Available online at www.sciencedirect.com
ScienceDirect
Polymer Degradation and Stability 92 (2007) 110−117
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Rubber aging in tires. Part 2: Accelerated oven aging tests

David R. Bauer*, John M. Baldwin, Kevin R. Ellwood

Ford Motor Company, Research Laboratory, MD-3182, P.O. Box 2053, Dearborn, MI 48121, United States

Received 15 June 2006; received in revised form 31 July 2006; accepted 4 August 2006
Available online 30 October 2006

Abstract

The kinetics of oxidation of wedge and skim rubber from tires aged at different oven temperatures with various fill gases have been measured for 5 different tires and compared to field results. We demonstrate that oven aging tires mounted on wheels and inflated to the maximum sidewall pressure closely reproduce the aging behavior measured for tires collected after customer use. Temperatures as high as 70 °C can be used to accelerate aging. Use of 50/50 blend of N_2/O_2 as a fill gas accelerates the oxidative aging by 30−40% relative to air. By combining elevated temperatures with oxygen enriched fill gas, it is possible to oven age tires to an age equivalent to 6 years in Phoenix in 8 weeks or less.

Keywords: Tires; Oxidation; Natural rubber; Oven aging; Acceleration factors

1. Introduction

In the previous paper [1], aging rates for skim and wedge rubber were reported for 5 tires aged in the field. This paper reports corresponding aging rates for rubber properties obtained by the same methods, the difference being these tires (i.e. the same sizes, brands and DOT construction codes as obtained from the field) were aged under different conditions in laboratory ovens. This work builds on previous studies of oven aging which focused on only one light truck tire type and brand [1−3]. The purpose of this initial study was to demonstrate the suitability of oven aging to replicate the aging that occurs in the field and to establish the range of parameters that can be used. Tires were mounted on wheels and inflated to pressures ranging from the maximum sidewall pressure to twice that value. Fill gasses ranged from pure N_2 to pure O_2. Most studies were carried out using either air or a 50/50 blend of N_2/O_2 as fill gas. Mounted tires were aged for times up to 12 weeks at temperatures ranging from 40 to 100 °C. The rubber properties that were measured as a function of aging time were identical to those employed in the field studies and included swelling ratio and peel strength of the skim rubber and elongation-to-break and modulus of the wedge rubber. Swelling ratios were used to estimate relative crosslink densities using the standard Flory−Rehner relationship [4]. The following conclusions can be drawn from these studies:

1. Rubber degradation of tires exposed in laboratory ovens is controlled by diffusion limited oxidation (DLO). The oxidation rate is uniform across the belt, which is entirely consistent with the degradation that is seen in the field [5]. That is, oven aging can reproduce the pattern of oxidation observed in field tires.
2. The same analysis used to extract oxidation rate parameters from the field data can be used to analyze the oven aged tires. Fig. 1 illustrates the shift analysis and fitting procedure used to extract rate data [6,7].
3. The source of oxygen that is responsible for the oxidation of the skim and wedge rubber comes from inside the tire. That is, tires oxidize *from the inside out*. This means that oven aging of tires *must* be carried out on tires that have been mounted on wheels and inflated.
4. The fill gas and inflation pressure strongly influences the rate of oxidation. Use of a 50/50 blend of N_2/O_2, when added to the air present in the uninflated tire, leads to an

* Corresponding author. Tel.: +1 313 594 1756; fax: +1 313 323 1129.
E-mail address: dbauer3@ford.com (D.R. Bauer).

0141-3910/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2006.08.014

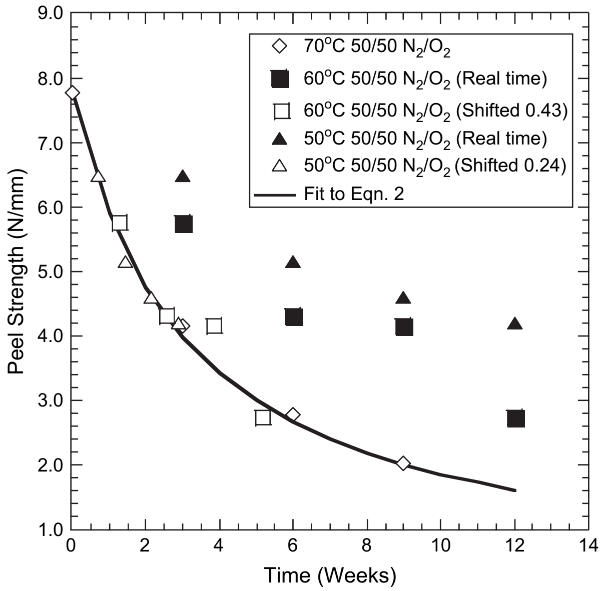

Fig. 1. Shift factor approach and fit to Eq. (2) for typical oven data. Data are for light truck tire [6,7].

O_2 concentration of ~43%. This blend has been found to increase the rate of skim and wedge rubber oxidation by 35 ± 5% relative to air. Increasing the inflation pressure also increases the rate of oxidation. For safety reasons, we have chosen the maximum sidewall pressure for the current oven aging study. It is also important to note that increasing the oxygen concentration inside the tire does not affect the basic mechanism of degradation.

5. The oxidation rate increases with increasing temperature up to 70 °C and then decreases rapidly above 80 °C. This result is consistent with diffusion limited oxidation. Finite-element models of rubber oxidation in tires confirm that the skim and wedge rubber becomes oxygen starved above 80 °C, resulting in the observed decrease in oxidation rate. Up to 70 °C, the apparent activation energy was ~69 kJ/mol, a value consistent with diffusion limited oxidation [3].

Based on the above conclusions, we limited our oven aging studies to 70 °C and below. The tires in this study have been described in the previous paper. The sizes and maximum inflation pressures are summarized in Table 1. Oven aging of the Small Car-BFG tire was carried out as part of a tire aging study conducted by the ASTM F9.30 committee on tires. Details of the ASTM study are described elsewhere [8]. It should be noted that the temperatures in this study were different from the other studies (55–75 °C). One important consideration is that the tires used in the Ford Motor Company oven aging study were manufactured at least 2–4 years after the youngest tires analyzed in the field aging study. Changes in rubber compounding and/or tire construction in this time period could influence relative aging rates complicating the comparison between field and oven aged tires. This possibility was evaluated by comparing the initial properties of the oven aged tires with the extrapolated initial properties of the corresponding field aged tires. From the comparison of oven aging oxidation rates with the corresponding field aging rates for properties with consistent initial values, we can derive acceleration factors for different oven aging conditions. These factors are consistent with both temperature extrapolations and finite-element models of rubber oxidation. The measured acceleration factor can be used to relate the "age" of a tire exposed in the oven to that of an average tire aged in Phoenix.

Table 1
Tire types used in aging study

Vehicle type-tire brand	Tire size	Maximum sidewall pressure (kPa)
SUV/Minivan-A	215/70R15	240
SUV/Minivan-B	235/75R16	300
SUV/Minivan-C	215/65R16	300
Large Car-C	225/60R16	240
Small Car-BFG	195/65R15	240

2. Experimental

Except for the ASTM study, tires were mounted and inflated to the maximum pressure listed on the sidewall prior to oven aging using either air or a 50/50 blend of N_2/O_2. In the case of tires inflated with the 50/50 blend of N_2/O_2, the atmospheric air present was not purged; the blend was added on top of it yielding a tire cavity concentration of approximately 41–44% O_2. In addition to these conditions, the ASTM tire was inflated to 30% and 60% above the maximum sidewall pressure. Two of the tires in this study (SUV/Minivan-A and SUV/Minivan-C) were aged at 50, 60, and 70 °C for up to 8 weeks, while the tires SUV/Minivan-B and Large Car-C were aged up to 8 weeks at 70 °C. The Small Car-BFG tire was aged at 55, 65, and 75 °C for up to 16 weeks. The specific protocol for this tire is described elsewhere. The ovens were calibrated as per ASTM E 145 with an A2LA approved, modified, method for temperature uniformity, consistency, airflow exchanges and airflow velocity.

3. Results and discussion

The decrease in peel strength of the skim rubber with oven aging for the Small Car-BFG tire is shown in Fig. 2. The decrease in elongation-to-break of the wedge rubber and the increase in crosslink density of the skim rubber and modulus of the wedge rubber for the same tire are shown in Fig. 3. These figures can be compared to Figs. 4 and 5 of the previous paper [1]. The equations used to extract rate constant values were the same as used previously. The crosslink density and the modulus were fit to a linear equation [6],

$$A(t) = A(0)(1 + \alpha t). \tag{1}$$

The peel strength and elongation-to-break data are fit to the following empirical equation,