Study of the Compound Effects on The Adhesion Layer Between Brass and the
Squalene Model Compound By GPC and TOF-SIMS

By

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ABSTRACT

Compound effects on the sulfidization reaction of brass were studied by GPC and TOF-SIMS using a squalene reaction medium. The absence of carbon black and cobalt salt retarded the decomposition reaction of accelerator and crosslinking reaction of squalene. Replacement of squalene with its saturated counterpart, squalane, suppressed the accelerator decomposition, the formation of copper sulfide layer and the formation of the cobalt-related compounds in the adhesion layer. Formation of the copper sulfide layer was enhanced by the absence of cobalt salt.

Keywords: brass, GPC, TOF-SIMS, squalene, adhesion, carbon black, cobalt, rubber

INTRODUCTION

The adhesion between brass-coated steel cord and rubber is one of the most crucial properties in the tire industry because it determines the durability of the tires during their service life and eventually retreadability. Numerous studies have been carried out to elucidate the mechanism of the adhesion between brass and rubber [1-3]. The effects of various compounding ingredients, ranging from accelerators to adhesion promotors, on brass-rubber adhesion were also studied [4-6]. Early studies to determine the effect of compounding ingredients on the adhesion strength between rubber and brass-coated steel
cord have been concentrated on the measurement of pull-out strength and rubber coverage ratio under the various compounding formulations and aging conditions. From these results, virtually all ingredients seem to have a certain effect on the adhesion strength before or after aging. However it is not easy to determine whether the ingredients affect the rubber properties or the adhesion layer itself. To study the changes in the rubber chemistry and the adhesion layer separately, squalene has been adopted as a model compound instead of rubber to facilitate the analysis after the curing process [7]. Squalene, the low-molecular-weight trans-isomer of natural rubber (Figure 1), has been successfully used to study the vulcanization mechanism of natural rubber [8-13]. Thus, in this paper, the effect of compounding ingredients on the sulfidization reaction in brass was studied using squalene as a model compound. The vulcanization rate of squalene was studied by Gel Permeation Chromatography (GPC) which can directly monitor the formation of crosslinked squalene. Investigation of the adhesion layer was done by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), which recently has been proved to be a very effective analysis method in monitoring the change in the adhesion layer of brass during the curing process [11].

EXPERIMENTAL

Materials

Hard-tempered 63/37 brass panels were purchased from Goodfellow Co. (Cambridge, England). They were polished to a mirror surface using 1200 grit SiC, followed by diamond paste of 45 µm, 6 µm and 1 µm, successively. After polishing, the panels were thoroughly rinsed with methanol, acetone, hexane and toluene in an ultrasonic bath to
remove any residues or contaminants. Squalene (C_{30}H_{50}) was purchased from J.T. Baker Co. (Phillipsburg, NJ, U.S.A.). Its purity was 99.9% as per GC. The rubber chemicals, ZnO, stearic acid, cobalt naphthenate adhesion promoter, ground sulfur, the accelerator N,N-dicyclohexylbenzothiazole sulfenamide (DCBS), and N326 carbon black were all obtained from Hankook Tire Akron Technical Center (Akron, Ohio) and used without further purification.

**Sulfidization of Brass Panels in the Squalene Medium**

Squalene 100 parts, ZnO 10, stearic acid 0.8, Co-naphthenate 2.0, N326 carbon black 10 were weighed and mixed in the beaker at 80°C and then cooled down to room temperature. The curatives, ground sulfur 6.4 and DCBS 0.8, were added to the mixture at 80°C to simulate the mixing process used in the rubber industry to achieve homogeneous mixing. The mixture was cooled down to room temperature and 5 ml aliquots were transferred to 10 ml vials. The brass panels were cut into 1×2 cm² pieces and placed in the vials. Nitrogen was purged through the squalene mixtures to prevent oxidation of the squalene or other side reactions. The reaction was initiated by lowering the vial holder into the heating bath which was kept at 150°C. The vial holder was rotated with a mechanical stirrer for 2 min. to reach the equilibrium temperature and vials were removed from the bath at regular intervals and immediately quenched in ice water to stop the curing reaction. The brass panels were thoroughly rinsed in toluene, acetone and hexane in an ultrasonic bath. The brass panels were stored in vials in a nitrogen atmosphere until analysis by TOF-SIMS.

**Analysis of Squalene Mixtures by GPC**
To analyze squalene mixtures by GPC, the reaction mixtures were placed in the refrigerator overnight for the particles to settle and 1ml aliquots were then taken and diluted with 10ml of HPLC grade tetrahydrofuran (THF). The THF solution of the reaction mixture was filtered off with a 0.45 µm membrane filter to remove the small particles. Analysis was done by GPC (Model; HP 1050) which has a 20µl loop volume with a Waters HR 0.5 GPC column which is capable of separating compounds up to a M.W. of 1000. 100µl of the sample solution was injected by a micro syringe. The mobile phase was THF and the flow rate was 1.0 ml/min. Chromatograms were obtained at 274 nm with a UV detector to minimize the peak overlap with the squalene monomer.

**Analysis of the Sulfidized Brass Panels by TOF-SIMS**

The sulfidized brass panels were analyzed by a Cameca TOF-SIMS Model IV using $^{69}$Ga$^+$ as the primary ion source with an energy of 25 keV in the bunched mode. The mass resolution (m/Δm) was 8000 measured at the $^{28}$Si$^+$ peak. The target current of the $^{69}$Ga$^+$ beam was 2 pA with a beam size of around 10 µm. The surface spectra were acquired for 30 s from a area of $500 \times 500 \ \mu m^2$. Depth profiling of the brass panels was performed using Ar$^+$ as the sputtering ion with an energy of 3 keV. The target current in the sputtering mode with Ar$^+$ was 50 nA. Data acquisition was done for 10 s per data point in the raster area of $20 \times 20 \ \mu m^2$ located in the center of the crater of $300 \times 300 \ \mu m^2$. The intensities of elements of interest were obtained by acquisition of the intensity from 0 - 1200 s of depth profiling. All SIMS data were normalized with respect to the total ion intensity. Peak assignments given throughout this paper are based on exact mass
measurements of the peaks with a deviation between observed and calculated mass of no more than 0.01 amu.

RESULTS AND DISCUSSION

Monitoring the Compounds Effects on the Crosslinking of Squalene by GPC

Formulations of the reaction mixtures were designed so that the effect of compounding ingredients such as double bonds in the polymer backbone, carbon black and cobalt salt could be studied (Table 1). A typical GPC chromatogram during vulcanization reaction is shown in Figure 2. Assignment of the peaks was done based upon the work of Borros who separated the peaks with preparative HPLC and further characterized them with mass spectrometry and NMR [8]. First, the concentration of the accelerator (DCBS) is plotted versus the reaction time in Figure 3. Measuring the decomposition rate of the accelerator is very important in understanding various features in the curing process because it is the very first stage of the vulcanization reaction determining the overall rate of the curing process. The formation of a small amount of mercaptobenzothiazole (MBT) from DCBS is the rate-determining step of the curing process. Once generated, MBT catalyzes the decomposition of DCBS with formation of MBTS, which leads to the formation of the active sulfurating species by reacting with ZnO/S₈ like a following scheme [14].
In the control formulation, DCBS started to decompose rapidly at the early stage of the curing process, so most of the DCBS had disappeared at the end of the reaction. Removing carbon black or cobalt salt from the formulation led to a retardation of the DCBS decomposition rate. The cobalt salt was observed to have a more significant effect than carbon black in retarding the accelerator decomposition. The most dramatic effect was observed when squalene was replaced with squalane, the saturated form of squalene. Only 40% of the DCBS had decomposed at the end of the reaction, leaving 60% of the accelerator intact. This result confirms the recent report that double bonds in rubbers directly participate in the decomposition of sulfenamide-type accelerator as shown in the following scheme [8,14]. The high electron density in the $\pi$ orbital of the double bond polarizes the S-N bond and makes it susceptible to the decomposition reaction. The sulfenamide moiety tends to accommodate the negative charge due to the large size of sulfur atom and the charge delocalization by the resonance.

To monitor the curing reaction, the concentration of crosslinked-squalene was measured by GPC and plotted in Figure 4. Removing cobalt salt and carbon black from the formulation resulted in a significant retardation of the overall vulcanization rate of squalene as it did to the accelerator decomposition rate. Carbon black has been speculated
to catalyze the formation of the two key elements in curing process, the active sulfurating intermediate and the accelerator-terminated polysulfidic pendant groups [15,16]. The effect of cobalt salt on the rate of vulcanization was observed to be even more significant. Cobalt salts are generally believed to take part in the rate-determining step of the cure process by lowering the activation energy of the formation of active sulfurating intermediates [17].

It was noticed that removal of the carbon black retarded the onset of vulcanization but did not change the final crosslink density. On the contrary, the absence of the cobalt salt not only retards the onset of vulcanization but lowers the final crosslink density as well. This result can be understood in terms of the DCBS decomposition rate. As was shown previously, when carbon black was removed from the formulation, DCBS decomposed slowly at first but at the end of reaction it disappeared completely. But when cobalt salt was removed from the formulation, a considerable amount of accelerator was observed to remain undecomposed at the end of reaction which resulted in low crosslink density.

**Study of Compound Effects on Brass Sulfidization by TOF-SIMS**

In our previous paper on investigating sulfidized brass panels using TOF-SIMS [11], it was shown that depth profiling by TOF-SIMS can provide copious amounts of information about the detailed composition of the copper sulfide films formed in the squalene mixtures. By plotting the intensity of the copper sulfide peaks, it was possible to monitor the formation of copper sulfides throughout the reaction. In Figures 5-8, the depth profiles of brass panels versus reaction time during curing process are shown for
the various formulations. There is not much difference between formulations in terms of basic features such as the coherence of the pair-elements (Zn-O, Cu-S, Co-C) or the growth of layers with reaction time. However detailed characteristic differences are observed between the formulations.

When carbon black was removed from the formulation (Figure 5), the width and intensity of the cobalt and ZnO layers increased significantly at the end of the reaction, as compared with other formulations. It seems that cobalt deposited on the brass surface so that a thick layer of cobalt was present at the end of the reaction.

Cobalt and carbon often show very similar depth profiles in TOF-SIMS because cobalt exists in part in the form of an organic cobalt species inside the adhesion layer [11,18]. When cobalt is removed from the formulation, the depth profile of elemental carbon can be interpreted as the distribution of crosslinked squalene which contains fragments of the accelerator. It was observed that the depth profile of elemental carbon without cobalt salt exhibited quite a distinctive maximum in the range where Cu and S showed strong intensity, while smeared maxima were shown with other formulations. Existence of the maximum carbon intensity where copper and sulfur show strong intensity confirms the concept of the inclusion of crosslinked-rubber inside the porous copper sulfide layer by physical or chemical interaction. [1-3]

When the mass spectrum was reconstructed from the raw data of depth profiling, more useful information about the detailed nature of the copper sulfide layer could be obtained.
Typical reconstructed mass spectra of untreated and treated brass panels are presented in Figure 9. As is clearly seen from the spectra, the composition of brass panel changed during the vulcanization reaction. The formation of new species was observed in the spectra and those new compounds were identified as copper sulfides [11]. From the various copper sulfide peaks in the TOF-SIMS spectrum, a strong Cu$_2$S peak was selected and its intensity was plotted versus reaction time in Figure 10. It was observed that the control formulation reached the maximum Cu$_2$S intensity within 10 minutes of reaction while other formulations did not reach a maximum until after 30 minutes. It seems that the copper sulfide growth rate strongly depends on the decomposition rate of the accelerator, which means that sulfur atoms are delivered to the brass substrate in the form of active sulfurating intermediates and not in the form of elemental sulfur. When cobalt salt was removed from the reaction mixture, a very high intensity of copper sulfide peaks was observed, compared to other formulations. This finding can be rationalized by considering the role of cobalt inside the copper sulfide layer, which is believed to suppress the migration of metal ions from the substrate to the surface [ ]. Removal of cobalt in the copper sulfide layer enhanced the migration of copper ions to the surface where they reacted with sulfur and were converted into copper sulfide.

It is noteworthy that the brass sulfidization rate is significantly retarded by the use of squalane. The absence of double bonds in squalane seems to suppress the formation of copper sulfide layer by delaying the decomposition of the accelerator and subsequently the formation of the sulfurating intermediate, which is the essential compound for the growth of the copper sulfide layer.
Another remarkable difference can be found for the cobalt intensity in the copper sulfide layer. The mass spectrum of the adhesion layer was reconstructed for the mass range of 90–120 and presented in Fig. 11. In this mass range, weak but characteristic peaks of the adhesion layer appeared. In the control formulation, various cobalt and copper-related peaks are observed at masses 91(CoS), 95(^{63}CuS), 97(^{65}CuS), 103(CoCS), 107(^{63}CuCS), 109(^{65}CuCS) and 118(CO₂). When carbon black was removed, the relative intensity of cobalt related peaks (CoS, CoCS, CO₂) to copper-related peaks (CuS, CuCS) increased significantly. Depth profiles of the formulation without carbon black (Figure 5) led to the same conclusion that cobalt deposited on the surface of the brass during the curing process. Substitution of squalene with squalane resulted in a sharp decrease of the cobalt incorporation into the adhesion layer. As is seen from the figure, the mass spectrum of the adhesion layer treated in the squalane medium resembles that of the adhesion layer treated without cobalt salt. It was observed that almost no cobalt-related compounds were found in the adhesion layer when squalene was replaced with squalane. This finding strongly suggests that cobalt incorporation into copper sulfide layer requires interaction between cobalt ions and the active sulfurating intermediates which are formed only after the accelerator decomposition. This trend could be confirmed when the intensity of cobalt ion is plotted with reaction time in Figure 12. The figure shows that the absence of carbon black led to the initial retardation of the incorporation of cobalt into the adhesion layer compared to the initial rise of cobalt intensity in control formulation. But after a certain induction period an abrupt increase of cobalt intensity in adhesion layer was observed.
From the GPC results, the accelerator in the absence of carbon black decomposed to completion only after a certain induction period. This can be the reason for the abrupt increase of cobalt incorporation in the adhesion layer when carbon black was eliminated. Thus it can be concluded that decomposition of the accelerator is the prerequisite of cobalt incorporation into the adhesion layer.

CONCLUSIONS

1. Decomposition of the DCBS accelerator is strongly influenced by the compounding formulation. The absence of carbon black and cobalt salts retards the decomposition reaction at initial stage and the decomposition reaction starts only after a certain induction period. Replacement of squalene with its saturated compound, squalane, greatly suppresses accelerator decomposition and only 40% of the original amount is decomposed.

2. The absence of carbon black slows down the crosslinking reaction of squalene but leads to the same final crosslink density as control formulation. Removal of cobalt salt not only retards crosslinking reaction but reduces the final crosslink density as well.

3. The formation of the copper sulfide layer is enhanced by the absence of cobalt salt. Use of squalane instead of squalene slows down the formation of copper sulfide layer.

4. The absence of carbon black leads to the deposition of the cobalt layer on the brass surface at the end of reaction. It is observed that replacement of squalene
with its saturated compound, squalane, prevents the formation of the cobalt-related compound in the adhesion layer.

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**Tables Captions**

Table 1. Formulation of Reaction Mixtures for Investigation of Compound Effects

**Figures Captions**

Fig. 1 Molecular Structure of Squalene

Fig. 2 Typical GPC chromatogram of squalene mixture after 10 min of curing reaction in the control formulation. Numbers in the chromatogram is the retention time of each peak.

Fig. 3 Change of DCBS concentration during vulcanization with various formulations
as determined from GPC

Fig. 4  Change of crosslinked squalene concentration during vulcanization with various formulation as determined from GPC

Fig. 5  Depth profiles of brass panels treated in squalene mixture without carbon black

Fig. 6  Depth profiles of brass panels treated in squalene mixture without cobalt salt

Fig. 7  Depth profiles of brass panels treated in squalane mixture

Fig. 8  Depth profiles of brass panels treated in squalene control mixture

Fig. 9  Reconstructed mass spectrum of untreated and sulfidized brass
( * : Cu$_2$S , ** : Cu$_3$S )

Fig. 10  Intensity change of Cu$_2$S peak during vulcanization (from TOF-SIMS spectra)

Fig. 11  Mass spectrum of adhesion layer in the mass range of 90 – 120 amu
(a) control (b) no carbon black (c) squalane (d) no cobalt salt

Fig. 12  Intensity change of cobalt in the adhesion layer during vulcanization (from TOF-SIMS spectra)
Table 1. Formulation of Reaction Mixtures for Investigation of Compound Effects

<table>
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<tr>
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<th>Squalane</th>
<th>Without Carbon Black</th>
<th>Without Cobalt Salt</th>
<th>Control</th>
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</table>
Fig. 1
Fig. 2

Crosslinked Squalene

DCBS

Sulfur

Intermediates

Absorption

Time (min)

mAU

0

2

4

6

8

10

12

5.042

5.538

6.025

6.384

6.942

7.564

8.101

9.131

9.906

11.452
Fig. 3

Absorption (mAU) vs. Time (min)

- Squalane
- No Carbon Black
- Control
- No Cobalt Salt
Fig. 4

Absorption (mAU) vs. Time (min)

- Control
- Without Carbon Black
- Without Cobalt Salt
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10

- Squalane
- No Carbon Black
- No Cobalt
- Control

Normalized Intensity vs. Time (min)
Fig. 11
Fig. 12