conventional cure compound during aging appeared to be significantly different from others compounds with different cure systems. It appeared to have a significantly larger increase in absorbance at 1710 cm⁻¹ and 1010 cm⁻¹. This suggests that the conventional cure, high polysulfidic material tended to oxidize with the formation of sulfoxide structures. This makes sense because it had the highest sulfur content. The compound with conventional cure(high polysulfidic content) also exhibited the greatest

decrease in cis alkene absorbance (1673, 836, and 3035cm⁻¹). During oxidation of compound, cis to trans rearrangements occurred more readily than other compounds. In summary IR results suggest that the new crosslinks formed during oven aging were oxygenated structures, probably sulfoxide linkages. By IR spectroscopy, the linkages formed during aerobic aging appeared to be oxygenated species (sulfoxide, ether, epoxide, or peroxide). The sulfur linkages were probably participating in the formation of crosslinks in the form of sulfoxide linkages. At higher temperature (e.g. oven aging) the oxygenated linkages rearrange to carbon-carbon linkages with the evolution of CO₂, CO, and SO₂.

At higher temperature (e.g., oven aging), the oxygenated linkages rearrange to carbon-carbon linkages with the evolution of CO₂ and SO₂ gases. The crosslinks formed during aerobic aging of belt-coat compounds were found to be of two types. The following mechanism is proposed to explain the results from the various techniques. The chemical structure of one type is probably sulfoxide (sulfur-oxygen). The second type is probably carbon-carbon. The former was the primary crosslink structure formed during field service. The later was the primary crosslink structure formed during oven aging. Temperature, presumably, is the key factor governing the structure of the crosslinks formed.

Table 2: Infrared Results				
	absorbance increase at 1010 cm ⁻¹ after aging	absorbance increase at 1710 cm ⁻¹ after aging	absorbance increase at 3400 cm ⁻¹ after aging	overall absorbance decrease associated with cis alkene after aging
Compound with Conventional Cure	89	470	215	-20

Figure 8: Infrared Spectrum of Aged and Un-aged compound
(High sulfur, unfilled compound)



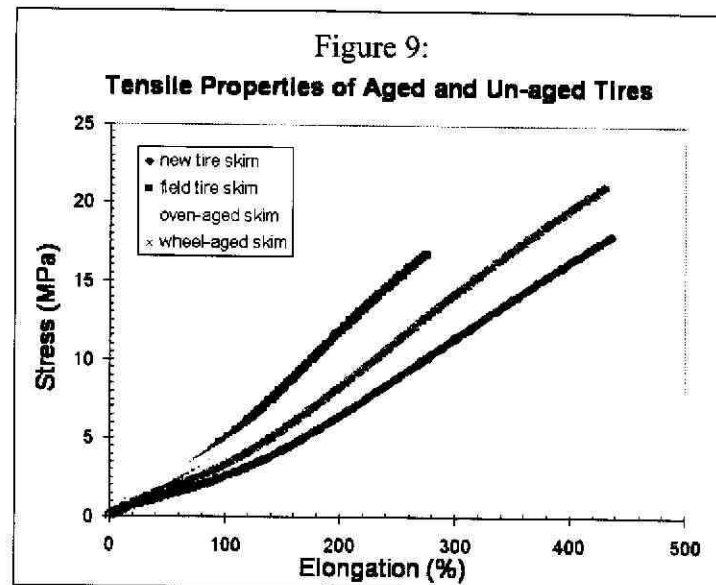
Physical Properties (Tensile and Crack Growth Resistance)

The samples and results of tensile testing are shown in Table 3. When compared to the new tire, the ultimate tensile strength and elongation at break of the field tire decreased approximately 9% and 35% respectively after 7 plus years in Phoenix. The tensile moduli at different strains for the field tire all increased relative to the new tire. For the tire oven aged at 60°C for 6 weeks, the ultimate tensile strength decreased approximately 24% while the elongation at break decreased 38%. The tensile moduli at different strains for the oven aged all increased to magnitudes similar to the field tire. The tire wheel tested for 168 hours exhibited a 17% increase in ultimate tensile strength and a 1% decrease in elongation at break when compared to the new tire. The tensile moduli at different strains for the wheel-tested tire all increased approximately half as much as the increase observed in the field tire.

Tire Description	Tensile Strength (MPa)	Elongation (%)	Modulus at 25% (MPa)	Modulus at 50% (MPa)	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)	Modulus at 400% (MPa)
New	18.0	427	0.92	1.48	2.74	6.81	11.81	16.65
Field	16.3	277	1.18	2.20	4.65	11.20		
Oven-aged	13.7	266	0.98	2.14	4.33	9.92		
Wheel-tested	21.1	421	1.07	1.79	3.47	8.63	14.61	20.03

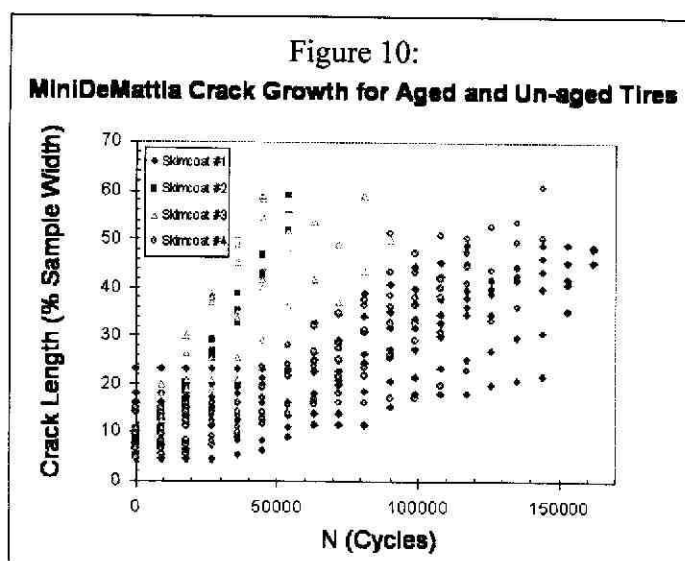
The stress-strain curves for the field, oven-aged, wheel-aged tires are shown in Figure 9. The tensile properties of the belt-coat compound of the oven-aged tire were similar to the field tire. This is a key observation. The field tire and the oven-aged tire had similar total crosslink densities, but differed in crosslink distribution. However, the tensile properties of the oven-aged tire were not significantly different from the field-aged tire. In addition, as will be discussed in a following section, the miniDeMattia crack growth resistance properties were not significantly different between the oven and field tires.

The belt-coat in the wheel-tested tire was not aged as much as the field or oven-aged tires. Presumably these wheel test conditions did not result in sufficient oxidation of the belt-coat (skim) compound, despite the fact that the belt edge may see very high temperatures.



The crack growth resistances of tire belt-coats and lab compounds were measured using the miniDeMattia technique (Table 4). The coefficient of variation expressed in percent is shown for the crack growth rates. The extracted tire belt-coat materials could be ranked by this technique (Figure 10). The new tire had the best crack growth resistance. The wheel-tested tire had less degradation in crack growth resistance than the field and oven-aged tires. The oven aged tire had similar crack growth resistance to the field aged tire. This is a key observation. The field tire and the oven-aged tire had similar crosslink densities, but differed in crosslink distribution. However, the crack growth resistance of the oven-aged tire was not significantly different from the field-aged tire.

Table 5: MiniDeMattia Crack Growth Rate Data			
Compound	Description	Crack Growth Rate (in/10 ⁶ cycles)	COV (%)
Belt-coat #1	New tire	0.30	26
Belt-coat #2	Field tire, 7.38 yrs / 44,385 miles of service in Phoenix, Arizona	1.08	8.0
Belt-coat #3	Oven aged tire, 60°C for 6 weeks, max sidewall pressure, 42% O ₂ inflation gas, capped	1.05	29
Belt-coat #4	Wheel-tested tire, 168 hours	0.43	22



Mechanisms Governing Property Changes during Oxidative Aging (Glass Transition Temperature and Crystallization Kinetics)

The glass transition temperatures (T_g) of aged and un-aged tire belt-coat compounds were measured to determine whether glass transition temperature was a fundamental criterion governing property changes during aging. Aging did not affect the glass transition temperature of these compounds (Table 5).

Table 51: TMA T_g Data	
Sample	T_g (°C)
Belt-coat #1	-52
Belt-coat #2	-49
Belt-coat #3	-48
Belt-coat #4	-49

Crystallization kinetics was measured to determine whether aging affects crystallizability of natural rubber tire belt-coat and lab compounds. It is well known that both filled and unfilled compounds of natural rubber and cis-polyisoprene crystallize on stretching¹³⁻²². The ability to crystallize on stretching is vital for its performance. In Figure 11 the crystallization rate of a unfilled, natural rubber based compound with an efficient cure was found to be significantly diminished after aging. The crystallization half-life approximately doubled after one (1) week at 70°C. Further aging (through 5 weeks) continued to slow the crystallization rate. Melting point was altered (decreased) by aging this compound (Table 6). The crystallization rate correlated with the effect of aging on physical properties (e.g., tensile elongation at break). For example, the tensile properties of this compound were significantly diminished after aging. Certainly the compounds extracted from tires crystallize on stretching; however, they may crystallize too fast or too slow to be detected by this technique.

In summary, the crystallization data suggests that the oxidation of natural rubber is associated with loss of crystallizability. Aging of a sulfur vulcanized elastomer compound caused a steady decrease in crystallization rate. The similarities between changes in crystallization rate and tensile properties are strong evidence that the loss of properties during aging of NR is explained, in part, by loss of its ability to crystallize on stretching. Crystallizability of natural rubber is affected by pendent side groups and cis to trans rearrangements. Pendant side groups and cis to trans rearrangements are possible during oxidation of natural rubber². Therefore, loss of crystallizability is a key factor governing property decay in natural rubber compounds.

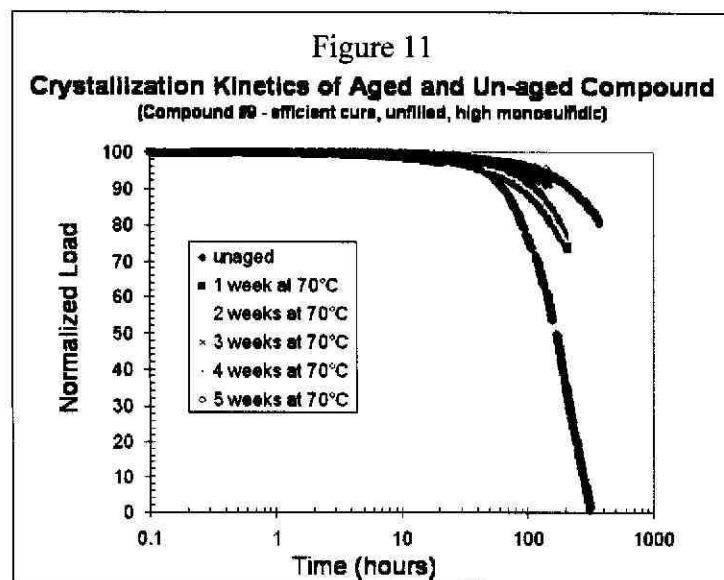


Table 2: Crystalline Melting Point		
Compound	Description	Melting Point
Unfilled Compound with an efficient cure	unaged	14.5°F
Unfilled Compound with an efficient cure	Aged 1 week at 70°C	-1.5°F
Unfilled Compound with an efficient cure	Aged 2 week at 70°C	1.5°F
Unfilled Compound with an efficient cure	Aged 3 week at 70°C	Not observed
Unfilled Compound with an efficient cure	Aged 4 week at 70°C	3.5°F
Unfilled Compound with an efficient cure	Aged 5 week at 70°C	2.4°F

Conclusions:

Aerobic aging of tire belt-coat compounds led to increased crosslink densities. Crosslink density was determined by solvent swelling in toluene and pulsed proton NMR relaxation time. Changes in crosslink distribution were followed using wet chemistry (thiol cleavage agents)¹⁹. By this technique the new crosslinks formed could appear to be either polysulfidic type or monosulfidic type. The formed crosslinks in the field tire were mostly "polysulfidic" and during oven aging they were mostly "monosulfidic". From ¹³C NMR spectroscopic analysis, no evidence was found for formation of more sulfur crosslinks in the field or oven-aged belt-coat compounds. By IR spectroscopy, the linkages formed during aerobic aging appear to be oxygenated species (sulfoxide, ether, epoxide, or peroxide). The triphenylphosphine results of the extractable sulfur in the network suggest that the original sulfur network stays intact during these aging conditions (not thermally reverted). However, the sulfur linkages are probably participating in the formation of crosslinks in the form of sulfoxide linkages. At higher temperature (e.g., oven aging), the oxygenated linkages rearrange to carbon-carbon linkages with the evolution of CO₂ and SO₂ gases.

The crosslinks formed during aerobic aging of belt-coat compounds were found to be of two types. The following mechanism is proposed to explain the results from the various techniques. The chemical structure of one type is probably sulfoxide (sulfur-oxygen). The second type is probably carbon-carbon. The former was the primary crosslink structure formed during field service. The later was the primary crosslink structure formed during oven aging. Temperature, presumably, is the key factor governing the structure of the crosslinks formed.

The oven-aged tire belt-coat and the field-service tire belt-coat compounds were obtained with the same total crosslink density, differing in crosslink types. Thereby, these two samples provided a comparison of the role of the crosslink types formed during aerobic aging on physical properties. In the tensile properties and crack growth rate, there was no significant difference between the field and oven-aged belt-coats.

The fundamental mechanism of property decay during aerobic aging was considered by examining crystallization kinetics before and after aging. The crystallization kinetic data suggest that oxidation of natural rubber is associated with loss of crystallizability on stretching. The crack blunting results from tensile testing also substantiates the loss in the ability to crystallize on stretching. The loss of crack blunting ability has been shown to be associated with the loss of the ability to crystallize on stretching²³. Crystallizability was presumably affected by pendant side groups and cis to trans rearrangements. Compound glass transition temperature was not a factor governing property changes during oxidation.

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