Aging

Paper No 25B

Some Key Questions about Wirecoat Compound Aging

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Presented at a meeting of the
International Tire Exhibition & Conference
Akron, OH
September 12-14, 2006

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Abstract

Oven aging has been suggested as an approach to aged endurance tire testing for passenger and light truck tires. Oxidative crosslinking has been shown to be the major aging mechanism in the beltcoat of these tires. Some key points were examined and reported herein to aid this development. This understanding may help designing aged tire tests which better simulate field (normal service) conditions. The following questions were examined by aging wirecoat compound extracted from a passenger tire. (1) What is the effect of aging temperature on the crosslink structure and properties? (2) If diffusion of oxygen slows during aging, what happens to the crosslink structure and properties? (3) What is the effect of strain (static or dynamic) during aging on the crosslink structure and properties?

Background

What happens to wirecoat compound if aging is initially aerobic and then followed by anaerobic aging? This service requirement may be prevalent in a number of tire types and service scenarios. For example, a large tire wirecoat at ambient temperature may age aerobically and then become anaerobic after the compound consumes the dissolved oxygen. This could be prevalent in earthmover, aircraft, and radial medium truck tires. Other scenarios could slow oxygen diffusion to the wirecoat compound. During wheel testing the internal tire components could initially have plenty of dissolved oxygen, after which they become oxygen starved. Diffusion limited conditions can be achieved when ever the outer compounds consume oxygen faster than oxygen can diffuse. This could be true in tire oven aging. This could occur when a nail hole is plugged, a tube tire receives a new liner or a repaired liner, or when the cavity gas is replaced by an inert gas.

Strategy for Determining What Happens to Properties and Chemical Structure of the Wirecoat Compound

The strategy for establishing determining the effect of aerobic aging followed by anaerobic aging was to study the physical and chemical property changes as a function of time at 80°C. Two wirecoat compounds were aged at 80°C in air oven for four weeks followed by anaerobic aging at 80°C for six weeks. Property changes were monitored as a function of time. Physical property changes were monitored by tensile properties. Chemical property changes were monitored using oxygen content and extractable sulfur using triphenyphosphine. To determine whether the aging was homogenous, modulus profiling and the diffusion limited oxidation model were examined. Filler/filler interactions and filler/rubber interactions were illuminated using dynamic mechanical property strain sweeps and stress-strain curves.

Experimental – Description of Compounds and Aging

Two passenger tire wirecoat compounds were mixed in the laboratory and differed in antioxidant package. Compound 1 had an antioxidant package (1 phr 6PPD, 1 phr TMQ, and 0.5 phr Wingstay 100) and Compound 2 did not have antioxidants in the recipe. Thin samples (1 mm) were molded to prevent diffusion limited oxidation.

Aging was performed in a forced air oven at 80°C for four week, followed by six weeks at 80°C in an anaerobic, stainless steel reactor.

Experimental – Test Methods

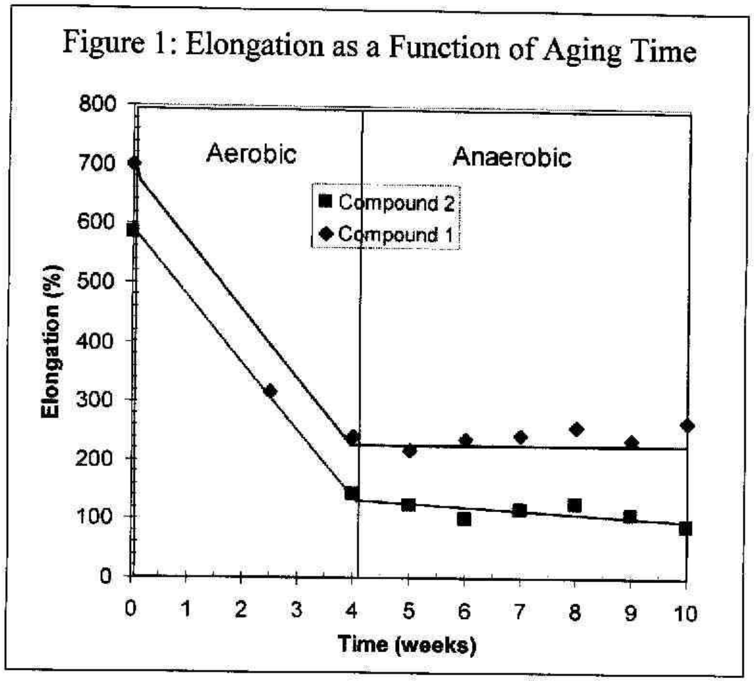
The tensile properties were measured per ASTM D 412-98A (2002) using ASTM D 638-02a Type V dumbbell die. Oxygen content was measured by elemental analysis. Triphenylphosphine (TPP) method for sulfur extraction was reported earlier.[1] TPP-extractable sulfur has been shown to correlate with polysulfidic crosslink levels in the compound. Modulus profiling and the Diffusion Limited Oxidation Model were reported earlier.[2]..Dynamic mechanical properties were measured in tension using a Metravib model VA2000.

Results and Discussion

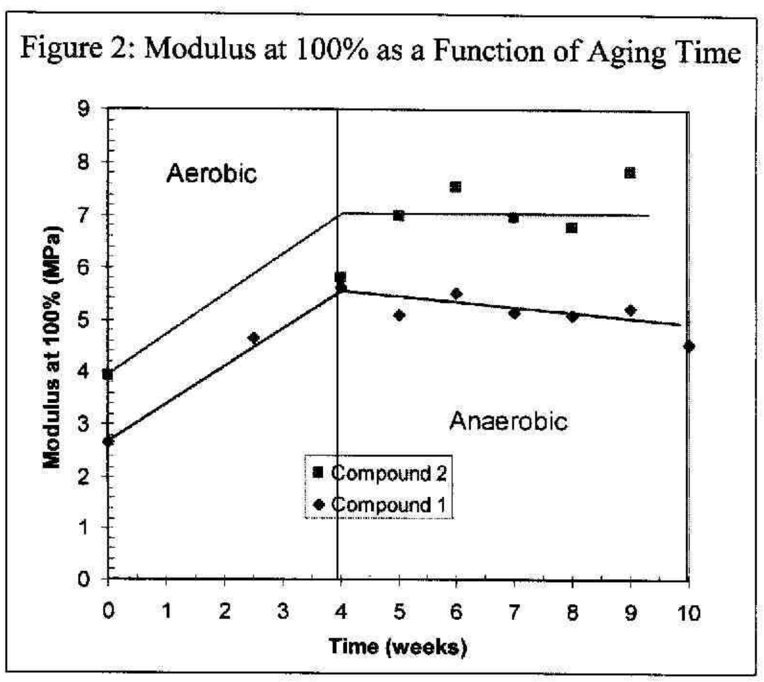
Two wirecoat compounds (natural rubber and high sulfur based) which differed in antioxidant content were aged at 80°C, initially under aerobic conditions and subsequently under anaerobic conditions. The physical properties and chemical properties were studied as a function of time. The homogeneity of aging through the thickness of the sample was examined because the aging could possibly be non-homogeneous due to diffusion limited oxidation. The low-strain property changes were studied because they reflect changes to the filler-filler interactions and the filler-rubber interactions.

Physical Property (Tensile) Changes

The tensile elongation decreased during aerobic aging at 80°C and then remained unchanged during anaerobic aging at 80°C (Figure 1).

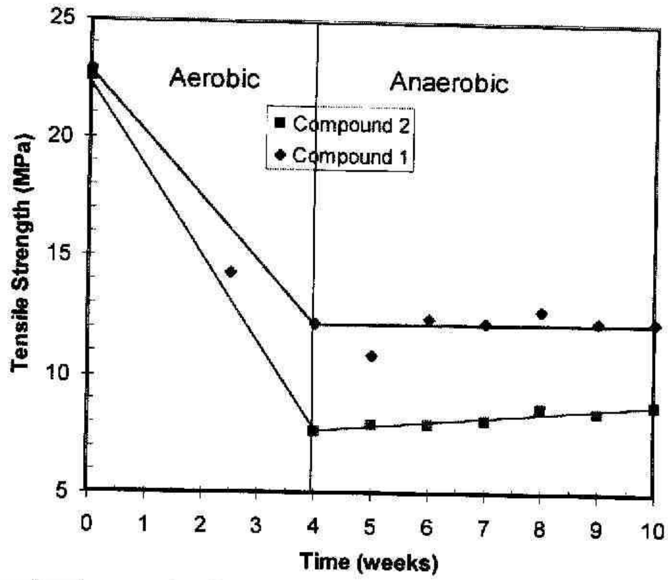


The tensile modulus at 100% increased during aerobic aging and then remained unchanged during anaerobic aging (Figure 2).



The tensile strength decreased during aerobic aging and then made no further change during anaerobic aging (Figure 3).

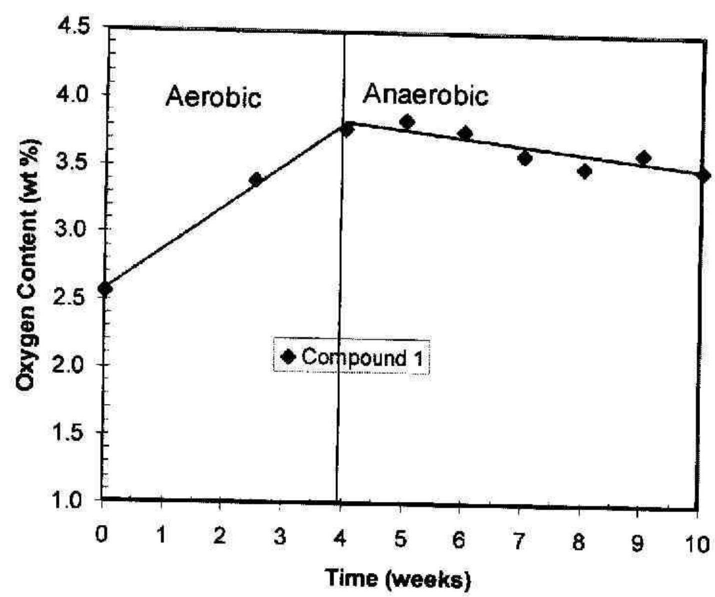
Figure 3: Tensile Strength as a Function of Aging Time



Chemical Property (Oxygen Content and TPP-Extractable Sulfur) Changes

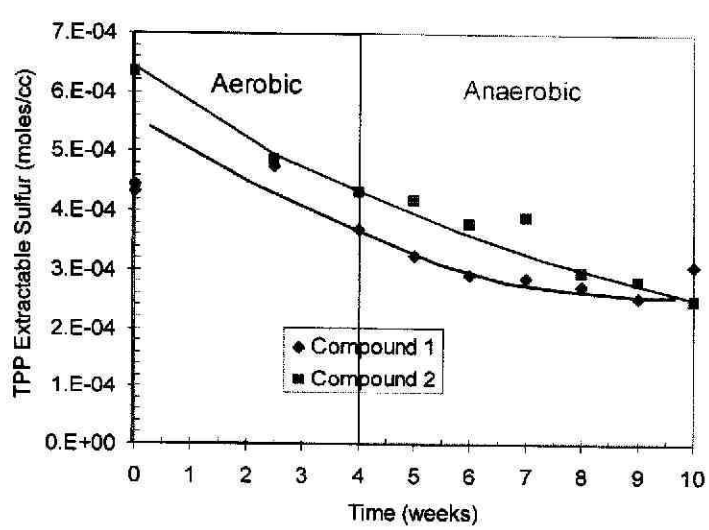
The oxygen content increased during aerobic aging and subsequently decreased during anaerobic aging (Figure 4). The increase in oxygen content is associated with the reaction of oxygen to formation of oxygenated structures. Oxidation is known to generate CO and CO_2 simultaneously. Probably CO and CO_2 continued to evolve during the anaerobic aging from oxygenated structures formed during the anaerobic conditions.

Figure 4: Oxygen Content as a Function of Aging Time



TPP-extractable-sulfur decreased during aerobic and anaerobic aging (Figure 5). This suggests that O_2 partial pressure did not affect thermal reversion reactions. Thermal reversion was governed by thermal (heat) history.

Figure 5: TPP-Extractable Sulfur as a Function of Aging Time



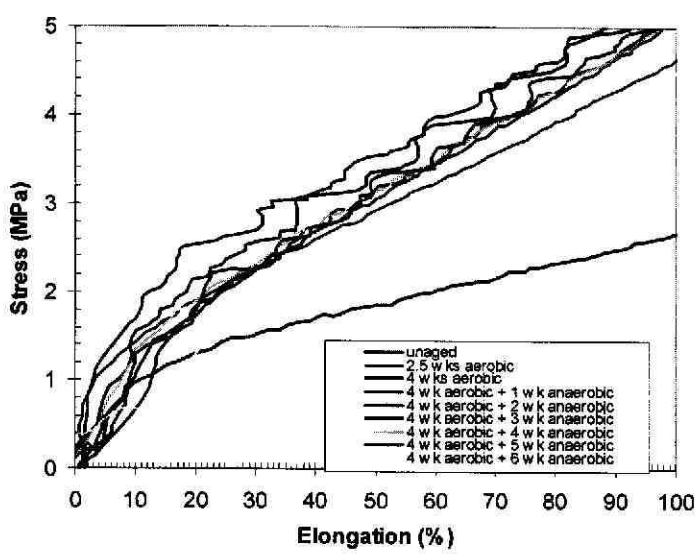
Homogeneity of Aging through the thickness

The Diffusion Limited Oxidation model and modulus profiling were used to check for non-homogeneous (diffusion limited) oxidation. The samples were molded to 1 mm gauge to prevent diffusion limited oxidation. No evidence of diffusion limited (non-homogeneous) oxidation was observed.

Low-strain Properties

Low-strain dynamic mechanical properties and tensile properties were examined. The low-strain modulus increased during aerobic aging and, subsequently, decreased slightly during anaerobic aging (Figure 6). This suggests that oxidation increased rubber-filler interactions and that anaerobic aging led to a loss in rubber-filler interactions. The reasons can only be hypothesized. Oxidation may impart interactions and bonding between rubber and filler. Thermal reversion ay reduce interactions and bonding between rubber and filler.

Figure 6: Low Strain Tensile Properties as a Function of Aging



Conclusions:

1. Physical and chemical properties were measured in wirecoat compounds which experienced aerobic aging at 80°C followed by anaerobic aging at 80°C.
2. During aerobic aging elongation to break and tensile strength decreased and modulus at 100% increased. During anaerobic aging no change in tensile properties were observed.

3. Tensile properties changed very little during anaerobic aging at 80°C. This suggests that any method to reduce oxygen in the wirecoat compound is helpful for tire durability.
4. Oxygen content increased during aerobic aging. During anaerobic aging oxygen content decreased, presumably from CO and CO_2 generated from oxygenated structures.
5. TPP extractable sulfur ("polysulfidic content") decayed during both aerobic and anaerobic aging. It appears to be independent of O_2 gas concentration.
6. No DLO aging was observed in these aged sheets.
7. The low strain modulus increased during aerobic aging and decreased during anaerobic aging.

References:

1. B Saville and A A Watson, *Rubber Chem. and Tech.* **40**, 100 (1967).
2. E R Terrill, U Karmarkar, and A Pannikottu Paper Number 116, Presented at a meeting of the Rubber Division American Chemical Society, Cleveland OH October 14-17, 2003.