

# Surface Treatment of Fluorinated Rubber with Triazine Thiols and Their Properties

KUNIO MORI,<sup>1,\*</sup> HIDETOSHI HIRAHARA,<sup>1</sup> YOSHIYUKI OISHI,<sup>1</sup> SAISO KIM,<sup>1</sup>  
KOSAKU TAMURA,<sup>1</sup> and AKIRA IWABUCHI<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry & Molecular Science and <sup>2</sup>Department of Mechanical Engineering, Faculty of Engineering, Iwate University, Ueda 4-3-5, Morioka 020, Japan

## SYNOPSIS

Fluorinated (FKM) vulcanizates were treated by immersing in an aqueous solution of triazine thiols, NaOH, and onium salts for 15–60 min at 50–95°C (W-Method). Treated FKM vulcanizates further were postcured in an air oven for 20 h at 200°C to complete the reaction. The onium salt of triazine thiols were found to be formed by a reaction among the triazine thiols, NaOH, and onium salts and to act as cross-linking agents to the surface of FKM vulcanizates. In the acetone solution of onium salts of triazine thiols, FKM vulcanizates were also treated by immersing for a few minutes at 20°C and then by heating in an air oven for 20 min at 200°C (A-Method). Triazine thiols were introduced as cross-links onto the FKM backbone. The degree of cross-linking in the surface increased by these treatments and the depth of cross-linking reached up to about 40 μm thickness by control of treating conditions. The coefficient of friction in FKM vulcanizates decreased as a result of the surface treatment up to about 0.5 from 2.6. FKM vulcanizates decreased the tensile strength by these surface treatments because of the generation of cracks on the surface at 50% or 100% elongation. The surface treatment of FKM vulcanizates suppressed markedly the fixing between FKM vulcanizates and stainless steel at 150°C. Especially, the A-Method was very effective treating for retarding the fixing between FKM vulcanizates and metals. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Fluorinated vulcanizates have good heat, oil, and ozone resistances as well as good rubbery elasticity, although they show a degree of high tackiness to various metals. The tackiness of vulcanizates has often been disliked on rubber packing and valves because of their fixing phenomenon.<sup>1,2</sup> The fixing phenomenon of vulcanizates is based on the easy motion of vulcanizate segments that is responsible for good rubbery elasticity. The prevention of fixing requires the loss of rubbery elasticity in vulcanizates, i.e., there is a relation of antinomy between nontackiness and good rubbery elasticity in vulcanizates.

Surface treatment is one of the best methods to impart simultaneously both nontackiness and good

rubbery elasticity to vulcanizates,<sup>3–5</sup> namely, it is possible to suppress the segment motion in vulcanizate surfaces by treating vulcanizates without loss of elasticity.

This article presents a new treating method for the surface of fluorinated vulcanizates and clarifies their surface properties.

## EXPERIMENTAL

### Reagents and Materials

Fluorinated rubber, vinylidene fluoride–hexafluoropropene copolymer (FKM, Tecnoflon NM) and curing agents [Tecnoflon M<sub>1</sub>: 2,2-bis(4-hydroxyphenyl)hexafluoropropane, and Tecnoflon M<sub>2</sub>: triphenylbutylphosphonium bromide) were obtained from Nippon Zeon Co. Ca(OH)<sub>2</sub> and MgO were commercially available. Triazine thiols such as 1,3,5-

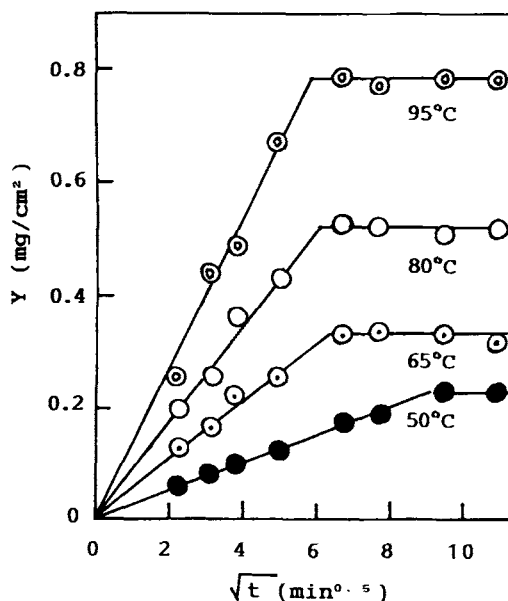
\* To whom correspondence should be addressed.

triazine-2,4,6-trithiol (TT), 6-anilino-1,3,5-triazine-2,4-dithiol (AF), 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB), and 6-dioctylamino-1,3,5-triazine-2,4-dithiol (DO) were supplied by Sankyo Kasei Co. Onium salts such as tetrabutylammonium bromide (TBAB), tetrabutylphosphonium bromide (TBPB), and tetraphenylphosphonium bromide (TPPB), NaOH, and others were of reagent grade.

Masterbatches containing FKM copolymer (100 parts), MT carbon black (20 phr), Tecnoflon M<sub>1</sub> (3.7 phr), Tecnoflon M<sub>2</sub> (1.5 phr), Ca(OH)<sub>2</sub> (6 phr), and MgO (3 phr) were mixed for 20 min in a Banbury mixer and then blended in a two-roll mill. The FKM compound was placed in a metal mold (20 × 50 × 2 mm) and heated for 20 min at 170°C under a press of 8 MPa to produce fluorinated (FKM) vulcanizates.

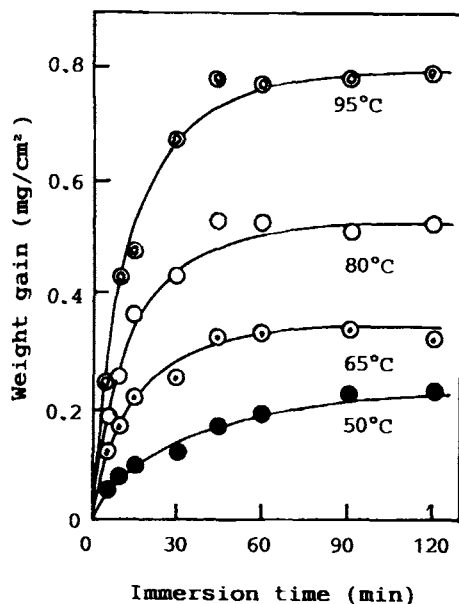
#### Synthesis of TBAB Salt of DB (DBMTA)

DB (0.05 mol) and NaOH (0.05 or 0.1 mol) were added into water (100 mL). The DB-NaOH aqueous solution was also poured into an aqueous solution (100 mL) of TBAB (0.05 or 0.1 mol). The aqueous solution was cooled up to room temperature to afford a white crystal, 6-dibutylamino-1,3,5-triazine-2,4-dithiol monotetrabutylammonium salt (DBMTA)

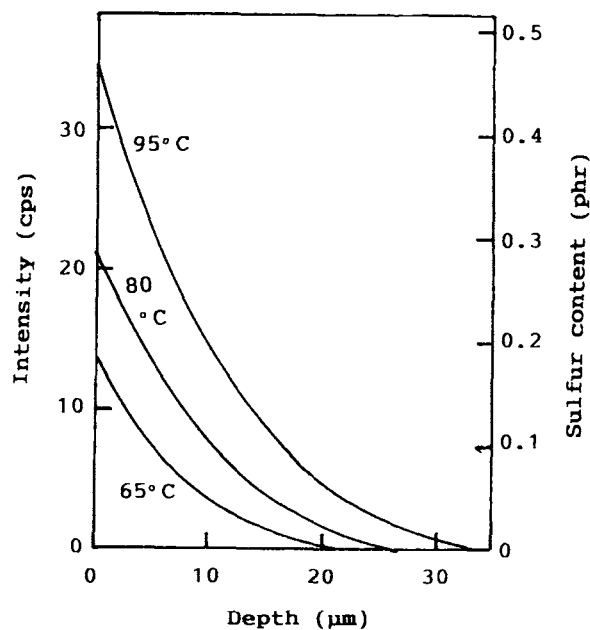


**Figure 2** Relation between  $Y$  and  $\sqrt{t}$  in the surface treatment of FKM vulcanizates. Conditions: same as in Figure 1.

in 98% yield after being stirred for 120 min at 95°C. DBMTA was recrystallized from a mixed solvent of methanol and benzene: mp: 81–81.5°C.



**Figure 1** Effect of immersion time ( $t$ ) and temperature on the weight gain ( $Y$ ) in the surface treatment of FKM vulcanizates with DB (10 mmol/L) in the presence of NaOH (20 mmol/L) and TBAB (20 mmol/L) in hot water.



**Figure 3** Effect of immersion temperature on the intensity of S  $K\alpha$  ray and its depth in FKM vulcanizates treated for 90 min with the W-Method. Concentration: DB, 10 mmol/L; NaOH and TBAB, 20 mmol/L.

ANAL: Calcd for  $C_{27}H_{55}N_5S_2$ : C, 63.09%; H, 10.81%; N, 11.61%; S, 12.47%.  
Found: C, 63.2%; H, 11.0%; N, 13.8%; S, 12.0%.

### Surface Treatment of FKM Vulcanizates

#### W-Method

Triazine thiols (5–15 mmol) and NaOH (10–30 mmol) were added to water (500 mL) at 50–95°C. Next, onium salts (10–30 mmol) were also added into water (500 mL). The aqueous solution of onium salts was poured into the aqueous solution of triazine thiols and NaOH under stirring at 50–95°C. FKM vulcanizates were sufficiently washed with methanol for removal of contamination on them and dried for 12 h at 50°C under a pressure of 5 mmHg. The vulcanizates were immersed into the above-obtained aqueous solution for 15–60 min at 50–95°C, after being weighed [ $w_1$ ]. The treated vulcanizates were sufficiently washed with methanol, then dried for 12 h at 20°C for removal of unreacted reagents at a pressure of 5 mmHg and weighed [ $w_2$ ]. The reaction weight is  $w_2 - w_1$  (mg/cm<sup>2</sup>).

#### A-Method

DBMTA (0.1 mol) was added into acetone (1000 mL) at room temperature. FKM vulcanizates were immersed into an acetone solution of DBMTA for 0.5–5 min at 20°C. The surface-swollen FKM vulcanizates were dried in air at room temperature and then heated in an air oven for 20 h at 200°C.

### Measurement and Tests

X-ray microanalyzer (XMA) measurements were made with an Energy Diffusion Type XMA-848 (Nippon Denshi Co.). FTIR spectroscopy was done with a Nippon Denshi FTIR JIR-5500, according to the ATR method. Surface energy was determined from the contact angles of water and methylene iodide on the vulcanizates.<sup>6</sup> The friction test was made with a reciprocating-type friction meter and the coefficient of friction between vulcanizates plates and a sector of an aluminum sphere was determined under a load of 0.05 MPa at 20°C. Tensile strength was measured by a Shimadzu Autograph P-100 with a tensile rate of 20 mm/min. The repeating of tensile was carried out 10 times at 50 and 100% elongation. The fixing test between vulcanizates and stainless steel was carried out at 150°C for 48 h under a loading of 0.05 MPa, according to the Mori Fixing Test Method,<sup>7</sup> and the fixing strength was determined.

## RESULTS AND DISCUSSION

### Surface Treatment Using Triazine Thiols, NaOH, and Onium Salts in Hot Water (W-Method)

We reported that poly(vinyl chloride) fibers are cross-linked, being immersed into an aqueous solution of DB, TBAB, and NaOH at 90°C.<sup>8</sup> So, to improve surface properties, the surface treatment of FKM vulcanizates has been tried by using DB, TBAB, and NaOH in hot water. Figure 1 shows the relation between the reaction weight ( $Y$ ) and im-

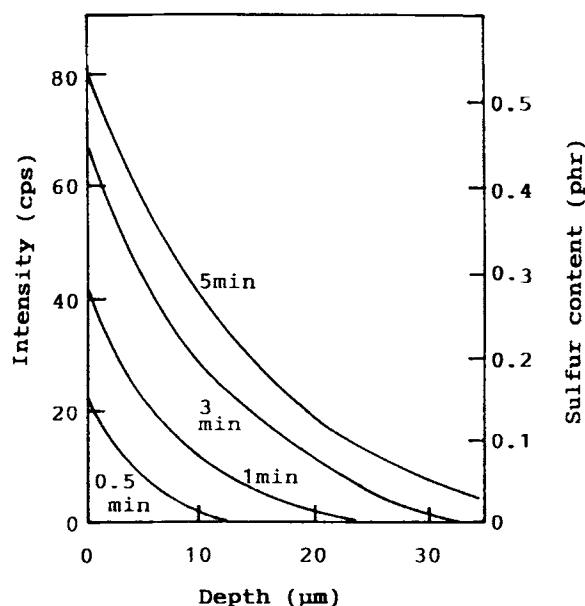
**Table I** Effect of Treating Conditions on Treatment Parameters

|  | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| D O (mmol/L)                                 |       |       |       |       |       | 5     |       |       |
| D B (mmol/L)                                 | 5     | 10    | 15    | 10    | 10    |       |       |       |
| A F (mmol/L)                                 |       |       |       |       |       |       | 5     |       |
| T T (mmol/L)                                 |       |       |       |       |       |       |       | 5     |
| NaOH (mmol/L)                                | 10    | 20    | 30    | 20    | 20    | 10    | 10    | 10    |
| TBAB (mmol/L)                                | 10    | 20    | 30    |       |       | 10    | 10    | 10    |
| TBPB (mmol/L)                                |       |       |       | 20    |       |       |       |       |
| TPPB (mmol/L)                                |       |       |       |       | 20    |       |       |       |
| $k$ (mg/cm <sup>2</sup> min <sup>0.6</sup> ) | 0.135 | 0.151 | 0.125 | 0.138 | 0.132 | 0.096 | 0.111 | 0.106 |
| $Y_m$ (mg/cm <sup>2</sup> )                  | 0.76  | 0.81  | 0.73  | 0.56  | 0.48  | 0.45  | 0.72  | 0.71  |
| $I_s$ (cps)                                  | 28    | 34    | 40    | 24    | 21    | 20    | 24    | 24    |
| Depth ( $\mu$ m)                             | 24    | 33    | 19    | 16    | 15    | 15    | 26    | 27    |

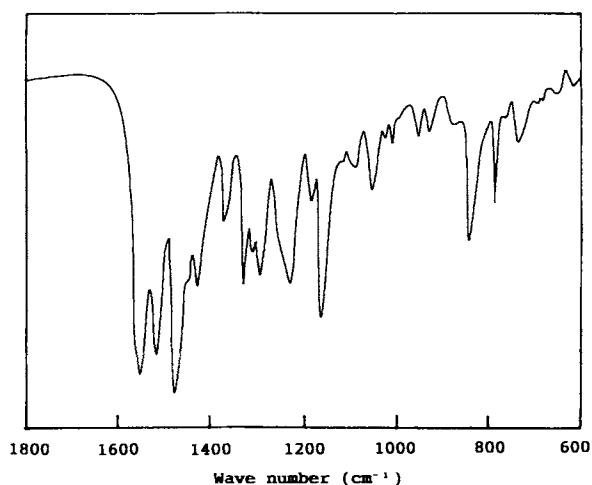
Conditions: for 120 min at 95°C.

mersion time ( $t$ ) at various temperatures in the surface treatment of FKM vulcanizates. The weight gain means the amount of reaction for DB.  $Y$  increased with an increase in immersion time and temperature and reached a plateau at a certain immersion time. Figure 2 shows the relation between  $Y$  and a root of  $t$ . Both relations were linear before the plateaus. The reaction obeys a parabolic law. Activation energy was calculated to be about 9.8 kcal/mol. The results show that the rate-determining step of the reaction is the diffusion process.<sup>9</sup> The presence of the plateau indicates that the reaction reagents no longer diffuse to the inner of FKM vulcanizates under the given conditions. The weight gain in the plateaus was dependent on the temperature.

To obtain information for the reaction weight to the depth direction, XMA was made for the sulfur atom ( $S K\alpha$ ). Figure 3 shows the relation between the intensity of the  $S K\alpha$  ray and its depth for the sulfur atom in the XMA analysis of the cut surface of treated FKM vulcanizates. The intensity means a measure of the concentration of the sulfur, namely, triazine thiols contained in FKM vulcanizates. In this figure, the sulfur content shows the intensity [ $I_s$ (cps)] of  $S K\alpha$  at the same level. An intensity of 10 cps corresponds to FKM vulcanizates with a 0.135 wt % sulfur content, which means a DB concentration of  $2.1 \times 10^{-5}$  mol/g<sub>FKM</sub>. The  $I_s$  decreased exponentially with an increase in the depth from the FKM vulcanizates' surface and reached zero be-



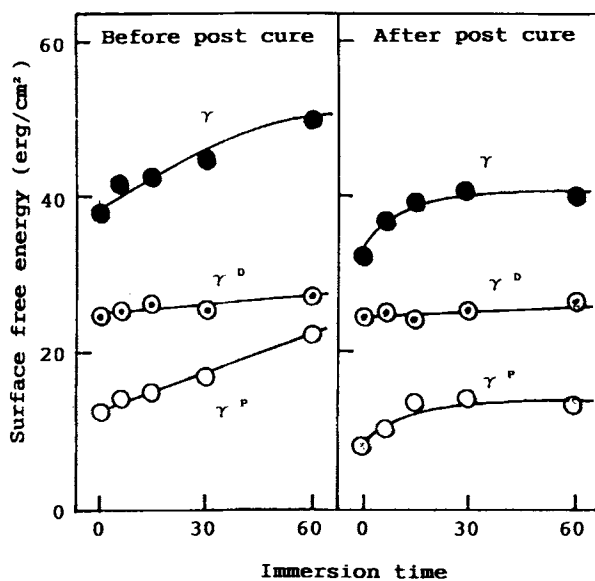
**Figure 4** Effect of immersion time on the intensity of  $S K\alpha$  ray, its depth, and sulfur content in the FKM vulcanizates treated with the A-Method.



**Figure 5** FTIR spectrum in the surface of FKM vulcanizates treated with the A-Method.

low about  $40 \mu\text{m}$ . With a decrease in treatment temperature, the  $I_s$  and depth decreased. This result shows that the rate-determining step of the reaction is also in the diffusion process.

Table I shows the effect of treatment conditions on the reaction rate ( $k$ ,  $\text{mg}/\text{cm}^2 \text{min}^{0.5}$ ), the plateau value ( $Y_m$ ,  $\text{mg}/\text{cm}^2$ ), the intensity of  $S K\alpha$  ( $I_s$ , cps), and the depth for the reaction ( $\mu\text{m}$ ). There were optimum  $k$  and  $Y_m$  for the change in the DB-NaOH-TBAB concentration in the range of 5 to 15 mmol/L, i.e.,  $k$  and  $Y_m$  reached the optimum value



**Figure 6** Changes in the surface free energy ( $\gamma$ ) with immersion time in FKM vulcanizates treated with the W-Method. Conditions: DB, 10 mmol/L, and NaOH and TBAB, 20 mmol/L, at  $95^\circ\text{C}$ .

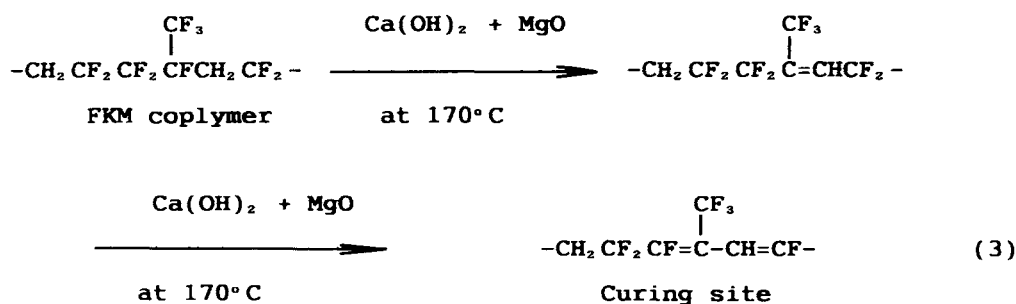
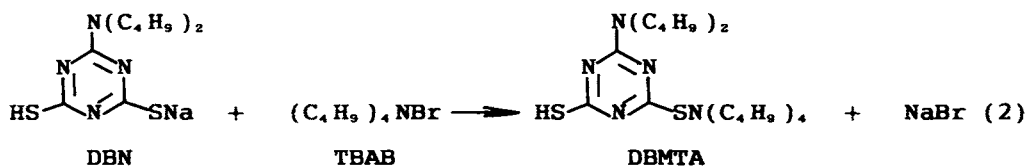
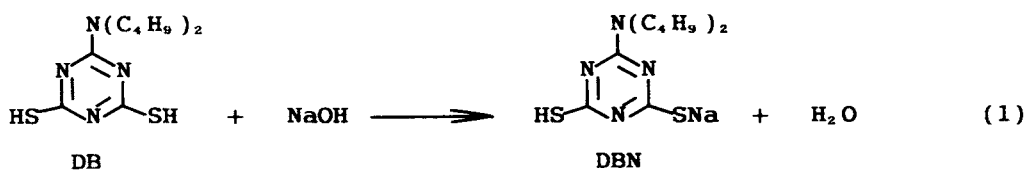
at the 10 mmol/L concentrations. The depth also had a maximum value at these concentrations, although  $I_s$  increased with concentrations in the above range. This is because at high DB–NaOH–TBAB concentrations the diffusion of reagents to the inside is retarded as the cross-linking degree of FKM vulcanizate surfaces increases.  $k$  and  $Y_m$  were dependent on the bulkiness of triazine thiols and the  $pK_a$  of the thiol groups, i.e.,  $k$  and  $Y_m$  increased with a decrease in acid dissociation constant ( $pK_a$ ) and decreased with an increase in bulkiness. The decrease of  $pK_a$  increases the reaction rate and the increase in bulkiness decreases the diffusion rate. Onium salts accelerated the reaction in the order of TBAB > TBPB > TPPB. This order agrees with that of the accelerating effect of onium salts in the curing of FKM polymer with triazine thiols.<sup>10</sup>

### Surface Treatment Using the Onium Salts of DB (A-Method)

DB reacted easily with onium salts in the presence of NaOH in hot water to yield the onium salts of DB (e.g., DBMTA) as described in the Experimental section. In this case, DBMTA was always formed regardless of the mixing ratio of three components. This reaction is expressed by reactions (1) and (2)

as described in a previous article.<sup>8</sup> Therefore, in the case of the surface treatment of FKM vulcanizates, a similar reaction among DB, NaOH, and TBAB may be estimated to occur, i.e., the formed DBMTA is eventually related to the surface reaction of FKM vulcanizates. Therefore, FKM vulcanizates were directly treated with DBMTA. Figure 4 shows the relation between the intensity the S  $K\alpha$  ray and the depth for the sulfur atom in the XMA measurement of the cut surface of FKM vulcanizates. FKM vulcanizates were immersed with DBMTA solution in acetone for various times at 20°C and heated for 20 h at 200°C in an air oven. With immersion time, both  $I_s$  and the depth increased. Over 5 min,  $I_s$  reached a constant value although the depth kept increasingly under a constant concentration.

In the immersion process, DBMTA immersed to the inner of FKM vulcanizates from the surface with the swelling of vulcanizates together, but did not react with FKM vulcanizates. The immersed DBMTA in FKM vulcanizates is easily removed by washing with methanol. In the heating process, the reaction between DBMTA and FKM occurred. A heating condition for 20 h at 200°C was actually selected for simplifying the production process, although was not required. The surface reaction occurred even under a mild condition for 3 days at



Scheme 1

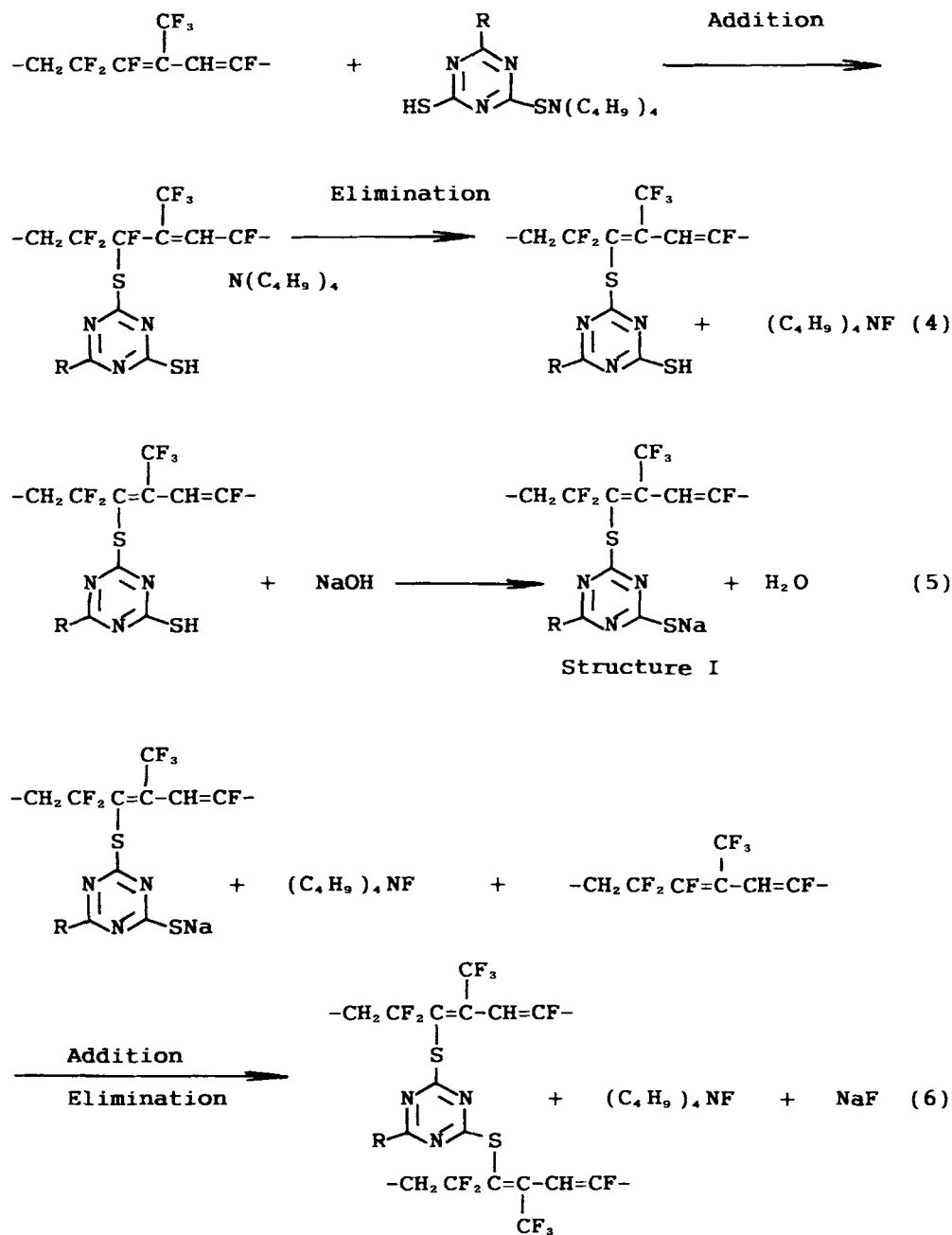
120°C in FKM vulcanizates after postcure for 20 h at 200°C. Because of its procedure, the A-Method is a very simple treating method compared to the W-Method.

### Reaction Mechanism for Surface Treatment

It is widely known that the FKM copolymer causes dehydrogen fluorination in the presence of  $\text{Ca}(\text{OH})_2$

and  $\text{MgO}$  at 170°C to produce a diene structure on the backbone as shown in Reaction 3.<sup>10,11</sup> The diene structure is a active reaction site for in FKM polymer. Many of the active sites remain on the surface of FKM vulcanizates after vulcanization.

On the other hand, DBMTA was formed from the aqueous solution containing three components of DB, NaOH, and TBAB even under a mild condition in a good yield. This means that DBMTA

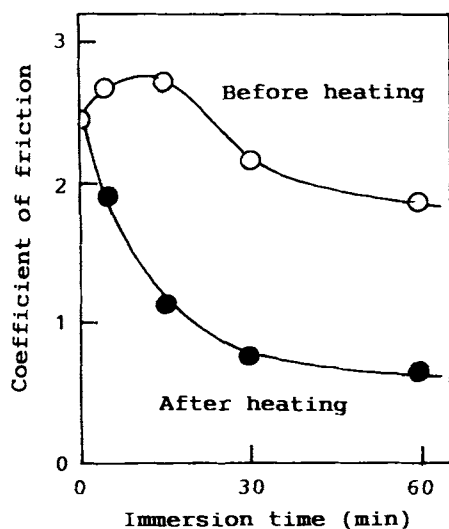


Scheme 2

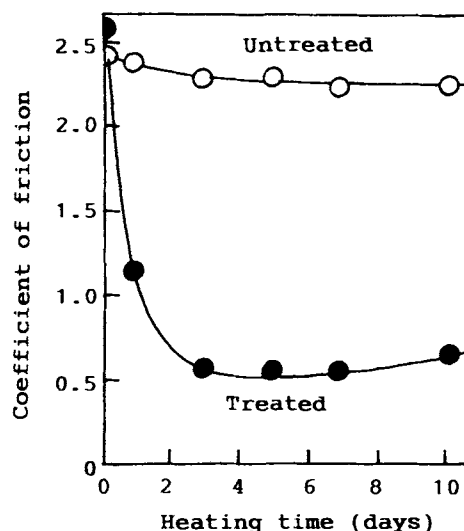
possibly reacts directly with FKM vulcanizates. Therefore, DBMTA is first formed by the reactions among DB, NaOH, and TBAB in hot water. The next-formed DBMTA is considered to cause, repeatedly, addition and elimination to the diene structure to produce the cross-links between FKM segments as shown in Reactions 4-6.<sup>10-12</sup>

To confirm the above mechanism, the cross-linking structure was investigated from the measurement of the FTIR spectrum on the surface of FKM vulcanizates treated with the A-Method. The samples were used for the measurement after the removal of unreactive compounds by extraction with tetrahydrofuran. From Figure 5, the absorption bands<sup>13</sup> based on a triazine ring appeared at 1552, 1477, 1378, 1195, and 849  $\text{cm}^{-1}$ . This suggests that DBTBA is introduced into the FKM polymer backbone. On the other hand, similar FTIR spectra were also observed for FKM vulcanizates, which are treated with the W-Method, before and after postcure for 20 h at 200°C, although these vulcanizates did not always have the same surface properties, as described later.

To make the reason clear, the surface free energy of both treated FKM vulcanizates was measured, as shown in Figure 6, i.e., the surface free energy for treated FKM vulcanizates before postcure increased with immersion time, although after postcure, it increased up to 15 min and soon become a constant value. The surface free energy of FKM vulcanizates treated with the A-Method was the same as that after postcure in the W-Method. The increase of surface free energy with immersion time before

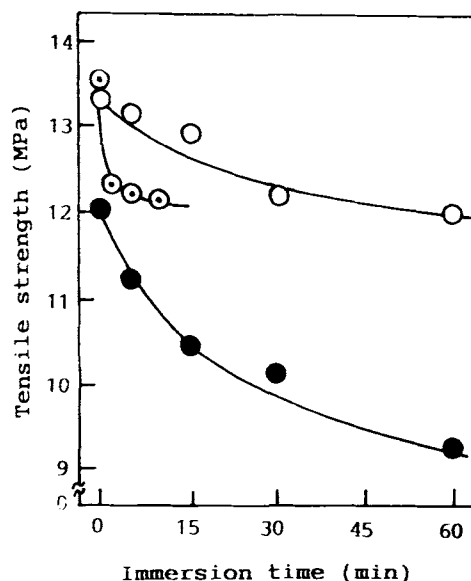


**Figure 7** Effect of immersion time on the coefficient of friction of FKM vulcanizates treated with the A-Method.



**Figure 8** Effect of heating time on the coefficient of friction of FKM vulcanizates untreated and treated with the A-Method.

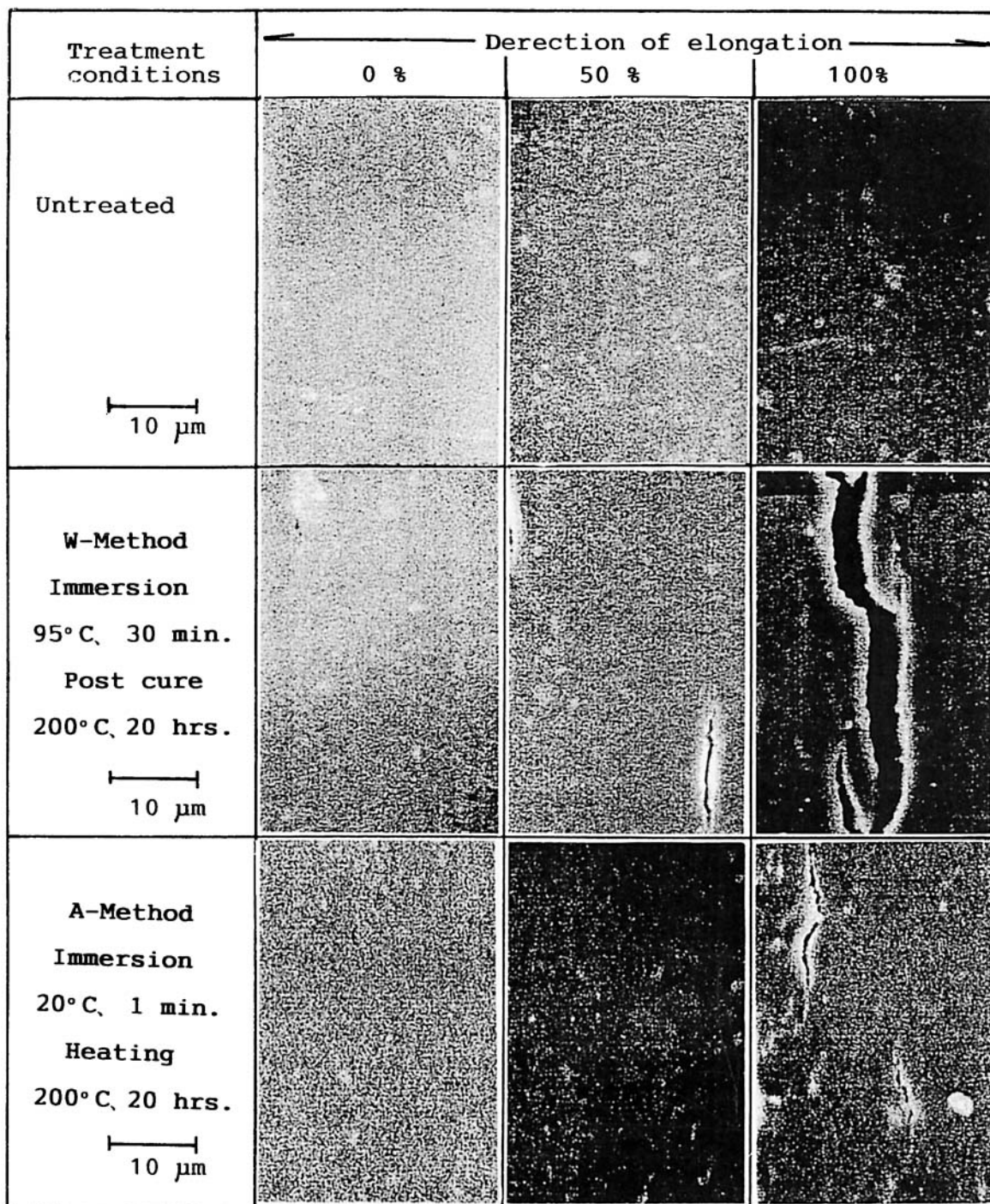
postcure is based on that of polar component ( $\gamma^p$ ) in surface free energy. This suggests that treated FKM samples before postcure in the W-Method contain Structure I in Reaction 5 as well as Structure II. The IR spectrum pattern of Structure I was very similar to that of Structure II.<sup>8</sup> Therefore, in the IR



**Figure 9** Effect of immersion time on the tensile strength of FKM vulcanizates treated with the W-Method: (○) after postcure at 200°C for 20 h and (●) before postcure), and (⊙) with the A-Method. W-Method: DB 10, mmol/L, and NaOH and TBAB, 20 mmol/L, at 95°C.

spectra measurement, it is hard to identify the small amount of Structure I in the large amount of Structure II. These results suggest that the cross-linking structure in the surface of FKM vulcanizates treated with the A-Method and the W-Method after post-

cure was expressed by Structure II and treated FKM vulcanizates with the W-method before postcure contain a small amount of Structure I. To have the reaction completed, it is important to heat-treat FKM vulcanizates at a high temperature. These re-



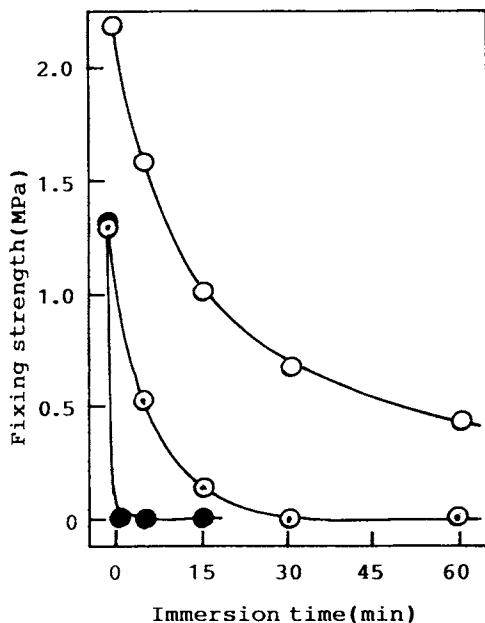
**Figure 10** Photographs in the surface of FKM vulcanizates treated with the W-Method and the A-Method.



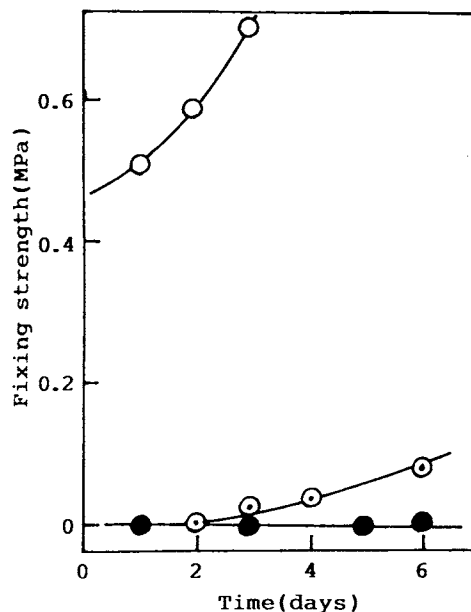
sults for the structure of the cross-linking chain support the reaction mechanism expressed by Reactions 1-6.

### Surface Properties of Treated FKM Vulcanizates

To understand surface properties, the coefficient of friction was investigated, as shown in Figure 7. The coefficient of friction in FKM vulcanizates treated with the A-Method decreased rapidly with immersion time and reached a constant value at an immersion time of 1 min. The coefficient of friction before postcure increased slightly with immersion time and then decreased slowly. The difference in the coefficient of friction before and after postcure is dependent on the degree of cross-linking, which is based on the formation of Structure II. Figure 8 shows the effect of heating time on the coefficient of friction for FKM vulcanizates immersed in the acetone solution. Untreated FKM vulcanizates hardly decreased the coefficient of friction after postcure at 200°C, although the network chain density increased from  $1.8 \times 10^{-4}$  to  $2.9 \times 10^{-4}$  mol/g after 10 h at 200°C. Treated FKM vulcanizates decreased the coefficient of friction up to near 0.5 after heating for 3 h at 200°C and had a constant value over 3 h. The decrease of the coefficient of friction



**Figure 11** Effect of immersion time on the fixing strength of FKM vulcanizates treated with the W-Method (○) after postcure at 200°C for 20 h and (○) before postcure, and (●) with the A-Method. W-Method: DB, 10 mmol/L, and NaOH and TBAB, 20 mmol/L, at 95°C.



**Figure 12** Effect of fixing time on the fixing strength of FKM vulcanizates treated with the W-Method (○) after postcure at 200°C for 20 h and (○) before postcure and (●) with the A-Method. W-Method: DB, 10 mmol/L, and NaOH and TBAB, 20 mmol/L, immersion for 30 min at 95°C. A-Method: Immersion for 2 min at 20°C.

depends on two effects of the increase in the cross-linking degree and the introduction of nonpolar butyl groups.

Figure 9 shows the relation between immersion time and the tensile strength of FKM vulcanizates treated with the W-Method and then postcured and with the A-Method. FKM vulcanizates before and after postcure that are treated with the W-Method decreased rapidly the tensile strength at a short immersion time and then slowly with immersion time. These decreases of tensile strength with surface treatment are considered to be due to the difference in the degree of cross-linking of the surface and the inside of treated FKM vulcanizates. To confirm the above estimation, a repeating tensile test was conducted 10 times at 50 and 100% elongation for untreated and treated FKM vulcanizates and the photographs of surfaces are shown in Figure 10. At 50 or 100% elongation in the treated samples, some cracks appeared on the surface. For FKM vulcanizates treated with the A-Method, it was generally hard to generate cracks by repeating the tensile test, compared to the W-Method. The low generation of surface cracks under low stress is favorable, especially for FKM functional valve sensors and packings.

### Fixing Properties

Like FKM functional valve sensors and packings, FKM vulcanizates adhere to metals during which both come into contact under stress at a high temperature. We have called this phenomenon "fixing."<sup>1,2</sup> Figure 11 shows the effect of immersion time on the fixing strength in the fixing test of untreated and treated FKM vulcanizates and stainless steel at 150°C. Fixing strength decreased with immersion time. FKM vulcanizates treated with the W-Method before postcure did not decrease in their fixing strength to zero after an immersion time of 60 min, although after postcure, they reached zero at 30 min. The A-Method was very effective in decreasing the fixing strength of FKM vulcanizates to metals with a simple treatment. The decrease of fixing strength with surface treatment is due to the decrease of segment motion in the surface of FKM vulcanizates and the coefficient of friction. The decrease of segment motion is brought about by increasing the degree of surface cross-linking. The decrease of coefficient of friction is provided by introducing non-polar parts on the surface of FKM vulcanizates. Figure 12 shows the effect of fixing time on the fixing strength in the fixing between stainless steel and FKM vulcanizates at 150°C. Treated FKM vulcanizates before postcure increased the fixing strength with testing time because they have small amount of thiol groups (—SNa). Thiol groups increased the fixing strength by reacting with the metal surface. Postcured treated FKM vulcanizates were hard to fix to metal surfaces. Especially, samples prepared with the A-Method did not fix at all to stainless steel after 6 days at 150°C.

### CONCLUSION

FKM vulcanizates were treated by immersing in the aqueous solution of triazine trithiols, NaOH, and onium salts and by postcuring (W-Method) or by heating after immersing in the acetone solution of DBMTA (A-Method). The A-Method's procedure was simpler than that of the W-Method. Triazine thiols were introduced as a cross-link into FKM

vulcanizates during surface treatment up to a thickness of about 40  $\mu\text{m}$ .

The coefficient of friction in FKM vulcanizates decreased by the surface treatment up to about 0.5 from 2.6, whereas FKM vulcanizates decreased the tensile strength by the surface treatment because of the generation of cracks on the surface at 50 or 100% elongation.

The surface treatment of FKM vulcanizates suppressed markedly the fixing between FKM vulcanizates and stainless steel at 150°C. Especially, the A-Method was a very effective treatment for retarding the fixing between FKM vulcanizates and metals.

### REFERENCES

1. K. Mori, S. Takamatsu, A. Watanabe, and Y. Nakamura, *Nippon Gomu Kyokaishi*, **60**, 412 (1987).
2. K. Mori and A. Watanabe, *Rubber Chem. Technol.*, **62**, 196 (1989).
3. K. Mori, A. Watanabe, S. Sakakida, and Y. Nakamura, *Nippon Gomu Kyokaishi*, **60**, 460 (1987).
4. K. Mori, S. Takamatsu, and A. Watanabe, *Nippon Gomu Kyokaishi*, **61**, 51 (1988).
5. K. Mori, S. Takamatsu, and A. Watanabe, *Nippon Gomu Kyokaishi*, **62**, 84 (1989).
6. Y. Nakamura, K. Mori, and K. Wada, *Nippon Gomu Kyokaishi*, **57**, 561 (1984).
7. K. Mori, Y. Nakamura, and H. Takagi, *Nippon Gomu Kyokaishi*, **60**, 165 (1987).
8. K. Mori and T. Jando, *Polym. J.*, **22**, 793 (1990).
9. J. K. Lee and G. Parravano, *Trans. Faraday Soc.*, **47**, 501 (1951).
10. K. Mori, S. Kim, and H. Harada, *Asahi Shoreikai*, **60**, 130 (1992).
11. W. W. Schmigel, *Kaut. Gummi Kunst.*, **137**, 31 (1978).
12. W. W. Schmigel and A. L. Logothetis, ACS Symposium Series 260, American Chemistry Society, Washington, DC, 1984.
13. K. Mori and S. Sai, *Kobunshi Ronbunshu*, **46**, 819 (1989).

Received February 2, 1993

Accepted June 18, 1993