Effects of Hot-Air Aging and Dynamic Fatigue on the Structure and Dynamic Viscoelastic Properties of Unfilled Natural Rubber Vulcanizates

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ABSTRACT: The effects of hot-air aging and dynamic tensile fatigue on the network structure and dynamic viscoelastic properties of unfilled natural rubber (NR) vulcanizates were investigated with magnetic resonance crosslink density spectrometry, Fourier transform infrared spectroscopy/attenuated total reflection (FTIR–ATR), and dynamic mechanical analysis. The results showed that there was a carbonyl weak absorption peak at 1723 cm^{-1} in the FTIR–ATR spectra of unfilled NR vulcanizates after hot-air aging; The crosslink density decreased continuously as the aging time increased. The dynamic modulus of an aged specimen declined considerably, and the value of tan δ after 72 h of aging greatly increased. There was a large difference in the FTIR–ATR spectra of unfilled NR vulcanizates before and after tensile fatigue. The peaks at 1597, 1415, and 1015 cm^{-1} increased concurrently with the tensile fatigue time. Initial analysis suggested that structures such as conjugated dienes appeared in the network structure. The modulus declined sharply, whereas the value of tan δ increased noticeably, after tensile fatigue. The effects of hot-air aging and tensile fatigue on the crosslink density and FTIR–ATR spectra of unfilled NR vulcanizates were different, but both affected the viscoelastic properties dramatically. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1911–1916, 2008

Key words: ageing; crosslinking; FTIR structure; viscoelastic properties

INTRODUCTION

Natural rubber (NR) remains the major general-purpose rubber because of its excellent cost/property ratio. NR plays an especially important role in products, such as tires, for which its dynamic properties are required. Nevertheless, hot-air aging and dynamic fatigue resulting from the presence of double bonds along the polymer backbone lead to a reduction in the dynamic viscoelastic properties and a shorter useful life of the products. Although much has been achieved through research in this area,[1–3] the evaluation of hot-air-aging resistance of rubber materials or articles used under dynamic conditions is still made by a comparison of the static tensile properties before and after hot-air aging. This is so largely because of the limitations of testing instruments. Dynamic fatigue resistance can be estimated only from the results of flexural fatigue measurements. Thus, the effects of hot-air aging and dynamic fatigue on the structure and dynamic viscoelastic properties have seldom been reported.

A focus on properties during the use of articles and materials is becoming more important. Thus, increasing attention is being paid to the dynamic viscoelastic properties of articles used under dynamic conditions and the evaluation of the influence of simulated dynamic conditions. The effect of hot-air aging and dynamic fatigue on the network structure and dynamic viscoelastic properties of unfilled NR vulcanizates, carbon black filled NR vulcanizates, and silica-filled NR vulcanizates will be investigated and analyzed in detail by dynamic mechanical analysis (DMA), Fourier transform infrared spectroscopy/attenuated total reflection (FTIR–ATR), and NMR crosslink density spectrometry during the course of this project. We hope to explore the method and basis for evaluating the properties of rubber articles used under dynamic conditions by examining the changes in dynamic viscoelastic properties.

This article reports only one part of the project. The effects of hot-air aging and dynamic fatigue on the network structure and dynamic viscoelastic properties of unfilled NR vulcanizates without antiaging agents are examined. The research on filled NR vulcanizates will be reported in a later publication.

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EXPERIMENTAL

Raw materials and basic formulation

NR SVR3L was from Dong Nai Rubber Co. (Dong Nai, Vietnam); others were bought from the market. The formulation was 100 NR, 1.0 accelerator N-tert-butyl-2-benzothiazole sulfenamide (NS), 5.00 phr zinc oxide, 2.00 phr stearic acid, and 3.0 phr sulfur.

Specimen preparation

The specimens were prepared on an open mill according to GB6038-1993. The optimum cure time (t_{90}) was tested at 155°C with a GT-M2000-A cure meter manufactured by Gaotie Science and Technology Co., Ltd. (Taiwan, China). The compression molding was carried out with an XIB press (manufactured by Qingdao Yadong Rubber and Plastics Machinery Co., Qingao, China) at a pressure of 10 MPa.

Hot-air aging was carried out at 100°C for 24, 48, and 72 h with a 401A aging oven (manufactured by Shanghai Experiment Instruments Factory, Shanghai, China) according to ISO 188:1998. Hot-air-aged specimens were stored at room temperature for 2–3 h for further analysis.

Dynamic tensile fatigue was tested with a tensile fatigue tester (manufactured by Jiangdu Test Machinery Factory, Jiangdu, China) according to GB/1688-1986 with elongation of 100% and a tensile frequency of 500 min^{-1}. The specimens after tensile fatigue were stored at room temperature before further analysis.

Tests and analysis

Tensile testing was carried out with a GT-AI-7000M universal material tester (manufactured by Taiwan Gaotie Co., Taiwan, China) at a tensile speed of 500 mm/min according to ISO 37:1994.

The crosslink density was measured with an MR-CDS 3500 crosslink density spectrometer (manufactured by IIC Innovative Imaging Crop, Blieskastel, Germany) with a magnetic field strength of 0.35 T and a resonance frequency of 15 MHz at 60°C.

A column-shaped specimen 5 mm in diameter and 8 mm long was put into the bottom of a glass tube. The tube with the specimen was allowed to settle for 5 min until the magnetic field and temperature were stable, and then the test started with the fixed parameters. The crosslink density of the vulcanizates was measured after the analysis of the data as follows:

$$M(t) = A_0 + A_1 \exp[-t/T_2 - (qM_2t^2)/2]$$
$$+ A_2 \exp(-t/T_2)$$

where $M(t)$ is transversal magnetization decay (s^{-2}), t is decay times (ms), qM_2 is the residual dipolar

moment ($\sim 10^{-4}$ s^{-2}), T_2 is the spin–spin relaxation time ($\sim$ ms), A_1 and A_2 are amplitude factors, and A_0 is the fitting factor (no physical meaning).

Dynamic mechanical properties were tested with a Netzsch 242 dynamic mechanical analyzer (Netzsch Instruments Co., Selb, Germany) with a frequency of 10 Hz, temperatures ranging from −80 to +80°C, a heating rate of 3°C/min, and the mode of double-cantilever deformation. Curves of tan δ and storage modulus E' as a function of temperature were examined.

Fourier transform infrared (FTIR) spectra were produced with a Vertex 70 spectrometer manufactured by Bruker Co. (Ettlingen, Germany), and the attenuated-total-reflection full-reflection mode was used to get the spectra.

RESULTS AND DISCUSSION

Effect of hot-air aging on the structure and properties of the unfilled NR vulcanizates

Magnetic resonance crosslink density spectrometry analysis

The crosslink density of vulcanizates changes as the aging time is increased, as shown in Figure 1. The basic theory of NMR crosslink density spectrometry is that ^{1}H-NMR relaxation involves intermolecular and intramolecular dipolar magnetic interactions of protons. In contrast to the isotropic tumbling of small molecules, the fast local motions of network chains fixed at both ends by permanent crosslinks are inherently anisotropic and, therefore, cannot average out the static dipolar interaction to zero. A small fraction (q) of the second moment (M_2) of these interaction remains, which can be measured and correlated to the dynamics of the crosslinked hydrocarbon chain segments.

As can be seen in Figure 1, the crosslink density of NR vulcanizates decreased as the hot-air-aging time increased, especially after 24 h. The crosslink density decreased by nearly one-third after 72 h of
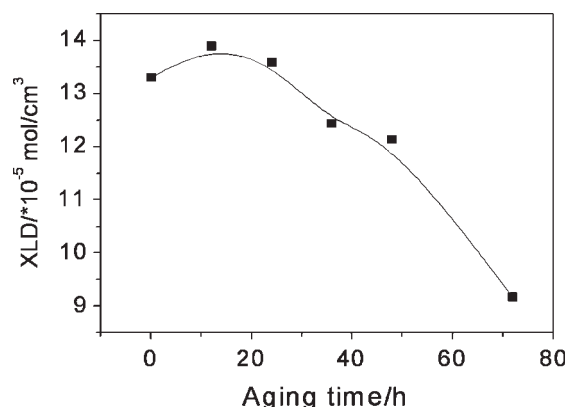

Figure 1 Influence of the hot-air-aging time on the crosslink density (XLD) of an unfilled NR vulcanizate.
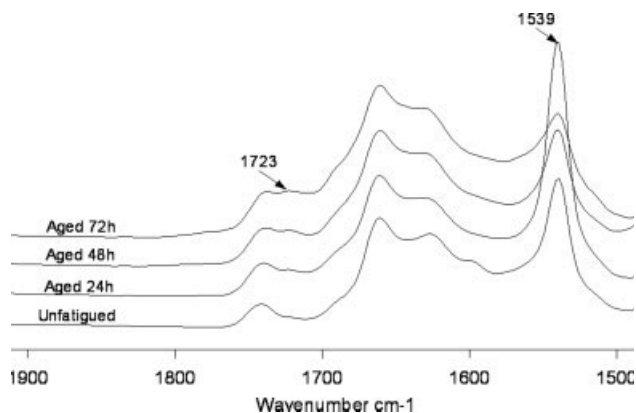
Figure 2 FTIR–ATR spectra of unfilled NR vulcanizates after various hot-air-aging times.

aging. The results indicated that hot-air aging obviously damaged the crosslink network in the vulcanizates, and this is in accordance with current thinking.

FTIR–ATR analysis

FTIR–ATR spectra of unfilled NR vulcanizates after various hot-air-aging times are shown in Figure 2.

By comparing the spectra before and after hot-air aging, we can see that there are no significant differences between them. Only the absorption peak at $1539 \mathrm{~cm}^{-1}$ slightly declines with an extension of the aging time. The spectral bands of zinc stearate and protein amide II in NR are responsible for the peak at $1539 \mathrm{~cm}^{-1}$,[4,5] and these should not affect the network structure, especially because the change is small. It should be noted that hot-air aging can be considered to be the combined effects of heat and oxygen. In the spectra, a weak carbonyl absorption peak appears at $1723 \mathrm{~cm}^{-1}$. One possible reason could be that even small amounts of oxygen absorbed by the polymer result in large changes in the bulk properties, whereas only a few oxygen-containing moieties are formed. Therefore, the peak observed by FTIR is weak.

DMA

The changes in the dynamic viscoelastic properties of hot-air-aged unfilled NR vulcanizates are shown in Figure 3.

The tan δ peak of aged specimens gradually moved to a higher temperature as the aging time increased in comparison with an unaged NR specimen, and the tan δ peak became smaller. Tan δ in the high-elasticity region first decreased and then after about 24 h started to increase again [Fig. 3(b)], whereas the curves of E' continuously decreased as the aging time increased [Fig. 3(c)]. The large difference for E' between 72-h-aged NR and unaged NR

indicates that the dynamic viscoelastic properties of the vulcanizates significantly changed after a long period of hot-air aging.

The changes during and after hot-air aging can be rationalized as follows. During aging, scission of the NR backbone occurs, and/or the crosslink networks are destroyed; the vulcanizate becomes weaker, and E' decreases. Scission of the backbone leads to an increase in the number of free chain ends, with a consequent increase in tan δ in the high-elasticity region. To date, the shift of the peak of tan δ to higher temperatures and its decline have not been reasonably described. Normally, the tan δ peak has been reported to move to lower temperatures, and the peak level increases.[6] That the results reported here could be reproduced several times suggests that the observations are real and require further investigation.

The changed viscoelastic properties after a long period of hot-air aging, especially the increase of tan δ
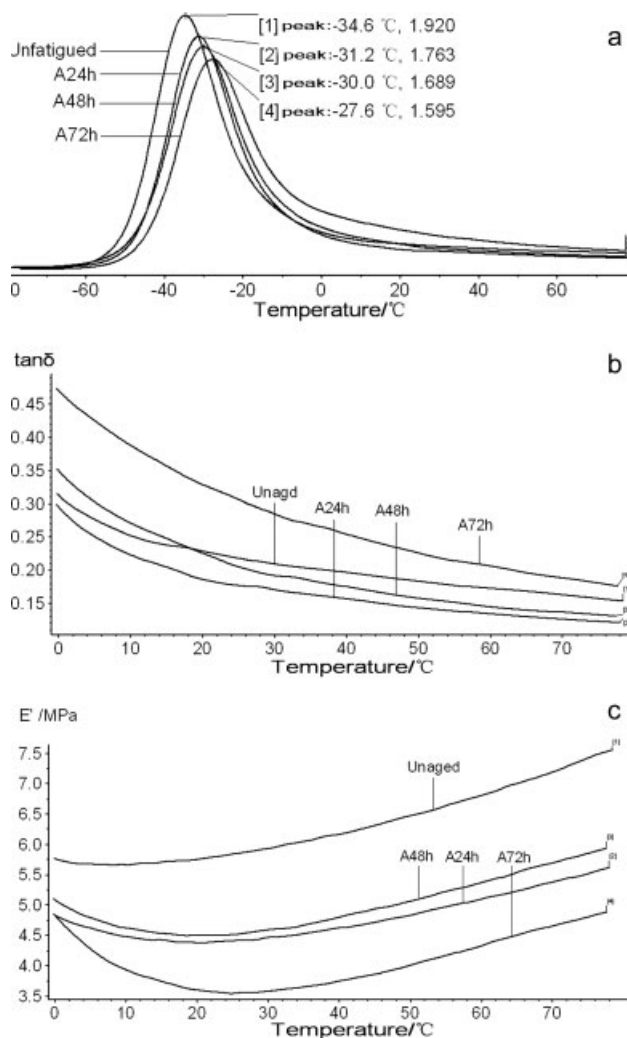

Figure 3 Dynamic viscoelastic properties of hot-air-aged unfilled NR vulcanizates.

TABLE I
Mechanical Properties and Crosslink Density of NR
Before and After Tensile Fatigue

Fatigue time (h)	Tensile strength (MPa)	Modulus at 100% (MPa)	Crosslink density by NMR (mol/cm^3 × 10^{-5})
0	25.655	0.973	14.16
1.5	21.088	1.07	14.48
3	13.534	0.54	14.34
4.5	6.029	0.573	13.99

Figure 5 Isomerization of the broken backbone of an unfilled NR vulcanizate in tensile fatigue.

and the significant decrease of E' in the high-elasticity region, will considerably affect the bulk properties of the materials or products made from such materials and used under dynamic conditions. For example, a tire would have increased heat buildup and greater rolling resistance leading to poorer handling and increased braking distance: this could have dire consequences.

Effect of tensile fatigue on the structure and properties of unfilled NR vulcanizates

Analysis of the changes in the tensile strength and crosslink density

As can be seen in Table I, the tensile strength and modulus at 100% decreased dramatically after 1.5 h of tensile fatigue. The modulus at 100% fell by 50% after 3 h of fatigue testing. This indicates that the effect of tensile fatigue on the static tensile properties is considerable.

The crosslink densities in Table I first increase and then decrease during these experiments. This is an opposite trend and a smaller change in comparison with hot-air aging. This suggests that the two aging mechanisms are different. Tensile fatigue is a mechanochemical process by which the vulcanizate undergoes constantly increasing stress under the pe-
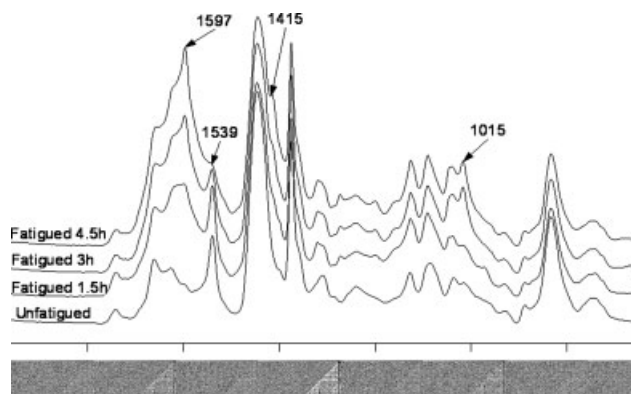
riodical force. The nonuniform network reacts to the stress field in a nonuniform manner leading to stress concentration and areas in which more bonds are broken.[7] In the early period of tensile fatigue, multiple sulfur bonds are broken. The resulting free sulfur radicals (S_{x-n}) can form new crosslinks and cause an increase in the crosslink density of the network. During the latter period of tensile fatigue, the molecular chains are broken because of the constant stress buildup causing a large decrease of the crosslink density and a deterioration of bulk properties.

FTIR–ATR analysis

As can be seen in Figure 4, the spectra change considerably during tensile fatigue. The peak at 1539 cm^{-1} declines, whereas the peak at 1597 cm^{-1} increases significantly; the shoulders at 1415 cm^{-1} gradually increase as the duration of tensile fatigue increases, and a new weak absorption at 1015 cm^{-1} appears. All these changes are different from those observed during hot-air aging. It is thought that because the tensile fatigue test was carried out at room temperature, the effect came mainly from the periodical force rather than from heating. Thus, the aging mechanisms of the two methods are different, and this difference influences the network structure. The peak at 1597 cm^{-1} in the spectra for tensile fatigue aging can be assigned to the stretching vibration absorption of the double bond of conjugated dienes, and the peaks at 1415 and 1015 cm^{-1} can be assigned to the in-plane and out-of-plane bending vibrations of the conjugated diene, respectively.[4,5] According to the literature, during the decomposi-
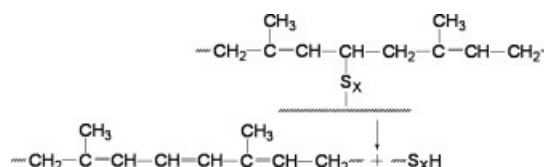

Figure 4 FTIR–ATR spectra of an unfilled NR vulcanizate before and after tensile fatigue.

Figure 6 Conjugated diene or triene resulting from broken C—S bonds.

tion of NR, the C—C bond between two α-methylenes can be broken, and this leads to free radicals and isomerization.[7,8] The conjugated diene end groups might form from an isomerization of a broken backbone during tensile fatigue, and structures such as conjugated dienes or trienes could also arise from C—S bond scission if a hydrogen atom is abstracted from α-methylenes[8] (see Figs. 5 and 6).

The peak at 1539 cm^{-1} is due to zinc stearate and protein amide II in NR; additionally, no obvious bands arising from oxygen-containing moieties were observed.

DMA

The curves of tan δ versus temperature after various durations of tensile fatigueare shown in Figure 7(a). The values of tan δ at different temperatures show no single trend, and the shape and width of the peak do not change significantly.
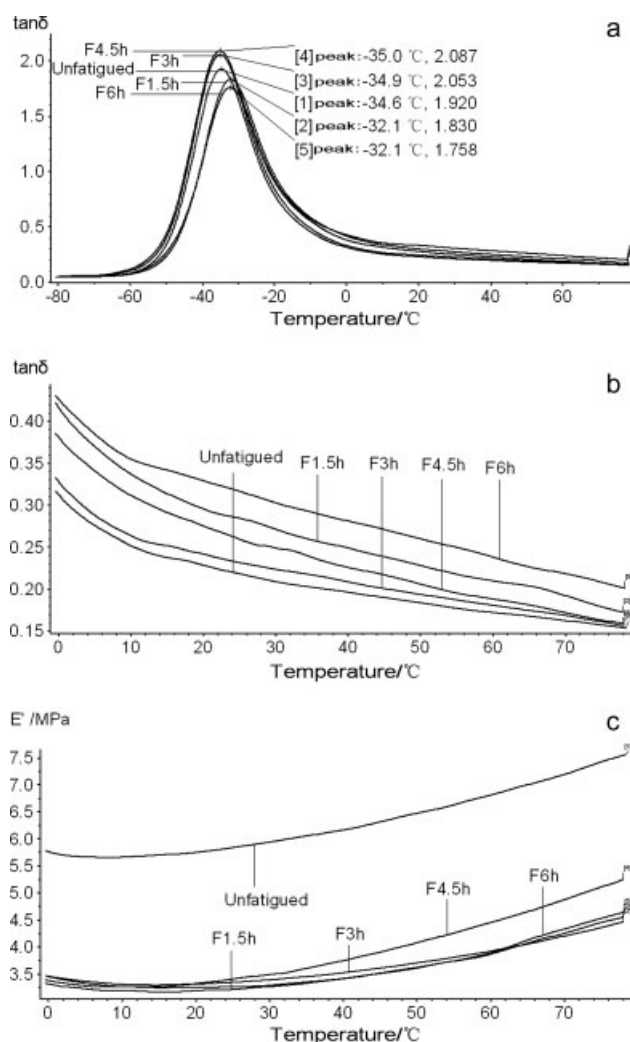

Figure 7(b) shows a detail of the tan δ versus temperature curve [Fig. 7(a)] for the temperature range of 0–80°C. The tan δ value of aged samples is considerably greater than that of unaged samples. Furthermore, tan δ increases with the duration of tensile fatigue for all samples. Combining the aforementioned observations with those from the FTIR–ATR analyses (discussed previously), we find that the development of terminal diene and triene structures as well as terminal thiol groups leads to an increase in tan δ reflecting reduced chain flexibility. In the initial stages of tensile fatigue (F1.5h), the breaking of multiple sulfur chains and the development of additional crosslinks are both responsible for the considerable increase in tan δ. Thereafter, for a short time, the increasing number of free chain ends dominates the development of tan δ: it decreases (F3h and F4.5h) in comparison with 1.5 h.

The changes of E' with the temperature in the high-elasticity area are shown in Figure 7(c). It indicates that E' of aged samples was much lower than that of unaged samples. However, there was no large difference among the values of E' with different tensile fatigue times. That the curves are similar and not dependent on fatigue duration is contrary to the results from static tensile testing. This may be an artifact from the use of unfilled specimens and needs to be investigated further.

CONCLUSIONS

There was a weak carbonyl absorption peak at 1723 cm^{-1} in the FTIR–ATR spectra of unfilled NR vulcanizates after hot-air aging, and the crosslink density decreased obviously as the aging time increased. The dynamic modulus of an aged specimen declined largely, and the value of tan δ after 72 h of aging greatly increased.

There was a large difference between the FTIR–ATR spectra of unfilled NR vulcanizates before and after tensile fatigue. The peaks at 1597, 1415, and 1015 cm^{-1} increased with the duration of tensile fatigue. The spectra suggested the development of structures such as conjugated dienes within the network. The modulus declined sharply, whereas the value of tan δ increased significantly, after tensile fatigue.

The effects of hot-air aging and tensile fatigue on the crosslink density and FTIR–ATR spectra of unfilled NR vulcanizates were different, but both affected the viscoelastic properties dramatically.

Figure 7 Dynamic mechanical properties of an unfilled NR vulcanizate before and after tensile fatigue.

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