Effect of a Small Amount of Sulfur on the Physical and Mechanical Properties of Peroxide-Cured Fully Saturated HNBR Compounds

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ABSTRACT: Sulfur can be used as crosslink coagent in unsaturated elastomer. In this work, a fully saturated HNBR with 39 wt % nitrile content was selected to investigate the effect of a small amount of sulfur acting as crosslink coagent on the physical and mechanical properties of peroxide-cured vulcanizates. First, selective cleavage of polysulfide ($-Sx-$) and monosulfide($-S-$) bond by combined thiol-piperidine treatment were performed and the existence of poly/monosulfide bond in sulfur-contained HNBR compounds was verified. Then, no-filler HNBR compounds with various content of sulfur were investigated to detect the influence of sulfur on the crosslink density and cure kinetics. The MDR results showed that the crosslink density of HNBR compounds reduced only when the amount of sulfur is 0.25 phr and above. Besides, the curing rate of no-filler HNBR compounds increased with the increasing of the amount of sulfur and reached a maximum at a dosage of 0.25 phr sulfur. Finally, physical and mechanical properties of fully formulated compounds were evaluated and it was found that the addition of small amounts of sulfur in fully saturated HNBR compounds could improve the dynamic properties of peroxide-cured HNBR compounds remarkably but at a cost of slightly higher compression set values and a small loss in heat aging resistance. In a conclusion, small amount of sulfur can impart the peroxide vulcanizates some "sulfide properties" like dynamic property, tensile strength, but at the same time, due to the introduction of sulfur, some "peroxide vulcanizates property" like heat-resistance property, hot air resistance were weakened slightly. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 41612.

INTRODUCTION

Sulfur cure of double-bond containing elastomers is known to give excellent mechanical properties and superior behavior under dynamic stress. Peroxide cure of elastomers does not require the presence of double-bonds and yields vulcanizates with much higher heat resistance, excellent compression set (CS) but worse mechanical and dynamic properties.[1] Fully saturated elastomers, such as low diene ethylene-propylene-diene rubber (EPDM), fluoro elastomers (FKM), ethylene-vinyl acetate copolymers and fully hydrogenated nitrile rubber (HNBR), etc. cannot be cured by sulfur but can be cured with peroxide or other cure systems depending on the available cure sites.[2] Compared with the $-S-$, $-S_2-$, and $-S_x-$ formed in sulfur-cured vulcanizates, peroxide vulcanization leads to a rubber network where polymer chains are linked to each other by very stable C—C bonds and as a result, peroxide-cured vulcanizates

would exhibit good high temperature properties such as excellent heat aging resistance and low permanent deformations at elevated temperature.[1,2] Thus, peroxide-cured rubber are used in applications where heat aging has to be minimal, where weather and ozone resistance is needed and CSs need to be low. However, some physical and mechanical properties, i.e., tensile strength, dynamic properties and in some cases the scorch time of peroxide vulcanizates are inferior to those achieved by sulfur cure. Therefore until now, peroxide curing systems are mainly used in special rubber products.

Crosslink coagents such as triallylcyanurate (TAC) are a type of organic molecules with multi-functional groups that are highly reactive to free radicals. In peroxide vulcanization system, crosslink coagents are always used as reactive additives to boost the efficiency of peroxide. Until now, various kinds of crosslink coagent have been developed and been divided into two groups

Additional Supporting Information may be found in the online version of this article.

depending on their chemical nature. Type I crosslink coagent is consist of polar molecules with a low molecular weight and activated double bonds, e.g., N,N-m-phenylenedimaleimide (BMI-MP) which can do favor to both the cure rate and crosslink density of the matrix rubber. Type II crosslink coagent, e.g., 1,2-polybutadiene is made up of less polar molecules. These coagents would lead to an increase in crosslink density of the vulcanizates, but unlike Type I, they are not capable of increasing the cure rate.

In recent years, in order to expand the application scope of peroxide, an increasing number of researches have been performed to study the effect of sulfur acting as a crosslink coagent in peroxide-cured vulcanizates to get sulfur-like properties. Scheele and Hummel[3] first investigated the effect of sulfur as an additive in peroxide vulcanization, they found out that although sulfur did not affect the decomposition rate of peroxide, it reduced the crosslinking efficiency of peroxide. They then classified sulfur as the Type II coagent and concluded that one sulfur may prevent the formation of one crosslink. Manik and Banerjee[4,5] explored the influence of sulfur in dicumyl peroxide (DCP)-cured natural rubber. Just as reported in Hummel's study, they asserted that the addition of a small amount of sulfur could reduce the crosslink density of peroxide vulcanizates. Das and Banerjee[6] then carried out similar studies based on peroxide-cured styrene butadiene rubber (SBR) vulcanizates and they claimed that when sulfur was added, the tensile strength was higher compared to those vulcanizates without sulfur. Besides, they suggested that the addition of sulfur would reduce the crosslink density as well as the resilience of peroxide vulcanizates. Fujio et al.[7] investigated the effect of sulfur on peroxide-cured EPDM and divinylbenzene (DVB) compounds. They concluded that the addition of small amounts of sulfur would improve modulus and rupture energy in addition to the cure rate of peroxide vulcanizates. However, they pointed out that when the amount of sulfur was too high (above 0.2 phr), the modulus was reduced. Later it was proven by Das[8] that sulfur would form coagent links in the peroxide-cured rubber network when small amounts of sulfur were added as a coagent in NBR/EPDM blends. These links would lead to better dynamic and mechanical properties. Further, Zhao et al.[9] studied the properties of EPDM/SBR blends cured with peroxide and sulfur coagent. They found out that the addition of a small amount of sulfur as a coagent to the peroxide cure system in EPDM/SBR compounds remarkably improved mechanical properties of the blends. However, studies mentioned above are mainly focused on the effect of sulfur on partially saturated rubbers which have unsaturated C=C bonds that can interact with sulfur directly. The effect of sulfur on fully saturated [remained double-bond content (RDB) $\approx$ 0] rubber has not yet been discussed.

Hydrogenated nitrile butadiene rubber (HNBR)[10] is a kind of highly saturated nitrile rubber. It was first synthesized by Bayer AG in 1977 through hydrogenation reaction of nitrile butadiene rubber (NBR)[11] and its vulcanizates properties have been described in 1983.[12] Except for the excellent oil resistance, abrasion resistance and low temperature flexibility[10] (it can be used under -40°C) that inherited from NBR, HNBR exhibits excellent heat resistance (can be used at 150°C), ozone resistance

and chemical resistance which are determined by its highly saturated structure.[10] However, considering the limitations of peroxide-cured highly saturated rubber, it was a target to investigate a possible effect of sulfur in peroxide-cured fully saturated HNBR.

In the present work, a fully saturated HNBR with 39 wt % nitrile content was chosen to explore the effect of the small amounts of sulfur on the physical and mechanical properties of peroxide-cured fully saturated HNBR. The high nitrile content HNBR selected for this study ensures high swell resistance in oily fluids such as those frequently encountered in oil exploration. It is expected that our study on the effect of small amounts of sulfur working as crosslink coagent on the physical and mechanical properties of peroxide-cured HNBR compounds will enlarge the application scope of HNBR and provide some new insights to understand the effect of sulfur in fully saturated rubber.

EXPERIMENTAL

Materials

Therban 3907 (HNBR 3907) used here was provided by Lanxess, Germany. It contains 39 wt % acrylonitrile and 61 wt % hydrogenated butadiene units. The residual double-bond content (RDB) is specified as below 0.9 wt % (considered as fully saturated) and its Mooney Viscosity is 70 MU (ML $1 + 4$, 100°C). Luperox F-40 (α,α'-bis(t-butylperoxy)diisopropylbenzene, BIBP) was purchased from Arkema. Liquid polybutadiene Ricon 153D (85 wt % 1,2 vinyl content, Mn 4700, 65 wt % on Ca-silicate) from Sartomer was used as coagent here for high tensile and high elongation values. Rhenogran S-80 (80 wt % soluble sulfur) was obtained from Rhein Chemie, Plasticizer TOTM (trioctylmellitate) from Xindi Chemical, anti-oxidants Vulkanox ZMB2 (zinc-methyl-mercaptibenzimidalzol) from Lanxess Chemicals and Naugard 445 (4,4'-bis (a,a-dimethylbenzyl)diphenylamine) from Pinshemg Chemical, carbon black N220 from Cabot, carbon black N774 from Evonik and Maglite DE (MgO) from Chinaway.

Formulations and Sample Preparations

No-filler (recipes are shown in Table I) HNBR compounds were prepared in a laboratory two-roll mill (SAGA Instruments Pte Ltd, C0840), the roller speed ratio was set to 1 : 1.2 and temperature of the cooling water is controlled under 50°C. The compounded rubber was then sheeted out and kept at room temperature for 16 h before being used for molding.

Formulas of carbon black filled HNBR compounds were shown in Table II. A master-batch was mixed in an internal mixer of 1.8 L (Farrel Corporation, KOMK4, Intermeshing) with a fill factor of 75% and the mixing procedure is illustrated in Table III.[13] The temperature of the cooling water was kept below 50°C and rotor speed was 40 r/min. The masterbatch was then split into two parts equally and their corresponding peroxide, coagent as well as sulfur were added on a two-roll mill (friction 1 : 1.2, temperature 50°C).

Characterization and Vulcanization

The cure characteristics were measured at 175°C using a MDR2000 from Alpha Technologies. $T_{90} + 3$ min was taken as the molding time at 175°C.

Table I. Formulations of No-Filler HNBR Compounds with Different Mass Ratios of Peroxide to Sulfur

Ingredient (phr)	Peroxide : Sulfur								
	6 : 0	8 : 0	10 : 0	10 : 0.05	10 : 0.1	10 : 0.25	10 : 0.5	10 : 0.75	10 : 1
HNBR	100	100	100	100	100	100	100	100	100
Peroxide	6	8	10	10	10	10	10	10	10
Sulfur	0	0	0	0.05	0.1	0.25	0.5	0.75	1
Ricon 153D	5	5	5	5	5	5	5	5	5

Swelling Test

Swelling tests of no-filler HNBR compounds before and after thiol treatment[14] were carried out to determine the total cross-link density and the content of ─S─ and ─Sx─ in HNBR compounds.

Molecular weight (M_{cs}) of the network chain between chemical crosslink points was determined using the Flory-Rehner relationship[15,16] as eq. (1).

$$M_{cs} = \frac{\rho\left(1 - \frac{2}{\phi}\right) V_1 V_{2m}^{\frac{1}{3}}}{\ln\left(1 - V_{2m}\right) + \chi V_{2m}^2 + V_{2m}} \tag{1}$$

where ρ is the density of the rubber network [kg/m^3], φ is the functionality of the crosslinks, V_{2m} is the volume fraction of polymer at equilibrium degree of swelling and V_1 is the molar volume of solvent [cm^3/mol]. χ is an interaction parameter between polymer and swelling agent. It is calculated according to the three-dimensional Hansen solubility parameters.[17]

The number of ─S$_x$─ and ─S─ linkages in these HNBR compounds can be quantified using crosslink density, μ_c. The μ_c in a tetra-functional network can be expressed as eq. (2):[18]

$$\mu_c = \frac{\rho}{2} * \frac{1}{M_{cs}} \tag{2}$$

where ρ is the density of the rubber network [kg/m^3].

Determination of Physical and Mechanical Properties

Zwick tensile tester was used to evaluate the mechanical properties of vulcanizates according to ASTM D412 and ASTM D624. In this test, to explore the heat resistance of sulfur-contained

HNBR compounds, five dog-bone-shaped samples were cut with a die and the tensile tests were performed at RT, 120°C and 150°C, respectively. The oil immersion (in IRM 903) tests at 100°C and 150°C were carried out according to ASTM D471. Hot air aging tests at 165°C for 3 days, 7 days and 10 days were performed according to ASTM D572. CS measurements at 100°C, 150°C, and 165°C after holding 24 h were carried out according to ASTM D395 to investigate the dependence of permanent deformation on temperature. DeMattia tests were carried out according to ASTM D430 and Demattia test after oil immersion in IRM903 at 100°C for 7days was performed. Tear analyzer with CCD system was performed in Lanxess, Leverkusen to investigate the dynamic tear propagation of HNBR compounds. Samples were tested at 70°C and deformations rates are 5.3, 6.9, and 7.5%, respectively. Goodrich flexometer tests were carried out to investigate the heat built-up at 55°C under dynamic conditions according to ASTM D623.

RESULTS AND DISCUSSION

The Existence of Sulfide Bond in No-Filler HNBR Compounds with Small Amounts of Sulfur

To investigate whether there exists polysulfide, disulfide and monosulfide bond in fully saturated HNBR compounds, compounds without sulfur and that with 0.25 /0.75 phr sulfur were treated with thiols and piperdine.

Nine samples (∼0.2 g) with 12 mm in diameter were cut with a die from the cured sheets for each compound. Samples of each compound were divided evenly into three groups. Three samples in the first group without pretreatment were completely immersed in monochlorobenzene (MCB) until the swelling at equilibrium occurred. The total number of crosslinks was calculated according to the weight of the samples before and after

Table II. Formulations of Fully Formulated HNBR Compounds in Phr

Ingredient (phr)	Peroxide : sulfur	
	8 : 0	9 : 0.25
HNBR	100	100
Peroxide	8	9
Sulfur	0	0.25
Ricon 153D	5	5
CB N220	20	20
CB N774	40	40
TOTM	5	5
Vulkanox ZMB$_2$	0.5	0.5
Naugard 445	1.0	1.0
Maglite DE	3	3

Table III. The Mixing Process of HNBR Masterbatch

Steps	Time (min)
Crumbing HNBR	1.00
Adding ZMB$_2$,Naugard 445, MgO, N220	1.00–2.30
Ram down, Mixing	2.30–3.30
Adding N774, TOTM	4.00–4.30
Ram down, Mixing	4.30–5.30
Ram up, Sweeping	5.30–6.00
Mixing	6.00–7.00
Dump batch	7.00
Sheeting	7.00-

Table IV. M_{cs} of HNBR Compounds in Phr Before and After Treatment with Thiol and Piperdine

M_{cs} Peroxide : sulfur	M_{cs}[a] (g/mol)	M_{cs}[b] (g/mol)	M_{cs}[c] (g/mol)
6 : 0	1909	2039	2123
8 : 0	1421	1533	1613
10 : 0	1154	1246	1347
10 : 0.25	1286	1502	1640
10 : 0.75	2006	3108	4872

[a] Refers to the M_{cs} calculated after swollen in MCB.
[b] Refers to the M_{cs} calculated after treatment with propane-2-thiol and piperidine removing polysulfide bond.
[c] Refers to the M_{cs} calculated after treatment within-hexanethiol and piperdine removing monosulfide bond.

the swelling.[19] The second group were first immersed into a solution of piperidine and propane-2-thiol[14] for 2 h under N_2 to cleave the polysulfide crosslinks followed by swelling in MCB. The total number of crosslinks after removing polysulfide bond was calculated by comparing the crosslink number of samples with and without piperidine/propane-2-thiol treatment.[19] Similarly, the concentration of monosulfide crosslinks in sulfur-contained HNBR compounds was evaluated according to the changes in the number of crosslinks before and after treatment with a piperidine and n-hexanethiol[19] solution.
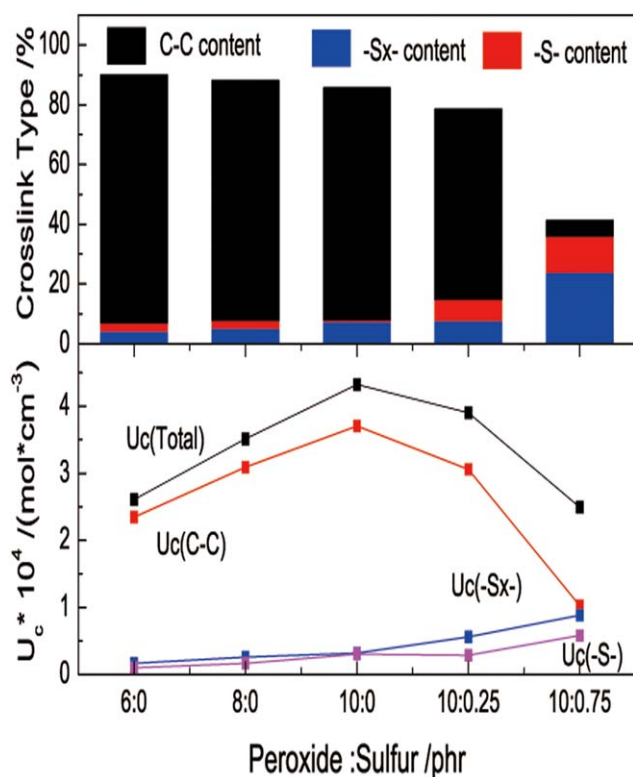

Figure 1. Lower panel: crosslink density of HNBR compounds in phr with different ratios of peroxide to sulfur. Upper panel: percentage of the three crosslink types in the investigated samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
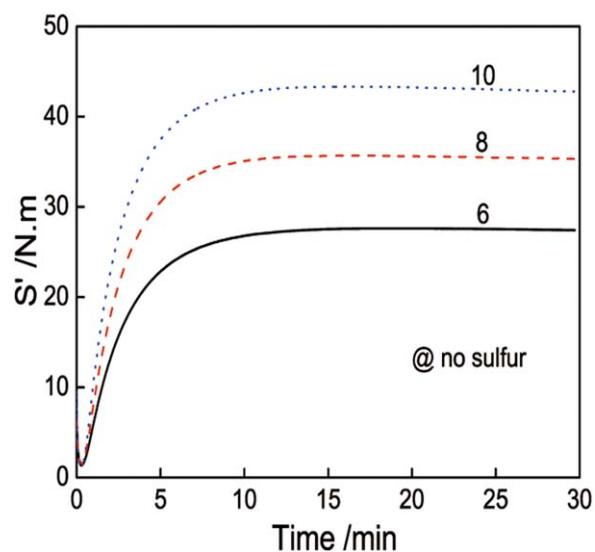

Figure 2. MDR curves of no-filler HNBR compounds with peroxide dosage from 6 to 10 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The results (average of three samples) are shown in Table IV. As illustrated in Table IV, M_{cs} (total) of no-sulfur HNBR compounds with and without thiol treatment are very similar. This implies that thiol-piperidine treatments do not change their rubber network obviously. The small deviation that exists may result from the loss of small molecules or uncrosslinked rubber. However, for HNBR compounds containing sulfur, M_{cs} obtained after consecutive treatment with piperidine and thiols are much larger than those untreated samples, implying a decrease of crosslink density and therefore the presence of sulfide crosslinks.

The crosslink type and the crosslink density of HNBR compounds with and without sulfur are given in Figure 1. It can be seen from Figure 1 that, consistent with the MDR data (shown in Supporting Information Table S1), the total crosslink density increases with the peroxide dosage increasing from 6 phr to 10 phr while it decreases upon the addition of a small amount of sulfur. Besides, for sulfur-contained HNBR compounds, the sulfide bond can be detected by the thiol and piperidine treatment and the more sulfur contained, the more sulfide bond existed.

Curing Behavior of Fully Saturated No-Filler HNBR Compounds with Small Amounts of Sulfur

Figure 2 shows the MDR curves of the no-filler HNBR compounds with various amount of peroxide. As expected, with the peroxide dosage increasing from 6 to 10 phr, the crosslink density and thus the maximum torques of no-filler HNBR compounds increased from 26 to 42 N.m. However, it can be seen from Figure 3 and Supporting Information Figure S1 that the addition of rather small amount of sulfur (0.05, 0.1 phr) has no obvious effect on the crosslink density, which can be indicated by the three almost overlapped MDR curves. Besides, the further increase of sulfur (from 0.25 to 1 phr), as shown in Figure 3 and Supporting Information Figure S1, would result in a persistent decrease of the maximum torques from 42 to 19 N.m. What's more, it should be noted that the torque of HNBR
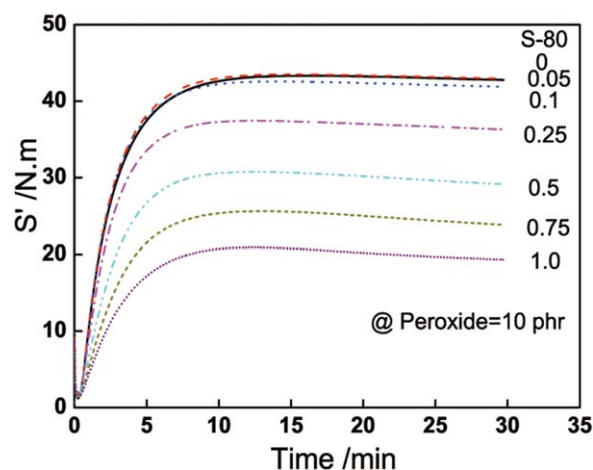
Figure 3. MDR curves of no-filler HNBR compounds with various amount of sulfur in phr and 10 phr peroxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compounds containing sulfur decreases after reaching the maximum torque, which can be explained by the reversion behavior in sulfur vulcanizates. And it should be noted that when the amount of sulfur is above 0.25phr, the reversion behavior is much more obvious. Then in the following study, 0.25phr sulfur was selected to investigate the effect of sulfur on the mechanical properties of the peroxide-cured HNBR compounds.

Cure rate was another important factor to evaluate the curing behavior. To elaborate the connection between the amount of sulfur and the curing rate, the dynamic kinetics was then calculated with the following eq. (3).[20–22]

$$\ln (M_H - M_t) = B - kt \qquad (3)$$

where M_H is the maximum torque and M_t is the torque at t in MDR curves (N.m), k is the constant of reaction rate, t is the curing time ($T_{10} < t < T_{90}$).

K values calculated are illustrated in Table V. It can be seen from Table V that the k values increase with the amount of peroxide increasing from 6 phr to 10 phr. While with the addition of sulfur, k increases to a maximum at a dosage of 0.25 phr sulfur and then decreases. Mooney scorch tests of fully formulated HNBR compounds with 0.05 phr sulfur at 130, 140, and 145°C showed shorter mooney scorch time compared to the counter-

Table V. k Values at 175°C of No-Filler HNBR Compounds in Phr

Peroxide : Sulfur	K (dNm/min)
6 : 0	0.369
8 : 0	0.417
10 : 0	0.424
10 : 0.05	0.449
10 : 0.1	0.47
10 : 0.25	0.496
10 : 0.5	0.457
10 : 0.75	0.411
10 : 1.0	0.383

part without sulfur (shown in Supporting Information Figure S2). This result verified our calculation of k value. So, the quantitative evaluation of cure behavior of the HNBR compound supported that 0.25 phr sulfur is appropriate to evaluate the effect of small amount of sulfur on the mechanical properties of the peroxide-cured HNBR compounds.

The Physical and Mechanical Properties of Fully Formulated HNBR Compounds with Small Amounts of Sulfur

As reported, sulfur-cured rubber exhibits excellent mechanical properties as well as better dynamic properties, while peroxide-cured elastomers own good high temperature properties such as excellent heat aging resistance and low permanent deformations at elevated temperature. The effect of sulfur on the physical and mechanical properties of fully formulated HNBR compounds was then investigated.

As shown in Supporting Information Figure S3, fully formulated HNBR compounds with 8 phr peroxide and the counterpart with 9 phr peroxide and 0.25 phr sulfur have almost the same crosslink density, so their physical and mechanical properties were compared to identify the influence of sulfur. It can be seen from Table VI, tensile elongation at break (TB) of sulfur-contained HNBR compounds tested at room temperature are slightly higher than those of no-sulfur HNBR vulcanizates. The results are consistent with the report by Das and Banerjee.[6] While TB values of sulfur-contained HNBR compounds tested at high temperature such as 120°C and 150°C are similar with that of no-sulfur HNBR compounds, implying that sulfur-contained HNBR compounds are more temperature-sensitive which probably results from the sulfide bond formed in fully saturated HNBR compounds. Besides, EB values of both sulfur-contained and no-sulfur HNBR compounds above 100% can still be reached at elevated service temperatures.

Temperature-resistance of HNBR compounds with and without sulfur were then comparatively evaluated by aging the samples in hot air for various periods at 165°C and the result are shown in Figure 4 and Supporting Information Table S2. As expected, the mechanical properties of HNBR compounds decreased after aging. The longer the aging time is, the lower the EB values are. And although the linear fitting curves shown in Supporting Information Figure S4 suggest that sulfur-contained HNBR compound is more temperature-sensitive, the absolute EB and TB value of both sulfur-contained and no-sulfur HNBR compounds are comparable after hot air aging due to the better mechanical properties of unaged sulfur-contained HNBR compounds. The higher temperature-sensitivity of sulfur-contained HNBR compounds maybe caused by the lower bond energy of carbon–sulfur and sulfur–sulfur bonds (C—S bond, 285 kJ/mol, S—S bond, 267 kJ/mol, C—C bond, 351 kJ/mol) which exist in sulfur-contained compounds. But this effect is not pronounced and the excellent aging resistance property of HNBR is still preserved (EB is still above 100% and can be used). Besides, it is found that the hardness of both no-sulfur and sulfur-contained HNBR compounds increase with the increase of the aging period.

As we all know, HNBR, similar to NBR, also provides better resistance against H_2S which is often associated with crude oil.[10] Then swell tests in oil and the subsequent tensile tests at

Table VI. Mechanical Properties of Fully Formulated HNBR Compounds in Phr at Different Test Temperature

Mechanical properties	8 : 0	Retention (%)	Standard deviation	9 : 0.25	Retention (%)	Standard deviation
TB[a] (MPa)	26.4	–	0.62	28.5	–	1.15
EB[a] (%)	253	–	7.51	279	–	21.02
TB[b] (MPa)	9.2	35	0.86	8.6	30	0.29
EB[b] (%)	140	55	2.85	134	48	10.59
TB[c] (MPa)	7.0	27	0.33	7.6	27	0.18
EB[c] (%)	116	46	0.48	120	43	1.34

[a] Refers to samples tested at room temperature.
[b] Refers to samples tested at 120°C.
[c] Refers to samples tested at 150°C.

elevated temperatures will reflect their target applications with high mechanical stress under elevated temperatures such as stator pumps in the oil field. Oil resistance properties of HNBR compounds were measured by immersion in IRM 903 at 100°C and 150°C for 7 days. It can be seen from Figure 5 and Supporting Information Table S3 that the changes of mechanical properties for both compounds after oil immersion are comparable, i.e., the EB and TB values of no-sulfur HNBR compounds immersed in IRM 903 at 100°C for 7 days are slightly superior while that of sulfur-contained HNBR compounds immersed in IRM 903 at 150°C for 7 days is better. And the initial modulus of sulfur-contained and no-sulfur HNBR compounds did not change after oil aging in IRM903 at elevated temperature as well. This can be detected from the original slope of their stress–strain curves. Besides, the initial modulus of sulfur-contained and no-sulfur HNBR compounds is almost the same as well. The Hardness of no-sulfur and sulfur-contained HNBR

compounds decreased when samples were stretched. This can be explained by the softening effect of oil that penetrating in samples. While for the unregular modulus of HNBR compounds, it is probably the synergistic effect of oil softening effect and the aging effect of the elevated temperature and air that co-exist in the oil. Furthermore, the weight loss (ΔM) and the volume loss (ΔV) of HNBR compounds during the oil immersion tests shown in Figure 6 and Supporting Information Table S3 indicates that the addition of sulfur in HNBR compounds lead to less the mass and volume loss.

As reported, generally sulfur vulcanizates display a higher CS value, therefore it is very necessary to study the effect of a small amount of sulfur on the CS properties of peroxide vulcanizates and the results are shown in Figure 7. As denoted in Figure 7, the higher the compressed temperature is, the larger the irreversible CS values are, and under high temperature the CS values of sulfur-contained HNBR compounds are obvious larger than that
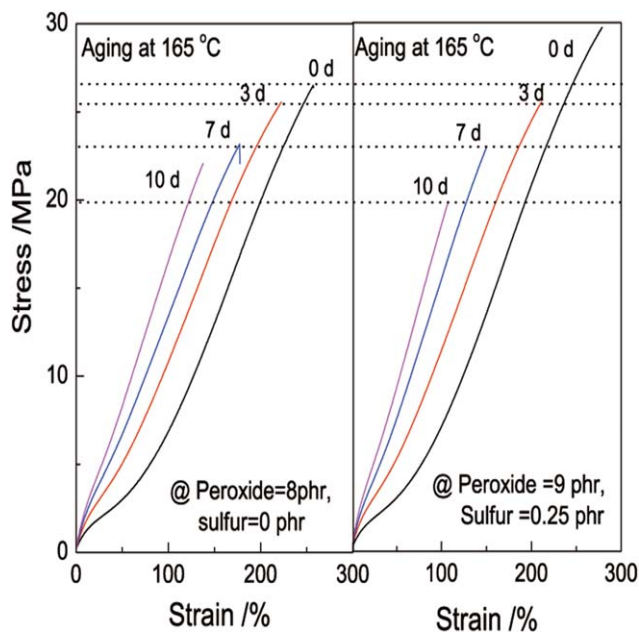

Figure 4. Stress–strain curves of no-sulfur (left) and sulfur-contained (right) HNBR compounds in phr after aging various periods at 165°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
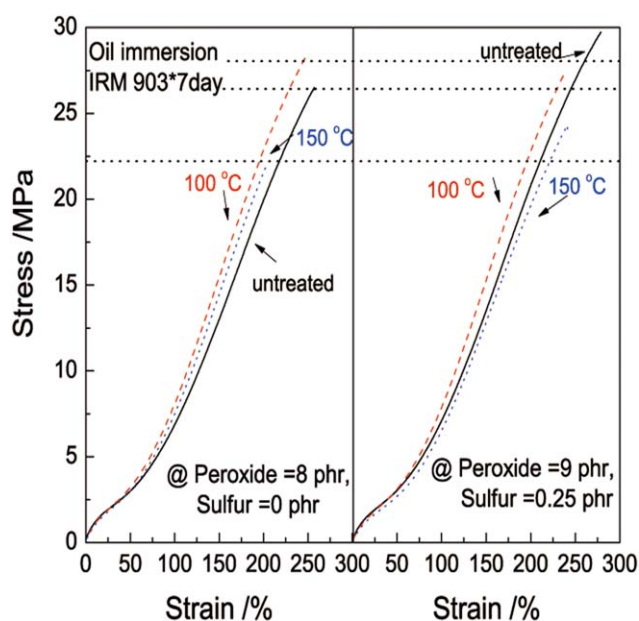

Figure 5. Stress–strain curves of no-sulfur (left) and sulfur-contained (right) HNBR compounds in phr after oil immersion at 100°C and 150°C for 7 days, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
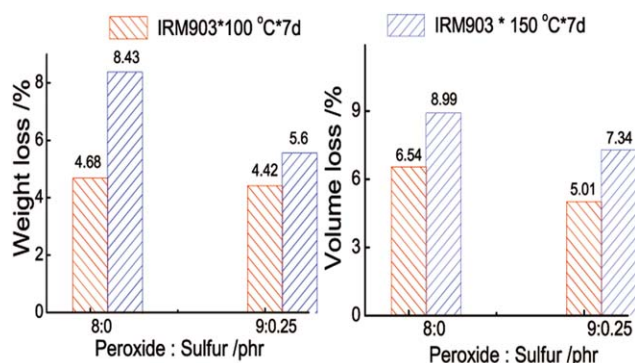
Figure 6. Quality loss (left) and volume loss (right) of sulfur-contained and no-sulfur HNBR compounds in phr after oil immersion at 100°C and 150°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Times consumed to reach third-level crack for HNBR compounds with and without sulfur. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of no-sulfur HNBR compounds, which verified the existence of sulfide bond in sulfur-contained HNBR compounds. What's more, it can be found from Supporting Information Figure S5 that sulfur-contained HNBR compounds is more temperature-sensitive than those no-sulfur HNBR compounds which is a consequence of the heat sensitivity of sulfide bond.

On the fact that peroxide-cured fully saturated HNBR compounds exhibit a poor dynamic property, sulfur was added as a crosslink coagent to improve the dynamic property of peroxide-cured fully HNBR compounds. Figure 8 shows the time needed to reach third-level crack of HNBR compounds obtained from demattia tests. As can be seen from Figure 8, regardless of testing at RT or after oil immersion, sulfur-contained HNBR compounds need longer time to reach the same level crack than the counterpart without sulfur, which means the sulfur-contained compounds has better dynamic properties than those no-sulfur
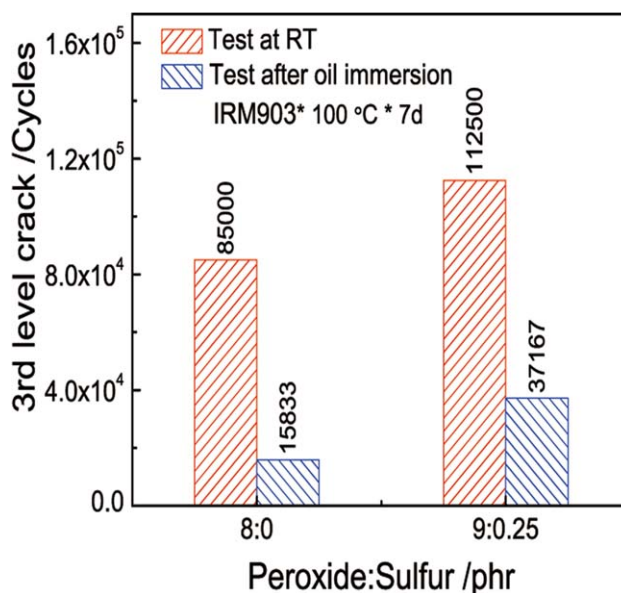
HNBR compounds. This can be attributed to the sulfide bond formed in the vulcanization process which has a better chain mobility.[8] Tear analyzer test results shown in Figure 9 also demonstrate that sulfur-contained HNBR compounds exhibit a better dynamic property.

Goodrich flexometer can be used to test the heat built-up behavior of HNBR vulcanizates by monitoring the temperature increment of samples subjected to dynamic compressive
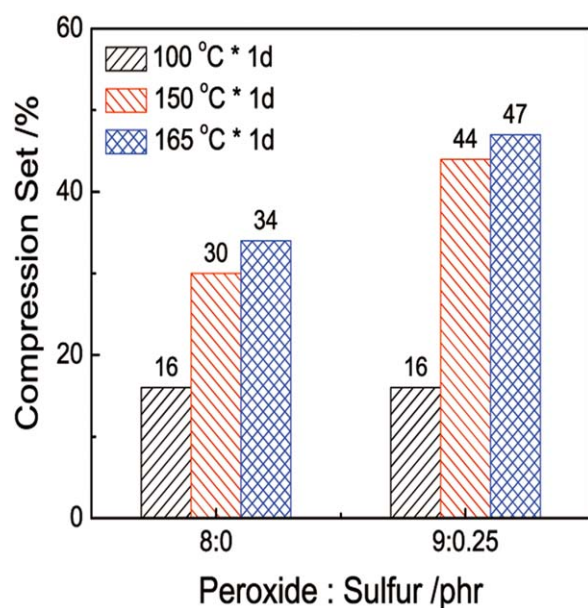

Figure 7. CS values of HNBR compounds in phr with and without sulfur after compressed at 100°C, 150°C, and 165°C for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
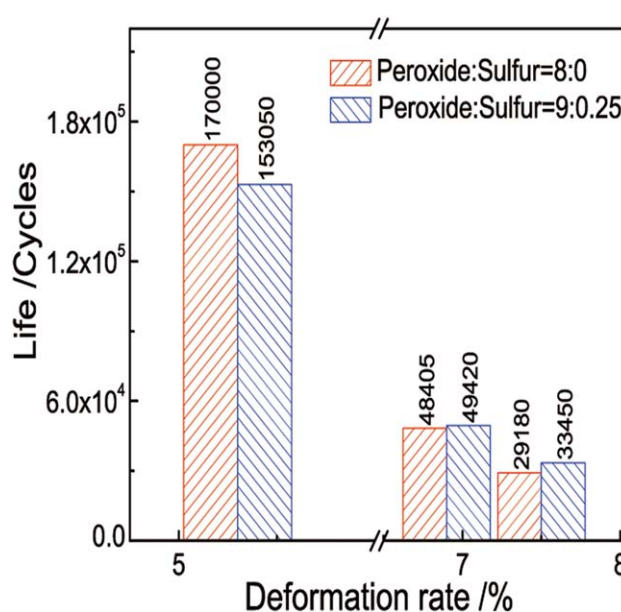

Figure 9. Tear analyzer results of sulfur-contained and no-sulfur HNBR compounds in phr at different deformation rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

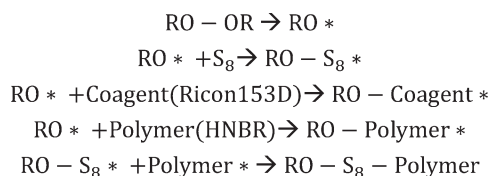**Table VII.** Goodrich Flexometer Results of HNBR Compounds in Phr with Different Peroxide to Sulfur Ratios

Peroxide : Sulfur	8 : 0	9 : 0.25
ΔT (°C)	51.4	46.4

strains.[23] Table VII shows that the temperature increment (ΔT) resulting from the heat built-up during the dynamic process of HNBR compounds with a small amount of sulfur (0.25 phr) is lower than that of HNBR compounds without sulfur. This behavior probably results from the di/polysulfide bonds formed in sulfur-contained HNBR compounds. Compared with C—C bond formed in no-sulfur HNBR compounds, di/polysulfide bonds possess better chain mobility which could provide an easy energy dissipated approach during the dynamic flexing process. Wang et al.[23] investigate the service life of rubber damping products with flexing test and found that the goodrich flexing test could provide a reliable information on the service life of those damping products. Thereby, it can be concluded that the service life of sulfur-contained HNBR compounds is longer than that of no-sulfur HNBR compounds when used under dynamic environment. And this result is in accordance with the above DeMattia test result.
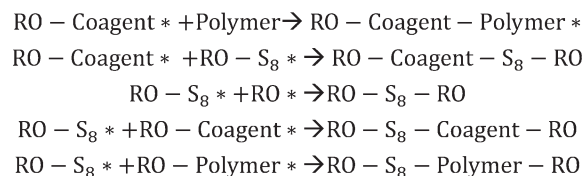
Reaction Mechanism of Sulfur in HNBR Peroxide Cure Process

A better dynamic property of fully saturated HNBR compound was obtained through the addition of a small amount of sulfur. Then what happened during the HNBR cured process? Why the curing rate and crosslink density of HNBR compounds is affected by the dosage of sulfur (behavior different at dosage below and above 0.25 phr) and why sulfide bond can be formed in the fully saturated elastomer?

To explain those phenomena, mechanisms are proposed tentatively. First, when the amount of sulfur is below 0.25 phr. The small amount of sulfur could act as a coagent increasing the cure rate like a type I coagent. This is in line with our finding that sulfur reduced the scorch time (shown in Supporting Information Table S1) compared to vinyl-BD which belongs to type II coagent. The react process can be illustrated as follows Scheme 1, where S_8 may stand for S_8 chains from the original 8-membered rings or any longer sulfur chains. During curing process, sulfur (dosage below 0.25 phr) added to polymer or peroxide-derived radicals[24] are able to maintain the chain crosslink reaction by H-abstraction to further form polymer radicals during which combining polymer

$$RO - OR \rightarrow RO*$$
$$RO* + S_8 \rightarrow RO - S_8*$$
$$RO* + Coagent(Ricon153D) \rightarrow RO - Coagent*$$
$$RO* + Polymer(HNBR) \rightarrow RO - Polymer*$$
$$RO - S_8* + Polymer* \rightarrow RO - S_8 - Polymer$$

Scheme 1. The crosslink scheme when the amount of sulfur below 0.25 phr.

$$RO - Coagent* + Polymer \rightarrow RO - Coagent - Polymer*$$
$$RO - Coagent* + RO - S_8* \rightarrow RO - Coagent - S_8 - RO$$
$$RO - S_8* + RO* \rightarrow RO - S_8 - RO$$
$$RO - S_8* + RO - Coagent* \rightarrow RO - S_8 - Coagent - RO$$
$$RO - S_8* + RO - Polymer* \rightarrow RO - S_8 - Polymer - RO$$

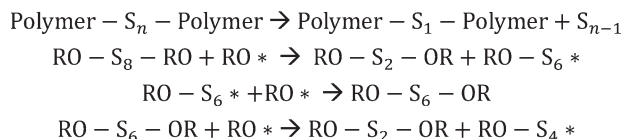**Scheme 2.** The crosslink scheme when the amount of sulfur above 0.25 phr.

and polymer-coagent radical together and thus increase the cure rate.

However, when the sulfur concentration is high (above 0.25 phr or more), other reactions such as radical recombinations without involving polymer which are not productive for crosslinking and thus a decreased crosslink density would take place as well. Besides, a recent study by Vandeputte et al.[25] on hydrogen abstraction indicates that it is unlikely that sulfur end-group radicals ($RO-S_8^\star$ and others) are strong enough radicals for hydrogen abstraction from fully saturated HNBR which does not contain any significant amounts of allylic hydrogen. This can explain why the crosslink density of HNBR compounds reduced under the existence of a small amount of sulfur and why the curing rate decreased when the sulfur dosage was above 0.25 phr. The related reaction process can be illustrated as following Scheme 2:

Additionally, the formation of mono/di-sulfide crosslinks in fully saturated HNBR compounds, unlike those formed in sulfur-cured vulcanizates, probably result from the crosslinks with longer sulfur chains that thermally desulfurize down to monosulfide crosslinks. It should be noted that the cure temperature of 175°C has been chosen to allow fast enough decomposition of the peroxide which is however high for sulfur cure and will therefore favor the formation of short sulfur crosslinks by a "digestion" of the S_8 ring as shown in the following Scheme 3.

CONCLUSIONS

The effect of the addition of a small amount of sulfur acting as a crosslink coagent on the curing, physical and mechanical properties of peroxide-cured fully saturated HNBR compounds was investigated in this work. No-filler HNBR compounds with various content of sulfur were first evaluated to study the influence of sulfur on their crosslink density and cure kinetics. Selective cleavage of polysulfide (—Sx—) and monosulfide(—S—) bond by combined thiol and piperidine treatment verified the existence of poly/monosulfide bond in sulfur-contained HNBR compounds. Subsequently, the physical and mechanical properties of fully formulated compounds were evaluated and it is found that the addition of small amounts of sulfur in fully

$$Polymer - S_n - Polymer \rightarrow Polymer - S_1 - Polymer + S_{n-1}$$
$$RO - S_8 - RO + RO* \rightarrow RO - S_2 - OR + RO - S_6*$$
$$RO - S_6* + RO* \rightarrow RO - S_6 - OR$$
$$RO - S_6 - OR + RO* \rightarrow RO - S_2 - OR + RO - S_4*$$

Scheme 3. The scheme of the formation of di/polysulfide in HNBR compounds.

saturated HNBR compounds can improve the stress–strain and dynamic properties of peroxide-cured HNBR compounds remarkably, at a cost of slightly higher CS values. Moreover, the addition of sulfur has no obvious influence on the aging and oil resistance properties of fully hydrogenated HNBR. Finally a cure reaction mechanism was given.

In a conclusion, small amount of sulfur can impart the peroxide vulcanizates some "sulfide properties" like better stretching and dynamic properties, but at the same time some "peroxide vulcanizates property" like CS are weakened slightly due to the introduction of sulfur. However, a scientific research on the mechanism of sulfur in peroxide vulcanization and a systematic study on the optimized ratio of peroxide to sulfur for balanced properties are still expected.

ACKNOWLEDGMENTS

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