Surface Modification of Vulcanized Rubber by Radiation Grafting, Part 1: Improvement in Friction Behavior

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ABSTRACT: Hydrophilic monomer, 2-hydroxyethyl methacrylate (HEMA), and hydrophobic monomer, 3-(methacryloyloxy)propyltris(trimethylsiloxy)silane (MPTS) were grafted on vulcanized rubber surface with simultaneous electron beam irradiation. Degree of graft polymerization was evaluated by composition ratio of imparted graft chain against trunk rubber. The composition ratio could be controlled by the monomer concentration and the irradiation dose. Grafted rubbers were evaluated by surface roughness and contact angle. Graft polymerization of HEMA decreased the contact angle from 93 to $\sim 70^\circ$ without considerable change of the surface roughness. In the case of MPTS, the contact angle increased approximately to 108°. The relationship between the contact angle of water on the modified surface and the friction at the moment of semi-dry was investigated as an application of the resulting rubber to wiper blade. The increase of the contact angle owing to the grafting of hydrophobic MPTS led to the decrease of $\Delta\mu$ (deference between semi-dry state and dry friction). Instead, the decrease of the contact angle by grafting of hydrophilic HEMA resulted in the increase of $\Delta\mu$. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2825–2830, 2010

Key words: electron beam; graft polymerization; surface modification; friction; rubber; wiiper blade

INTRODUCTION

Rubber is a low modulus material and undergoes large deformation. For this reason, it is used for the material of wiper blade in windshield wipers. Characteristics of friction between blade rubber and windshield glass affects the whole windshield wiper driving system.[1] There is a serious frictional problem which is called "semi-dry friction." This semi-dry friction is caused in transition state from wet friction to dry friction. It often causes unexpected overload in windshield wiper motor. This phenomenon can be elucidated by the suction force caused by meniscus, which is formed in the contact area because of capillary condensation from vapor in the ambient atmosphere.[2,3] This suction force affected by contact angle of water becomes smaller when the contact angle of the water increases.[4,5] For the blade rubber, it is presumed that such a suction force depends on the contact area between rubber blade and windshield glass. Hence, it may be possible that semi-dry friction is reduced by the surface modification technique that can change hydrophobic and hydrophilic property of the rubber surface.

We focused on simultaneous electron-beam-induced graft polymerization as the surface modification. Graft polymerization is to induce the aiming functions such as hydrophilicity,[6,7] mechanical properties,[8] and morphology of core/shell composite[9] to a rubber. Other studies indicated that the electron beam initiated graft polymerization of polyfunctional monomers onto the rubber improved the mechanical and surface characteristics of ethylene propylene rubber,[10] ethylene propylene diene rubber,[11] and acrylic ruber.[12] In this study, we investigate the surface modification technology of the natural rubber with graft polymerization of hydrophilic and hydrophobic monomers by simultaneous electron beam irradiation to improve the friction characteristics. For the application of the modified rubbers to wiper rubbers in the cars, the difference between the maximum semi-dry friction and the dry friction is especially essential factor for specification of wipe-driving motor. Effect of the modified surface on the friction characteristics was clarified in details.

EXPERIMENTAL

Material

Standard Malaysian rubber (SMR CV60) was used as unvulcanized natural rubber. The unvulcanized natural rubber was mixed with carbon black (Asahi

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#60, Asahi Carbon Co.), zinc oxide (Sakai Chemical Industry Co.), stearic acid (Kao Corporation), and dicumyl peroxide (NOF Co.) at the blending weight per 100% rubber of 50, 5, 2, and 5. Then this mixture was kneaded using two rollers at 50°C and molded into sheet, 2 mm thick, by heat pressing at 170°C for 13 min. The sheet obtained was cut into pieces of 30 mm × 40 mm and used as trunk rubber after washing with methanol. Monomers of 2-hydroxyethyl methacrylate (HEMA) and 3-(Methacryloyloxy)propyltris(trimethylsiloxy)silane (MPTS) were purchased from Kanto Chemical Co. and Shin-Etsu Chemical Co., respectively. Industrial-grade methanol (Taiyo Kagaku Co.) and ion exchanged water were used without further purification.

Graft polymerization by simultaneous irradiation of electron beam

HEMA was dissolved in water and 30, 50, and 70% of HEMA solution were used for graft polymerization. The trunk rubber sheet and 10 g of HEMA solution was put into a polyethylene bag. After the inside air is substituted with nitrogen gas, graft polymerization was conducted by irradiating electron beams of 3 to 20 kGy under the conditions of 2 MeV, 1 mA, and 1 kGy/pass. In the case of MPTS, methanol was used for solvent and grafting was carried out in the same way. After grafting, each grafted rubber was soaked in methanol for HEMA grafting and acetone-hexane mixture (1 : 1) for MPTS grafting, respectively, for 1 h to remove homopolymer. Then, the grafted rubbers were dried under the reduced pressure for 24 h.

Analysis of surface grafting

Composition ratios of graft polymer to natural rubber on the surface of the grafted rubbers were evaluated by ATR-FT/IR analysis (AVATAR 370FT/IR: Thermo Nicolet). The definitions of Composition ratio are as follows:

$$\text{Composition ratio}_{\text{HEMA}} = (A_h/A_{h0})/(A_n/A_{n0} + A_h/A_{h0})$$

$$\text{Composition ratio}_{\text{MPTS}} = (A_m/A_{m0})/(A_n/A_{n0} + A_m/A_{m0})$$

where A_h, A_m, and A_n are the absorbance at 1720 cm^{-1}, 1730 cm^{-1}, and 1375 cm^{-1} of the grafted rubbers, respectively. A_{h0}, A_{m0}, and A_{n0} were absorbance measured by using polymers of HEMA, MPTS, and the trunk rubber. The polymers of HEMA and MPTS were obtained by radiation-induced polymerization. The peaks of 1720 cm^{-1}, 1730 cm^{-1}, and 1375 cm^{-1} were assigned to $\nu_{C=O}$ of poly-HEMA, $\nu_{C=O}$ of poly-MPTS, and δ_{CH3} of the trunk rubber, respectively.

Analyses of surface characteristics

The surface roughness after grafting was measured by confocal laser scanning microscope (OLS1100: Olympus Corporation). Scanning step of *Z*-axis was 100 nm. Surface roughness was expressed by ten-point mean roughness (Rz). The contact angle of water against the grafted rubber surface was measured by a contact angle meter following ASTM D7334-08 (CA-X made by Kyowa Interface Science Co.). Friction behavior between the glass disk and the grafted rubber in the transition state from wet to dry friction was measured by a pin-on-disk type abrasion tester following ASTM G99-90 (Shinto Scientific Co.). The grafted rubbers cut into pieces of 10 mm^2 were washed with methanol before the measurement. Each piece was attached to the arm tip at the angle of 45° against the glass disk surface and subjected to the friction under the condition at 25°C with 70% of relative humidity. Vertical load during friction was 147 mN and the speed was 1.27 m/s.

RESULTS AND DISCUSSION

Graft polymerization

Two kinds of the monomers, HEMA and poly-MPTS, were grafted onto the trunk rubber, 2.65 g in weight, in the condition of 50% monomer and 10 kGy irradiation. After grafting, the weight gains are 0.6 (0.016 g) and 0.1 (0.0030 g) for HEMA, and poly-MPT, respectively. For graft polymerization that takes place at the surface of rubber, the degrees of grafting were less than 1% and quite low. The surface of grated rubber was analyzed by FTIR, since the surface seemed to be modified by graft polymerization. For the surface analysis of the grafted rubber, ATR-FT/IR spectra of the trunk rubber, poly-HEMA, and poly-MPTS were compared as shown in Figure 1. The absorption peaks of 1375 cm^{-1}, 1730 cm^{-1}, and 1720 cm^{-1} were intrinsic for vulcanized natural rubber, MPTS graft polymer and HEMA graft polymer, respectively, as these absorption peaks did not overlap with any other peaks. The peaks of 1720 cm^{-1}, 1730 cm^{-1}, and 1375 cm^{-1} were assigned to $\nu_{C=O}$ of poly-HEMA, $\nu_{C=O}$ of poly-MPTS, and δ_{CH3} of the trunk rubber, respectively.[13] Using these peaks, we calculated the composition ratios of the trunk rubber to the graft polymer on the modified rubber surfaces.

The composition ratios were plotted against dose in Figure 2. When HEMA was grafted on the trunk rubber in the monomer concentrations of 30, 50, and 70%, the composition ratio became large with the

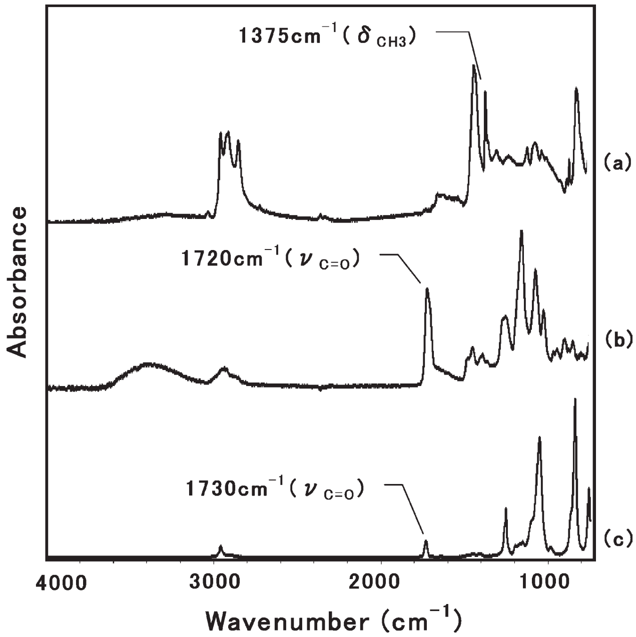

Figure 1 ATR-FT/IR spectra of (a) trunk rubber, (b) poly-HEMA, and (c) poly-MPTS.

increase of the dose. The grafting was enhanced more at higher HEMA concentration. The composition ratio reached to 0.92 under the conditions of 20 kGy and 70% concentration. On the other hand, the composition ratio for the MPTS grafting did not increase so much and it was only 0.19 under the conditions of 20 kGy and 100%. The composition ratio of the HEMA graft polymer was four times that of the MPTS graft polymer under the same conditions. This is because of the difference in reactivity of grafting. As the molecular structure of MPTS is bulkier than that of HEMA, the graft reactivity of MPTS is lower than that of HEMA. These results imply that HEMA can be easily grafted on the surface of the trunk rubber. The adjusting of monomer concentration and dose in the grafting can control the composition ratio in a certain range.

Then, the change of surface roughness caused by graft polymerization was evaluated using confocal laser scanning microscope. Figure 3 shows confocal laser scanning micrographs and roughness of HEMA grafted rubber surface. The surface roughness maintained the value of the raw trunk rubber until composition ratio of 0.84. In case of MPTS, the surface roughness is considered not to be affected by grafting since the maximum composition ratio was 0.2.

Contact angle because of graft polymerization

The surface property was evaluated by contact angle by using the different composition ratios of HEMA and MPTS grafted rubber. Effect of the composition ratio on the contact angle of water is shown in Figure 4. The contact angle of the raw trunk rubber, which was irradiated with electron beam, dipped water, and methanol solvent are 94.3,90.1,95.0°, respectively. In the case of HEMA grafting, the contact angle gradually became smaller as the composition ratio increased. The contact angle decreased from 92.6° to 73.4° when the composition ratio was varied from 0 to 0.92. It clearly indicates that the hydrophilic properties are achieved on the natural rubber surface by performing graft polymerization of HEMA onto it. In the case of MPTS grafting, the contact angle intensively increased as the composition ratio became larger. The contact angle changed from 92.6° to 108.1° when the composition ratio increased up to only 0.14. This result reveals that the hydrophobic properties are given on the natural rubber surface by graft polymerization of MPTS onto it on the contrary to the HEMA grafting. In these surface modifications, radicals are formed on natural rubber and monomer by irradiating electron beam. Graft chain of each monomer propagated in the surface area of the trunk rubber. In this way, graft polymer of HEMA or MPTS is imparted in the surface of the trunk rubber. As a result, the surface layer of the trunk rubber containing the hydroxyl group of HEMA leads the hydrophilic property. In the contrary, MPTS gives the hydrophobic property, by the trimethylsiloxy group. Accordingly, the grafting of hydrophilic HEMA and hydrophobic MPTS could modify the water contact angle of natural rubber in the range from 70 to 108°.

Semi-dry friction

When the wiper rubber system is designed, the friction affects the specification of driver motor[1]).

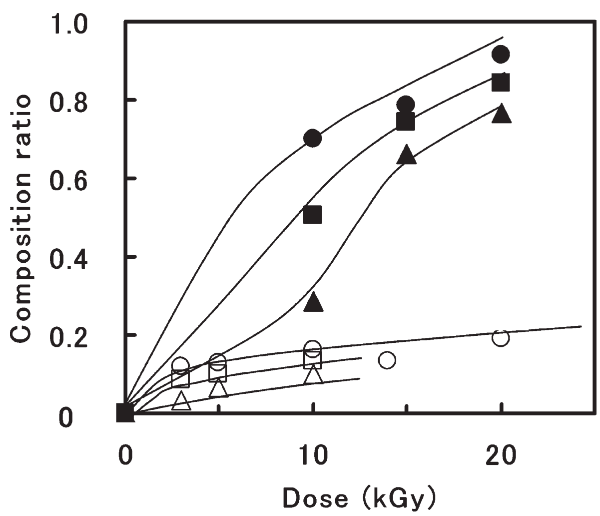

Figure 2 Effect of dose on composition ratios in different concentrations of HEMA and MPTS: (▲) 30% HEMA, (■) 50% HEMA, (●)70% HEMA, (Δ) 30% MPTS, (□) 50% MPTS, and (○) 70% MPTS.

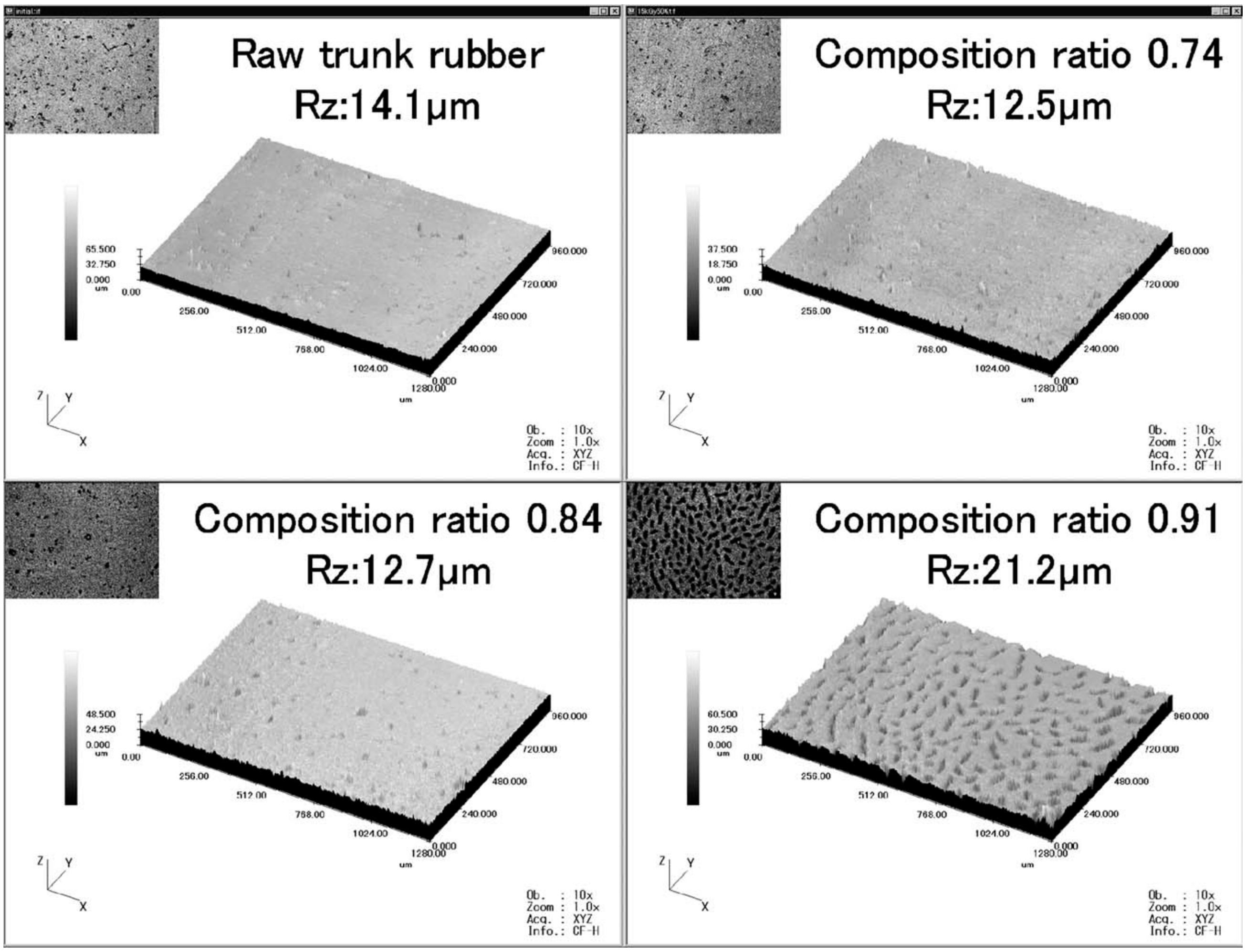

Figure 3 Confocal laser scanning micrographs and ten-point mean roughness (Rz). of HEMA grafted rubber surfaces.

Especially, the maximum friction has been observed in the semi-dry state which is transition state from wet to dry state. In this reason, friction property for rubber was evaluated by semi-dry state. Figure 5 shows the changes in the coefficient of friction from wet to dry friction for trunk rubber, HEMA grafted and MPTS grafted rubbers. The contact angles of water were 92.6°, 72.1°, and 106.6° for trunk rubber, HEMA-grafted rubber, and MPTS-grafted rubber, respectively. All coefficients of friction showed steep increase until the wet state shifted semi-dry state. In the semi-dry state, the coefficient of friction decreased gradually and came to a certain level at dry state. The maximum coefficient of friction is defined as coefficient of friction at semi-dry state, μ_{sd}. The coefficient of friction at the dry state is defined as μ_d. The difference of μ_{sd} and μ_d is expressed as $\Delta\mu$.

As mentioned before, surface properties are changed by graft polymerization. We considered that these modifications were connected with semi-

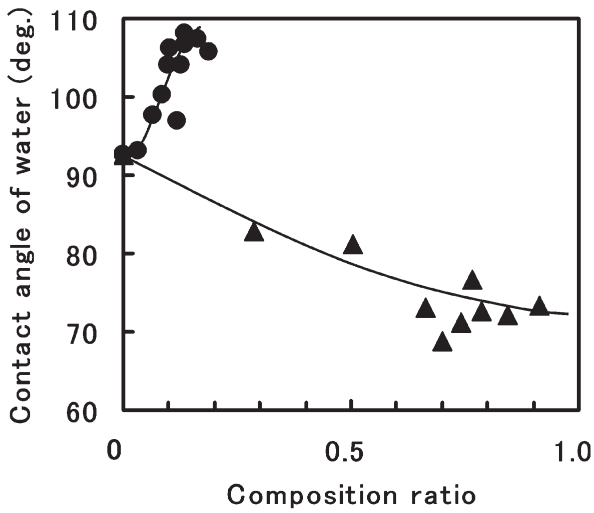

Figure 4 Effect of the composition ratio on the contact angle of water: (▲) HEMA grafted rubber and (●) MPTS grafted rubber.

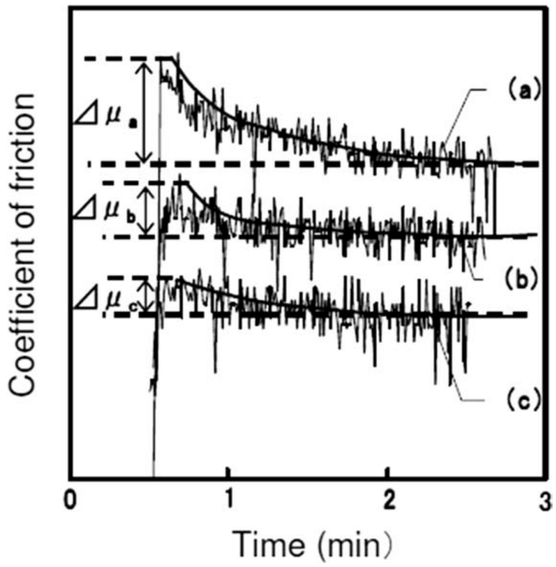

Figure 5 Coefficient of friction from wet to dry state: (a) HEMA grafted rubber (Contact angle = 72.1°, prepared by 50% HEMA and 20 kGy), (b) Trunk rubber (Contact angle = 92.6°), (c) MPTS grafted rubber (Contact angle = 106.6°, prepared by 50% MPTS and 10 kGy).

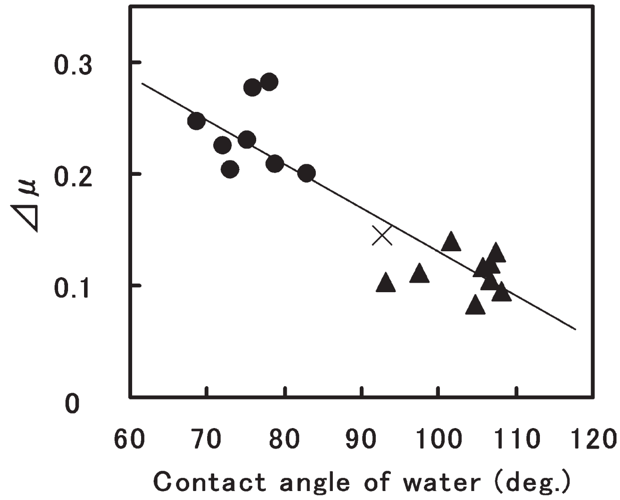

Figure 7 Relationship between contact angle of water and Δμ: (×) Trunk rubber, (●) HEMA grafted rubber, and (▲) MPTS grafted rubber.

dry friction. Effect of the composition ratio on the Δμ is shown in Figure 6. In the case of MPTS, Δμ became smaller as increase in the composition ratio. On the other hand for HEMA, Δμ became lager as increase in the composition ratio. These results are attributed to hydrophobic and hydrophilic property introduced by graft polymerization, respectively.

Then, to investigate the effect of contact angle on Δμ, the relationship between Δμ and water contact angles of the trunk rubbers and grafted rubbers were plotted in Figure 7. It was found that Δμ decreases with an increase of the contact angle. Owing to hydrophobic properties obtained by MPTS grafting, Δμ decreased. On the contrary, Δμ increases by hydrophilic properties obtained by HEMA grafting.

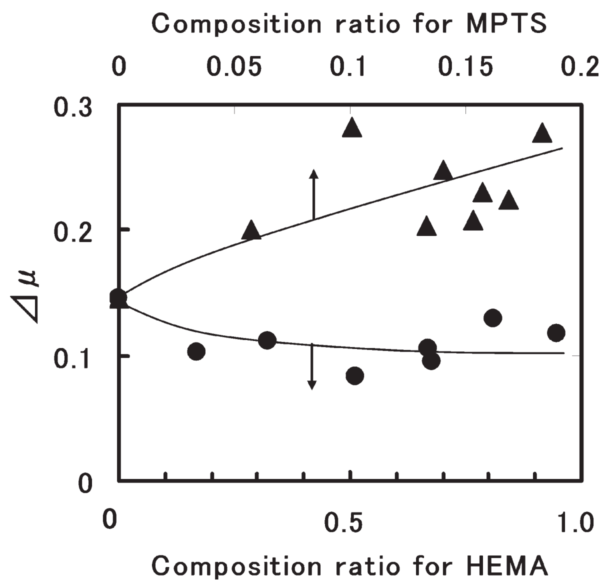

Figure 6 Effect of composition ratio on Δμ: (▲) HEMA grafted rubber and (●) MPTS grafted rubber.

The behavior of Δμ changes can be elucidated by the suction force caused by meniscus. Generally, a meniscus is formed in the contact area between two solids because of capillary condensation from vapor in the ambient atmosphere.[4] The meniscus may have the suction force between contacting solids. This suction force, F, will be represented by the following equation and is determined by the surface energy of the liquid forming meniscus and the contact angle of the liquid against the solid:[4,5]

$$F = 2\pi R\gamma_L(\cos\theta_1 + \cos\theta_2)$$

where F is meniscus force, R is radius of rubber, γ_L, surface energy of liquid, θ_1, contact angle between water and glass, θ_2, Contact angle between water and rubber.

The coefficient of friction at semi-dry is controlled by the suction force of the meniscus. In this case, the meniscus force changes with the change in the contact angle, θ_2, between water and rubber. Hence, Δμ becomes smaller as the increase in the contact angle between water and modified rubber. In this study, Δμ could be reduced to half of the untreated rubber by graft polymerization of MPTS.

CONCLUSIONS

We performed the graft polymerization of HEMA and MPTS by simultaneous irradiation of electron beam onto the vulcanized natural rubber and investigated the characteristics of graft polymerization, the contact angle of water on the modified surface, and friction behavior at the semi-dry state. After graft polymerization of HEMA and MPTS, the composition ratio of the modified surface could be determined by IR measurement. The contact angle of the trunk rubber, 92.6° was modified from 73.4 to 108.1. The increase in the contact angle owing to hydrophobic properties by graft polymerization of MPTS led to the decrease of Δμ. This result suggests that the friction at the moment of semi-dry can be controlled by providing the hydrophobic properties by graft polymerization.

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