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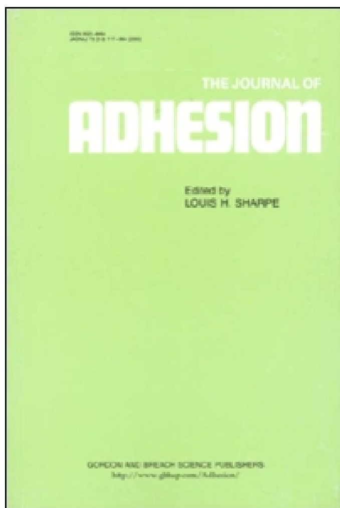

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Effect of Tetrachlorobenzoquinone on the Adhesion between Rubber Compound and Brass-plated Steel Cord

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The adhesion between tetrachlorobenzoquinone (TCBQ)-loaded rubber compound and brass-plated steel cord was studied to understand the role of TCBQ as an adhesion promoter. With loading of TCBQ in the rubber compound the cure rate became slow, but the change in physical properties was not significant. An improvement of the adhesion was obvious with low loading of TCBQ at the range of 0.5 phr while an adverse effect was observed with high loading at 2 phr. The addition of TCBQ for the improvement of adhesion has a greater effect before aging because TCBQ contributes to form a large surface area of copper sulfide *via* accelerated copper diffusion into the rubber bulk. However, higher TCBQ loading as well as longer aging time leads to a great extent of copper migration into the rubber and excess growth of zinc oxide layer, resulting in decreased adhesion. The adhesion interphase before aging, between a thin brass film and a rubber compound, investigated using AES showed no difference except that sulfur increased with increasing TCBQ loading. On the other hand, the adhesion interphase was changed after humidity aging. The copper content decreased at the adhesion interphase while it increased in the rubber layer with increasing addition of TCBQ.

Keywords: Adhesion interphase; rubber-to-brass bonding; adhesion promoter; AES; depth profile; tetrachlorobenzoquinone

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1. INTRODUCTION

Brass-plated steel cord for the belt and carcass of tires has been used as a reinforcing material in order to enhance the structure-maintaining function. Brass plating on the steel cord reacts with sulfur in the rubber compound during the curing process of tire manufacturing, forming an adhesion interphase between the rubber compound and the steel cord. Therefore, the adhesion interphase with sufficient thickness and stable structure is essential for a good adhesion.

Copper and zinc sulfides and oxides and hydroxides of copper and zinc are formed at the adhesion interphase due to the reaction of brass with sulfur, oxygen and water in the rubber compound [1 – 3]. Adhesion becomes weak when the copper sulfide layer is not sufficiently grown, but the excessive growths of copper sulfide and zinc oxide bring about their own cohesive failures. Severe migration of copper sulfide and zinc oxide into the rubber compound also leads to poor adhesion [4]. In an attempt to obtain information about the adhesion interphase, a depth profile has been measured by a surface analysis technique using X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) [1 – 6]. The adhesion sample, prepared by attaching the rubber compound with a thin brass film deposited on a glass, is useful to get homogenous and reproducible depth profiles of the adhesion interphases, compared with a mechanically-broken rubber compound-steel cord sample [7, 8].

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Since zinc is oxidized more easily than copper, depending on the fabrication and storage conditions, a zinc oxide layer formed on the surface of a brass-plated steel cord is readily found. A thick zinc oxide layer leads to poor adhesion because of the hindered formation of an adhesion interphase due to a reduced reaction rate between copper and sulfur, while the zinc oxide layer with a proper thickness has the effect of suppressing the excessive growth of copper sulfide as it controls the reactivity of copper. During the adhesion between the brass-plated steel cord and rubber compound, a zinc oxide layer is formed additionally on the adhesion interphase as a result of the reaction of oxygen or water contained in the rubber compound with the zinc in the brass. When the zinc oxide layer becomes thicker, as by humidity aging treatments, the adhesion layer can easily be ruptured because of the loss of zinc metal. However, optimum thickness of the zinc oxide

layer contributes to the adhesion stability, especially in promoting the stability of copper and zinc which, in turn, results in the suppression of the excessive growth of copper sulfide.

Tetrachlorobenzoquinone (TCBQ) was introduced as a new organic adhesion promoter by Barnhart and McKinstry [9]. But almost nothing has been reported thus far about its role in enhancing the adhesion between the rubber compound and brass-plated steel cord. So, it would be helpful for the design of new organic promoters to verify the function of TCBQ at the site of the adhesion interphase. Generally, it is known that copper and aromatic rings are apt to form a chelate or ligand. One recent study [10] also mentioned the formation of copper complexes of various benzoquinones.

The aim of this study is to show how TCBQ acts as an adhesion promoter. The effect of TCBQ on the adhesion between a rubber compound and brass-plated steel cord was examined, based on the formation and degradation of the adhesion interphase from the depth profile of the rubber compound/brass film samples. The adhesion force and rubber coverage of a rubber compound loaded with TCBQ were compared with those of a TCBQ-free compound. Influences of aging as well as TCBQ concentration on the adhesion of TCBQ-containing rubber compounds were also carefully observed.

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2. EXPERIMENTAL

2.1. Stock Preparation

Five rubber stocks with different amounts of TCBQ were prepared. Formulations for the masterbatch and final mixed compounds are given in Table I.

The loading amounts of TCBQ were 0, 0.5, 1.0, 2.0, and 4.0 phr. All the rubber compounds were mixed as described in ASTM D-3184 using an internal mixer (Banbury Mixer model 82, Farrel Co., U.S.A.). Ingredients for the masterbatch were mixed for 10 min at a rotor speed of 40 rpm and dumped at 150°C. After the masterbatch had been cooled down to room temperature, the final mixing components were added and mixed for 5 min at 30 rpm and dumped at 90°C. After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill (model MKIII, Farrel Co., U.S.A.).

TABLE I Rubber compound recipes

Material	Trade name	Manufacturer	Content (phr)
Masterbatch			
NR	SMR-100	Lee Rubber Co., Malaysia	80
BR	BR-01	Kumho Petrochem. Co., Korea	20
carbon black	N351	Lucky Co., Korea	50
processing oil	A#2	Michang Co., Korea	5
activator	ZnO	Hanil Co., Korea	10
antioxidant	Kumanox-RD[1]	Monsanto Co., U.S.A.	1
Final Mixing			
activator	Stearic acid	Pyungwha Co., Korea	1.5
TCBQ	Vulkor [2]	Uniroyal Chem. Co., U.S.A.	var.
accelerator	SantocureMOR[3]	Monsanto Co., U.S.A.	0.7
sulfur	Crystex HS OT 20	Akzo Co., The Netherlands	5

[1] 2,2,4-trimethyl-1,2-dihydroquinone.
[2] 2,3,5,6-tetrachloro-1,4-benzoquinone.
[3] 2-(Morpholinothio)-thiobenzothiazole.

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Rheocurves were recorded using a Monsanto Rheometer 100 at 160°C. T_{90} time and maximum torque were obtained from those rheographs. Mooney viscosity was also measured by a Monsanto MV-200 machine according to ASTM D-1646.

Hardness of vulcanizates was measured using a Shore A durometer according to ASTM D-2240, and tensile properties were determined by a tensile tester (model 6021, Instron, U.S.A.) according to ASTM D-412.

2.2. Adhesion Test

By the procedure described in ASTM D-2229, specimens for the T-test were cured at 160°C on a cure press. Curing was maintained to be 5 minutes more than T_{90} time. The brass-plated steel cords, with 4×0.28 construction in which 4 steel wires having the same diameter of 0.28 mm were twisted together, manufactured by Hyosung T & C Co., Korea, were used. The plating weight of the brass was 3.6 g/kg and the copper content 63.6%. For humidity aging, specimens were placed in a humidity chamber at 85°C under 85% relative humidity for 5, 10 and 15 days. Thermal aging was performed at 90°C.

Pullout force was determined as the maximum force exerted by the tensile tester on the T-test adhesion sample during the pullout test,

with 10 mm/min of crosshead speed. Rubber coverage was also noted visually. Each value reported is an average of the six tested specimens. For the fracture mode at the surface of the steel cord resulting from the T-test, a scanning electron microscope (JEOL JSM 7400, Japan) was used.

2.3. Observation of Depth Profile of Adhesion Interphase

A thin brass film with the Cu/Zn ratio of 70/30 was sputtered onto a glass plate (Marienfeld, Germany, 75 × 25 mm) using an RF magnetron sputter for 120 sec at 2×10^{-6} Torr. The thickness of the film was confirmed to be 150 nm by SEM (JEOL JSM 7400, Japan).

A brass-on-glass plate was sandwiched between two uncured pads of each rubber compound, and then placed in a pad mold. Curing and aging conditions for the rubber compound/brass film samples were kept to be the same as in the preparation of T-test adhesion specimens.

Depth profiles from the outer brass surface to the bulk of rubber were recorded on an Auger spectrometer (Perkin–Elmer Phi 670). Surface concentrations were determined from Auger peaks of detected elements with compensation of their sensitivities every 0.5 min. The sputtering rate for the brass film was determined to be 25 nm/min. It is difficult, however, to determine precisely the sputtering rate for the adhesion interphase because it includes various chemical components with variable concentrations. Therefore, the sputtering time instead of the absolute depth is used to indicate the depth of the adhesion interphase for this paper.

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3. RESULTS

3.1. Physical Properties of TCBQ-loaded Rubber Compounds

Cure rates of the rubber compounds were varied with the loading amounts of TCBQ as indicated in Table II. T_{90} time increased with an increase in the loading level of TCBQ, whereas the change in T_2 time decreased slightly. Therefore, the cure rate index (CRI), calculated

TABLE II Cure properties for various rubber compounds with different loading levels of TCBQ by oscillating disc type rheometer [1]

TCBQ loading (phr)	Time (min) T_2	T_{90}	CRI [2] (min^{-1})	Torque (J) min	max
0	2.7	6.4	27.0	1.36	5.41
0.5	2.3	7.5	19.2	1.44	6.16
1.0	2.1	8.8	14.9	1.44	5.88
2.0	1.8	10.5	11.5	1.44	6.23
4.0	1.3	12.8	8.7	1.57	6.02

[1] The rubber compounds were sheared to 1° and 1.67 Hz at 160°C.
[2] Cure Rate Index = $100/(T_{90}-T_2)$.

from T_{90} and T_2 values, decreased with an increase in TCBQ loading. Maximum torque increased with an increase in TCBQ loading, indicating a high crosslinking density.

Viscosity changes, with corresponding time, for the green compounds at 125°C are shown in Table III. T_5 time, indicating the onset of scorch time, shortened with increasing TCBQ loading, and viscosity deduced from torque increased steadily with TCBQ loading.

The physical properties of unaged vulcanizates are summarized in Table IV. Hardness increased with TCBQ loading. 5% modulus increased with increasing TCBQ loading, and 200% modulus increased up to 1 phr of TCBQ loading. Upon further increase in TCBQ loading, 200% modulus decreased. 300% modulus increased with increase in TCBQ loading up to 0.5 phr. A further increase in TCBQ loading resulted in decrease of 300% modulus.

Tensile strength and ultimate elongation decreased continuously with TCBQ loading. Compared with the unaged vulcanizate, modulus increased but tensile strength decreased upon aging thermally (Tab. V).

TABLE III Mooney viscometer test results [1] for various rubber compounds containing different loading levels of TCBQ

TCBQ loading (phr)	Time (min) T_5	T_{35}	Torque (J) initial	min	at 4 min
0	18.0	26.4	4.28	3.49	3.59
0.5	10.4	19.2	4.58	4.15	4.05
1.0	7.9	16.3	4.55	4.42	4.05
2.0	4.7	8.8	4.61	6.41	4.38
4.0	3.4	5.5	5.31	12.72	5.64

[1] The rubber compounds were sheared to 2 rpm at 125°C.

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TABLE IV Tensile properties for various rubber compounds with different loading levels of TCBQ

TCBQ loading (phr)	*Hardness*	*Modulus (MPa)* 5%	100%	200%	300%	*T.S.** *(MPa)*	*E.B.*** (%)
0	62	0.36	2.83	7.30	12.9	24.7	500
0.5	65	0.44	3.75	9.45	15.9	24.3	481
1.0	66	0.49	3.77	9.27	15.1	24.3	444
2.0	67	0.51	3.78	9.20	14.9	23.2	436
4.0	68	0.50	3.75	8.58	14.2	20.0	410

* T.S. = Tensile strength.
** E.B. = Elongation at break.

TABLE V Tensile properties of rubber compounds aged thermally at 105°C for 5 days

TCBQ loading (phr)	*Hardness*	*Modulus (MPa)* 5%	100%	200%	300%	*T.S.** *(MPa)*	*E.B.*** (%)
0	74	0.55	7.72	–	–	7.67	100
0.5	76	0.66	7.55	–	–	8.86	102
1.0	77	0.68	8.23	–	–	8.87	107
2.0	78	0.77	8.41	–	–	10.08	105
4.0	78	0.75	9.00	–	–	9.56	105

* T.S. = Tensile strength.
** E.B. = Elongation at break.

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3.2. Adhesion Properties of TCBQ-loaded Rubber Compound

Pullout force and rubber coverage of TCBQ-loaded rubber compound before and after humidity aging are shown in Figure 1. There were considerable increases in the pullout force and rubber coverage with TCBQ loading before aging. Pullout force increased abruptly up to 0.5 phr of TCBQ loading and was constant from 0.5 to 2 phr. However, it decreased when TCBQ loading exceeded 2 phr, even though the force value is still higher than that of TCBQ-free rubber compound. Rubber coverage showed the same trend as the pullout force. The enhancement in rubber coverage at an unaged state was considerable. Humidity aging deteriorated adhesion properties. With an increase in aging time, pullout force decreased. After aging for 15 days, pullout force increased at first with TCBQ loading up to 1 phr. Over 1 phr of TCBQ loading pullout force decreased abruptly and the pullout force for the samples loaded at 4 phr was considerably less than

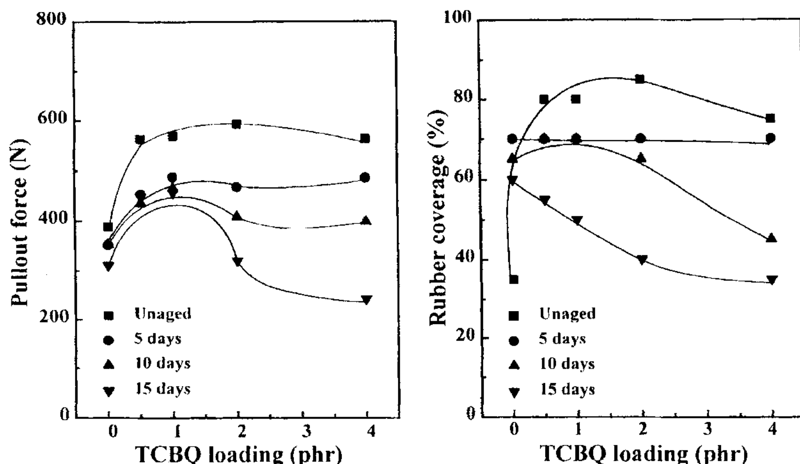

FIGURE 1 Adhesion properties of TCBQ-loaded rubber compounds. Humidity aging: 85°C and 85% relative humidity for 15 days.

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that of TCBQ-free compounds. Rubber coverage showed different behaviors for different humidity aging times. Rubber coverage of TCBQ-free rubber compound became high after humidity aging. On the other hand, rubber coverage of TCBQ-loaded rubber compound showed little improvement after humidity aging. With increasing humidity aging time, rubber coverage became poor with the rubber compound with a high level of TCBQ loading. The adverse contribution of TCBQ to rubber coverage was more significant with an increase in the amount of TCBQ and aging time.

The enhancement in adhesion properties with TCBQ loading was also observed after thermal aging as shown in Figure 2. The trend of pullout force for thermally-aged adhesion samples with TCBQ loading was similar to that of humidity-aged adhesion samples, whereas the rubber coverage of the pulled-out steel cord was different. Rubber coverage of thermally-aged samples increased dramatically with addition of TCBQ, and a rubber coverage as high as 80 to 100% could be attained for all samples. This improved rubber coverage of the TCBQ-loaded adhesion sample suggests that cohesive failure of the rubber layer instead of the adhesion layer occurred dominantly, indicating that the adhesion interphase became relatively stable compared with the rubber layer with thermal aging.

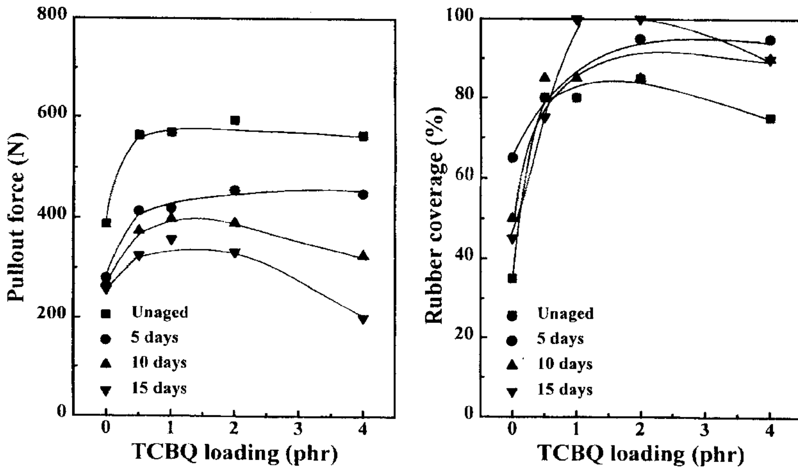

FIGURE 2 Adhesion properties of TCBQ-loaded rubber compounds. Thermal aging: 90°C for 15 days.

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The contributions of TCBQ loading on the adhesion properties can be summarized as: (1) The enhancement in adhesion properties was significant at a low loading level below 1 phr; (2) The pullout force and rubber coverage declined for the aged samples with high loading of TCBQ such as 2 and 4 phr; (3) Severe degradation of adhesion induced by TCBQ was observed after aging treatment at high loading. This summary suggests that the contribution of TCBQ loading to improved adhesion is significant at low loading. The disappearance of such enhancement by high loading of TCBQ indicates the presence of two contradicting contributions, a positive and a negative influence, of TCBQ on adhesion. At high loading, the negative contribution of TCBQ compensates for the positive enhancement observed at low loading.

3.3. Characterization of Adhesion Interphases

The AES depth profiles of the adhesion interphase between TCBQ-free rubber compounds and brass film at an unaged state is shown in Figure 3. At the outer surface, after 1 min of sputtering, carbon, zinc, and oxygen were detected. Since zinc has a high affinity for oxygen, the concentration of zinc at the outer surface is high compared with that of copper due to zinc migration to the surface. Carbon at the outer

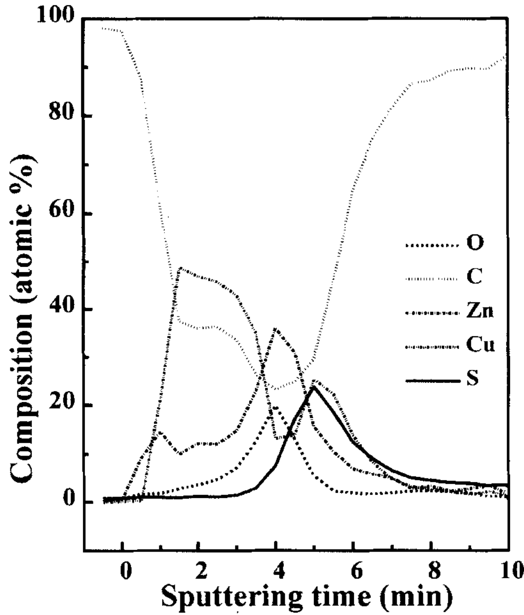

FIGURE 3 Depth profiles of the adhesion interphase between TCBQ-free rubber compound and brass film.

surface is thought to be due to partial contamination. The nearly-constant ratio of copper to zinc is observed at the region of sputtering time from 1 to 3 min, showing the unreacted brass layer. Copper content decreased after sputtering at 4 min and a peak of copper content was observed at the sputtering time of 5 min. At the same depth a peak of sulfur content was also observed. Peaks of zinc and oxygen were observed after sputtering of 3 ∼ 3.5 min. After sputtering of 8 min, the concentrations of copper, zinc, oxygen and sulfur diminished and that of carbon increased very rapidly, indicating the bulk rubber. This depth profile is a typical adhesion interphase between the rubber compound and the brass film [7, 11]. The peaks of zinc and oxygen observed at the brass layer and those of copper and sulfur observed at the rubber layer is in good accordance with van Ooij's mechanism [11], in which adhesion is built up through the penetration of copper sulfide to the rubber bulk.

Figure 4 shows the depth profiles of the unaged adhesion interphase prepared from the brass film and the rubber compound with various

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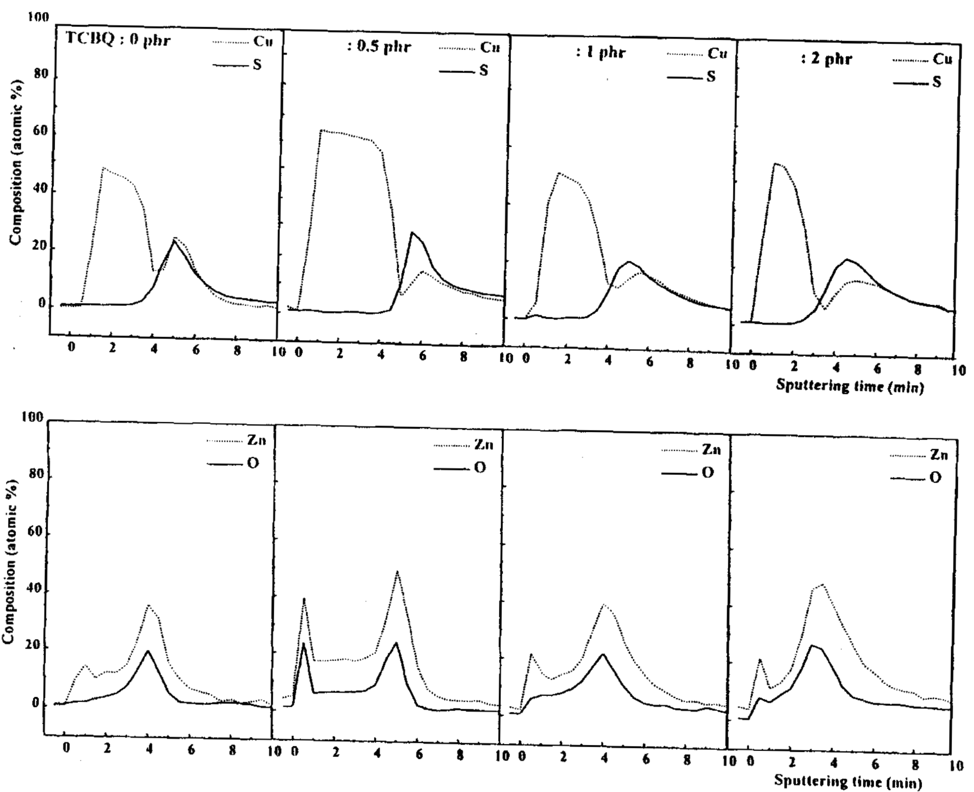

FIGURE 4 Depth profiles of copper and sulfur (top), and zinc and oxygen (bottom) for the unaged rubber compound/brass film adhesion samples with respect to TCBQ loading.

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TCBQ loading levels. For clarity, concentrations of copper and sulfur (upper) and zinc and oxygen (lower) are shown separately. The schematic shapes of the adhesion interphase are almost the same even when the loading amount of TCBQ is changed from 0 to 2 phr. But the relative concentration of sulfur to copper at the interphase is varied with TCBQ loading. With increasing TCBQ loading in the rubber compound of the adhesion sample, the ratio of sulfur to copper increases, indicating some of the copper disappears at the adhesion interphase.

With increasing TCBQ loading, the copper content in the brass layer decreases while that of the rubber compound increases. This indicates the migration of some copper from the adhesion interphase to the rubber layer. The concentration profiles of zinc and oxygen are similar in shape, and show the same tendency for different TCBQ loadings. For the rubber compound with higher TCBQ loading of 2 phr, the copper content in the adhesion interphase was found to be lower, however, zinc content was relatively high.

Usually the adhesion interphase spreads widely after humidity and thermal aging because sulfides and oxides of copper and zinc are formed additionally and they grow toward the bulk rubber. Therefore, it is relatively difficult to observe the distinct structure of the adhesion interphase after a long aging treatment. Figure 5 shows the depth profiles of the adhesion interphase after humidity aging for 15 days for various TCBQ loadings. Compared with those before aging, relative intensity and width of the sulfur peak against copper became remarkably larger. Considering that the sputtering time axis was three times as long as before aging, largely copper sulfide was thought to be formed and diffused into the rubber layer by the aging treatment. At the aged adhesion interphase, the distribution profiles of copper and sulfur, and zinc and oxygen were similar for the TCBQ-free compound and the compound with excess TCBQ of 2 phr. The profiles were also similar for those compounds with TCBQ loading of 0.5 phr and 1.0 phr, respectively. When a small amount of TCBQ was added, the adhesion interphase appeared to be maintained to a certain degree after the aging treatment, while it was significantly deformed for the compounds which contain no or excess TCBQ. In TCBQ-free compounds, no discrete peak of oxygen could be detected in the

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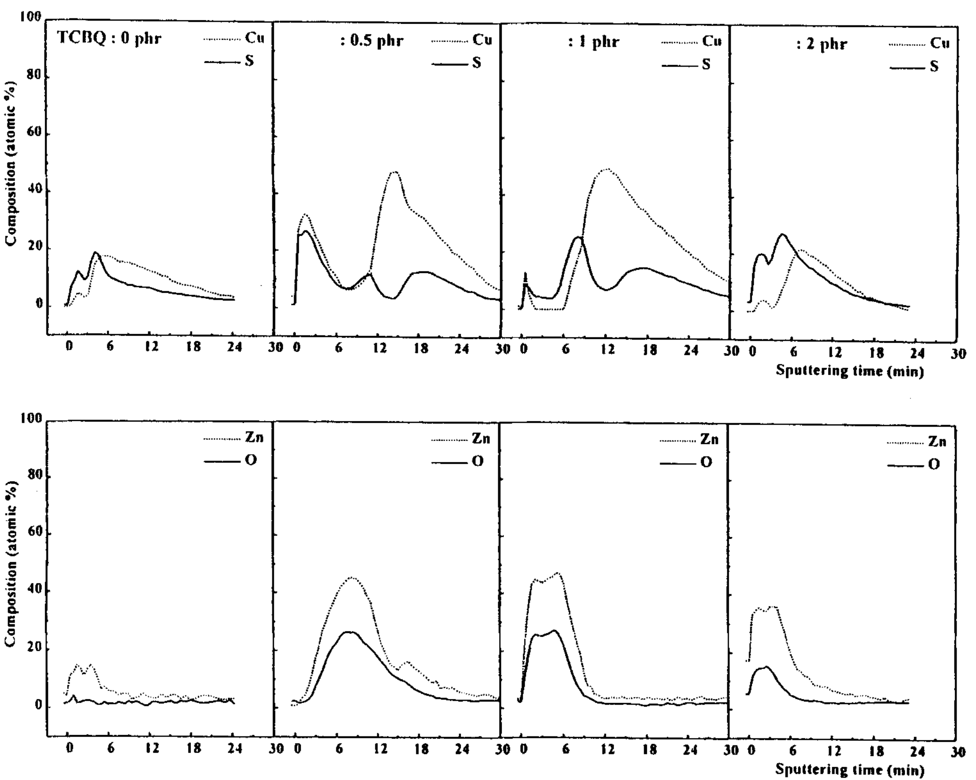

FIGURE 5 Depth profiles of copper and sulfur (top), and zinc and oxygen (bottom) for the humidity-aged rubber compound/brass film adhesion samples with respect to TCBQ loading. Humidity aging: 85°C and 85% relative humidity for 15 days.

adhesion interphase and the detection of zinc was also limited, indicating the occurrence of severe dezincification.

The small amounts of residual copper and sulfur in the adhesion interphase represent the fact that the adhesion interphase is nearly destroyed. Contrary to the TCBQ-free compound, peaks of copper, sulfur, zinc, and oxygen could be observed after humidity aging for the compounds having good adhesion properties *via* TCBQ loading of 0.5 or 1.0 phr. The adhesion layer became thicker and broader since most of the copper and zinc, which did not react during vulcanization, had completed their reactions. One peculiar fact is that copper moved into the rubber layer to a large degree instead of gathering around the adhesion interphase and the maximum of copper content could be seen after the sputtering time of 12 min. At the same time, large amounts of sulfur rather than copper were detected at the sputtering range of 4 to 8 min on which copper sulfide had been detected immediately after vulcanization. On the other hand, oxygen and zinc gathered together generally at the surface, though there existed a slight difference depending on the specimens. No more zinc was detected after the sputtering time of 8 min except for the compound with TCBQ loading of 0.5 phr. That is, copper diffusion to the rubber layer can be enhanced by the addition of TCBQ.

One of the most important factors for good adhesion stability is the optimum thickness of the zinc oxide layer. Zinc oxide has been considered as a diffusion barrier against the driving force of a growing adhesion layer such as the diffusion of copper ions into the adhesion layer. Zinc oxide concentrated in common in the adhesion interphase of the TCBQ-loaded rubber compounds. Although some differences in the distribution profile were present depending on the loading volume, zinc oxide was observed mainly in the adhesion interphase while copper migrated into the rubber matrix. This result shows a discrepancy when it is compared with the TCBQ-free compound in which little zinc is detected due to dezincification in the adhesion interphase. Zinc oxide formation is accelerated because the activity of zinc increases by the rapid movement of copper *via* TCBQ loading. The ZnO layer controls the reactivity of copper in brass with sulfur.

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4. DISCUSSION

With increasing amount of TCBQ in the rubber compound, the cure rate decreased. As shown in Table II, the CRI of the rubber compound containing 1 phr of TCBQ declined to one-half that of the TCBQ-free rubber compound. The slow cure rate of TCBQ-loaded rubber compounds induces slight decreases in tensile strength and elongation.

The adhesion properties are improved by TCBQ loading in the rubber compound. The enhancement is significant at a low loading and in the unaged state. However, when the TCBQ loading was as high as 2 phr or more, the enhancement disappeared. This improvement in the adhesion with TCBQ loading was also observed after thermal and humidity aging.

The schematic shapes of the unaged adhesion interphase investigated from various rubber compound/brass film samples were similar regardless of the amount of TCBQ loading. But the concentrations of sulfur and oxygen at the interphase were, depending on the loading amount of TCBQ and aging treatment, quite different. Copper sulfide and zinc oxide are the major components at the interphase of the TCBQ-free rubber compound and they increase concomitantly after the aging treatment [12, 13].

No conspicuous difference due to TCBQ loading is found from the adhesion interphase investigated immediately after curing; however, the adhesion interphase after humidity aging changes to a large degree by the addition of TCBQ. Because of the severe dezincification at the adhesion interphase of the TCBQ-free compound, only a small amount of copper and sulfur is detected, whereas almost no zinc and oxygen is detected. On the contrary, for the compounds with TCBQ loading of 0.5 or 1.0 phr, the adhesion interphase maintains its structure even after humidity aging of 15 days. Though the adhesion interphase was destroyed when excess TCBQ was added at 2.0 phr, the adhesion interphase of the compound with less TCBQ could be retained. Especially, zinc oxide exists, forming layers at the adhesion interphase. Copper and zinc peaks are seen in the bulk rubber. The fact that copper, which is present in the adhesion interphase, could be observed in the rubber layer after humidity aging of TCBQ-loaded compounds, indicates a possibility of acceleration of copper diffusion by TCBQ.

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Considering that the adhesion could be attained *via* copper sulfide formation through the reaction between copper in brass and sulfur in the rubber compound, copper diffusion in the rubber bulk can be thought to be a positive effect accelerating the formation of the adhe-sion layer. The effect of improved adhesion before aging by the addition of a small amount of TCBQ can be attributed to the accelerated reaction of sulfur at the interphase with copper which is enhanced to diffuse by TCBQ. Thus, the improved adhesion is explained in terms of the enlarged surface area of copper sulfide, because copper moves easily in the rubber bulk and the reaction between copper and sulfur occurs at many places rather than a limited region.

The enhancement in adhesion by the accelerated formation of copper sulfide can be predicted from the facts that it decreases with increasing TCBQ loading or that it disappears in the aging treatment. This is attributed to the lowered adhesion property due to the absence of copper at the adhesion interphase even as copper sulfide is formed abundantly by the diffusion of copper into the rubber matrix when the addition of TCBQ increases. Deterioration in the adhesion property by the aging treatment can be explained, as shown in Figure 5, by the fact that the movement of copper in the rubber compound becomes prominent.

In TCBQ-loaded compounds, zinc oxide gathers mainly on the adhesion interphase. Since, when zinc oxide layer grows to excess, adhesion fails within this layer, overgrowth of zinc oxide has been considered to be detrimental to adhesion. Nevertheless, the zinc oxide layer with adequate thickness can raise the stability of the adhesion interphase by suppressing the migration of copper and sulfur as suggested by Ishikawa [14]. When the mobility of copper increases by TCBQ loading, the degree of freedom of zinc increases *via* this effect and the formation of zinc oxide is also promoted (Fig. 4). However, this zinc oxide layer can contribute to an increase in the stability of adhesion by constraining the diffusion of moisture during humidity aging.

The adhesion property of the rubber compound is enhanced to a great degree by the addition of a small amount of TCBQ. Especially, it is more effective in improving the initial adhesion than the stability against aging. The enhancement of adhesion by TCBQ loading seems

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to be related primarily to the increase in the mobility of copper. That is, the large copper sulfide surface produced by the movement, which is facilitated in organic rubber compounds, of complexing between TCBQ and copper improves the adhesion property. Hence, when 2 phr or more of TCBQ is added, the effect on the increase of adhesion should vanish because copper migrates too much into the bulk rubber rather than into the adhesion interphase. The reason why effects of TCBQ loading on the enhancement of adhesion disappear after humidity aging for 15 days, when the movement of copper becomes prominent as shown in Figure 5, can be explained in the same manner. In addition, the formation of the zinc oxide layer is also promoted in the TCBQ-loaded rubber compounds by an increased reactivity of zinc due to copper diffusion. In so far as no severe migration of the copper sulfide layer into the rubber occurs, the stable zinc oxide layer suppresses the diffusion of outside water, contributing to the promotion of stability against humidity aging. However, with the gradual increase of TCBQ loading, or of humidity aging time, the addition of TCBQ brings about the loss of the adhesion stability rather than improvement of adhesion because the adhesion interphase becomes empty of copper due to copper migration.

On the other hand, the rubber compounds containing TCBQ show different behaviors. In the rubber compound with TCBQ loading of 0.5 and 1.0 phr, copper migrates to the rubber layer and it gathers together in the rubber rather than at the adhesion interphase. However, zinc oxide is generally present at the adhesion interphase, forming layers. For the TCBQ-free rubber compound, almost no zinc and oxygen is detected at the adhesion interphase due to severe dezincification, and the intensities of copper and sulfur are also very weak. The concentration of sulfur at the adhesion interphase after humidity aging increases with TCBQ loading, and that of oxygen increases up to 0.5 phr of TCBQ loading. After humidity aging for 15 days, the oxygen content at the interphase for the TCBQ loading of 0.5 phr became larger. But the acceleration of sulfide formation by TCBQ loading is obvious qualitatively from the depth profiles shown in Figures 4 and 5.

Zinc oxide is detected at the most in the adhesion interphase, but the effect of zinc oxide on adhesion is complicated. The zinc oxide layer prevents the migration of copper and zinc to the interphase during the

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aging treatment, enhancing the stability of the adhesion interphase [14]. However, excessive formation of the zinc oxide layer leads to a fatal failure because of its weak mechanical strength [11]. Thus, the excessive growth of the zinc oxide layer in humidity aging should be suppressed for stable adhesion. On the other hand, low content of zinc oxide at the interphase induces the excessive growth of copper sulfide and, therefore, the adequate formation of zinc oxide plays a key role in stable adhesion.

One plausible explanation of how TCBQ acts as an adhesion promoter is the controlling of zinc oxide formation. The optimum formation of zinc oxide can be controlled by TCBQ loading, resulting in the enhancement of adhesion. On the other hand, lack of the formation of zinc oxide to regulate the migration of materials at the interphase is induced by the high loading of TCBQ. The lack of a zinc oxide layer compensates the enhancement due to TCBQ loading, countering the positive contribution of TCBQ on the adhesion.

The adhesion between the rubber compound and brass-plated cord is improved by TCBQ loading at a low level. Since TCBQ does accelerate the adhesion degradation, some negative effect of TCBQ as an adhesion promoter is observed at 2 phr of loading and after 15 days of humidity aging. These results support the possibility of TCBQ as an organic adhesion promoter in suppressing dezincification at the adhesion interphase. But the mechanisms for the reaction of TCBQ with oxygen and sulfur as well as the optimal level of oxides and sulfides at the interphase should be studied more for the broad application of TCBQ.

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5. CONCLUSION

The adhesion between rubber compound and brass-plated steel cord is remarkably enhanced by the addition of a small amount of TCBQ. With low loading at 0.5 phr, both pullout force and rubber coverage increase to a large degree. However, with an increase in the loading level to more than 2 phr, the adhesion worsens. The addition of TCBQ is effective for enhancement of adhesion before aging, while the stability against aging declines with TCBQ loading. Copper diffusion into the bulk rubber occurs considerably at the adhesion interphase

of TCBQ-loaded rubber compounds, and the diffusion increases after humidity aging. The enhancement of adhesion by TCBQ loading can be attributed to the accelerated copper diffusion by TCBQ which contributes to the formation of a copper sulfide layer with a large surface area. The zinc oxide layer formed at the adhesion interphase also contributes to the promotion of adhesion stability. With an increase in TCBQ loading or in aging time, there results a decrease of adhesion because the copper content at the adhesion interphase becomes too low and the zinc oxide layer too thick.

References

[1] van Ooij, W. J. and Kleinhesselink, A., *Appl. Surface Sci.* **4**, 324 (1980).
[2] van Ooij, W. J., *Kautsch. Gummi, Kunsts.* **30**, 739 (1977).
[3] van Ooij, W. J., *Kautsch. Gummi, Kunsts.* **30**, 833 (1977).
[4] Hammer, G. E., Shemenski, R. M. and Hunt, J. D., *J. Vac. Sci. Technol. A* **12**, 2388 (1994).
[5] Kurbatov, G. G., Beshenkov, V. G. and Zaporozchenko, V. I., *Surf. Interface Anal.* **17**, 779 (1991).
[6] Kurbatov, G. G., Zaporozchenko, V. I., Gorayev, V. M., Gofman, A. M., Kukharenko, Y. A. and Goryaev, V. M., *Mittwoch Sektion B* **26**, 161 (1991).
[7] Seo, G., *J. Adhesion Sci. Technol.* **11**, 1433 (1977).
[8] Coppens, W., Chambaere, D. and Lievens, H., *Rubbercon'87* **45A** (1987).
[9] Barnhart, R. R. and McKinstry, P. H., *J. Elastomers Plast.* **10**, 216 (1978).
[10] Shah, M. A., Bergethon, P. R., Boak, A. M., Gallop, P. M. and Kagan, H. M., *Biochim. Biophys. Acta* **1159**, 311 (1992).
[11] van Ooij, W. J., *Rubber Chem. Technol.* **57**, 421 (1984).
[12] Lievens, H., *Kautsch. Gummi, Kunsts.* **39**, 122 (1986).
[13] van Ooij, W. J., Giridhar, J. and Ahn, J. H., *Kautsch. Gummi, Kunsts.* **44**, 348 (1991).
[14] Ishikawa, Y., *Rubber Chem. Technol.* **57**, 855 (1984).

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