

Surface Modification of Vulcanized Rubber by Radiation Grafting, Part 2: Improvement in Performance of Wiper Rubber

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ABSTRACT: Surface of natural rubber was modified by radiation-induced grafting of hydrophilic monomer, 2-hydroxyethyl methacrylate (HEMA), to improve the properties of surface hardness, dry friction, wiping performance, and wear duration. The ratio of grafted-HEMA to the rubber near the surface layer of HEMA-grafted rubber was analyzed by FT-IR and expressed as composition ratio. The composition ratio was controlled from 0.29 to 0.93 by changing HEMA concentration and dose in graft polymerization. When this composition ratio was higher than 0.8, the surface hardness was higher than 70 and the coefficient of dry friction lower than 0.65. Those values

became better than those of commercially available chlorinated-rubber in terms of wear and friction against glass. The surface hardness in wet state became very close to natural rubber since grafted-HEMA was softened by contacting with water. As a result, the grafted-HEMA rubber realized 95% and higher wiping performance of water on glass. Additionally, the wear resistance was eight times higher than chlorinated rubber. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2172–2176, 2012

Key words: graft copolymers; rubber; surface modification; fractionation of polymers; mechanical properties

INTRODUCTION

Friction of automotive wiper rubbers is one of the critical design factors for mechanical parts of wiper. Especially, friction in dry condition is a significant factor to adjust the size of wiper system and motor output characteristics because it is much higher than that in wet condition.¹ On the other hand, physical damage of wiper rubber owing to dusts on the windshield depresses wiping performance. Therefore, both properties of low dry-friction and high wear-resistance are required for a practical wiper rubber.

Principally, rubber materials have high frictional feature arising from their flexibility. A hardened layer on the rubber surface can decrease the friction by reducing the contact area between the rubber and the frictional surface.² Such reduction of dry friction is achieved by hardening the surface of wiper rubber by soaking it in sodium hypochlorite solution.³ This chlorination treatment is widely employed as a surface treatment of wiper rubber to reduce friction between surfaces of rubber and glass in the dry con-

dition. However, chlorination causes environmental problems such as the generation of chlorine and acidic wastewater in addition to the consumption of large electric power for the treatment process. Thus, development of alternative technologies for chlorination has been desired.

We focused on the surface modification by simultaneous graft polymerization induced by irradiation of electron beam as a novel technique. Graft polymerization is capable of imparting the desired functions such as hydrophilicity,^{4,5} mechanical properties⁶, and morphology of core/shell composite⁷ into rubber. Graft polymerization of polyfunctional monomers onto the rubber led the improvement of the mechanical and surface characteristics of ethylene propylene rubber⁸, ethylene-propylene-diene rubber⁹ and acrylic rubber.¹⁰

In the previous study, hydrophilic monomer, 2-hydroxyethyl methacrylate (HEMA), and hydrophobic monomer, 3-(Methacryloyloxy)propyltris(trimethylsiloxy)silane (MPTS), were grafted on vulcanized rubber surface by simultaneous grafting with electron beam irradiation to optimize the hydrophilicity.¹¹ In the present study, we investigated the surface modification of wiper rubber with graft polymerization of HEMA by simultaneous electron beam irradiation to improve friction characteristics, wiping performance, and wear resistance which are critical requirements of wiper rubber.

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EXPERIMENTAL

Material

Natural rubber, standard Malaysian rubber (SMR CV60), was used as trunk polymer for graft polymerization. The standard Malaysian rubber mixed with carbon black, zinc oxide, stearic acid, and dicumyl peroxide in the ratio of 100/50/5/2/5 was kneaded using two rollers at 50°C and molded into sheet in 2 mm thickness by heat pressing at 170°C for 13 min. This sheet was cut into pieces of 30 mm × 40 mm and used as trunk rubber after washing with methanol. 2-Hydroxyethyl methacrylate (HEMA) was obtained from Kanto Chemical Industrial-grade methanol of Taiyo Kagaku and ion exchanged water were used without further purification. Chlorinated rubber was prepared by soaking the trunk rubber in 0.5% sodium hypochlorite acidic solution for 5 min at 25°C.

Graft polymerization method by the simultaneous irradiation of electron beam

HEMA was dissolved in water and was prepared to a certain concentration. Ten grams of each solution was put into a polyethylene bag with one piece of the trunk rubber. Nitrogen bubbling was performed in each bag for 1 min and then the bags were sealed. Graft polymerization was conducted by irradiating electron beams of 10 to 20 kGy under the conditions of 2 MeV, 1 mA, and 1 kGy/pass. After grafting, each rubber was soaked in methanol for 1 h to remove homopolymer. Then, the HEMA-grafted rubbers were dried under the reduced pressure for 24 h.

Analysis of grafted rubber

Composition ratios of HEMA-grafted rubbers to natural rubber near the surface layer of the grafted rubbers were evaluated by ATR-FT/IR analysis (AVATAR 370FT/IR: Thermo Fisher Scientific K.K.). When the composition ratio of the HEMA-grafted rubber is termed as X that can be calculated by the following equations:

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

where A_h (stretching of C=O, $\nu_{\text{C=O}}$) and A_n (vending of methyl group, δ_{CH_3}) are peak heights originated from HEMA and rubber in HEMA-grafted rubber, respectively. A_{h0} ($\nu_{\text{C=O}}$) and A_{n0} (δ_{CH_3}) are peak heights for HEMA and trunk rubber.

Depth profiles of HEMA-grafted rubbers were observed by backscattered electron image (BEI) with SEM-EDS (JED-2140: JEOL) after grafted rubber was

soaked in the 2% osmium tetroxide aqueous solution for 5 h.

Surface hardness of the grafting layer was evaluated by international rubber hardness degree (IRHD) of ISO 48. IRHD was measured by the depth penetration of a ball indenter with a microhardness gauge (MD-1, Kobunshi keiki). Surface hardness was observed from wet state to dry state at 25°C after soaking of the grafted rubbers into water for 1 min.

Friction behavior and wear resistance between the glass disk and the HEMA-grafted rubber was measured by a pin-on-disk type abrasion tester (Shinto Scientific) at 25°C with 70% of relative humidity. The grafted rubbers cut into pieces of 10 mm² were washed with methanol prior to the measurement. Each piece was attached to the arm tip at the angle of 45° against the surface of glass disk. Vertical load during friction was 147 mN and the sliding velocity was 1.27 m/s. Wear resistance was evaluated based on the depth of wear after dry friction for 2 h. The depth of wear was evaluated by observing the cross section of worn rubber using SEM-EDS. Wiping performance was measured by the pin-on-disk type abrasion tester, also. Wiped area was observed by the digital microscope. Wiping performance was evaluated by the area of unwiped streaks left on the glass surface using the following equation:

$$\text{Wiping performance (\%)} = \frac{\text{wiped area}}{\text{wiped area} + \text{unwiped area}} \times 100$$

RESULTS AND DISCUSSION

The surface of trunk rubber was modified by graft polymerization of HEMA. Figure 1 shows the ATR-FT/IR spectra of the trunk rubber and the HEMA-grafted rubber. This is HEMA-grafted rubber prepared by irradiating electron beam of 20 kGy in 70% HEMA aqueous solution. HEMA-grafted rubber showed isolated peak at 1720 cm⁻¹ assigned to stretching of C=O group ($\nu_{\text{C=O}}$) of HEMA. Peaks at 1375 cm⁻¹ were attributed to vending (δ_{CH_3}) of methyl group of trunk rubber.

The composition ratios of grafted rubbers obtained under different conditions of monomer concentrations and doses were calculated and plotted against dose in Figure 2. The composition ratios indicate the molar fraction of HEMA to rubber near the surface layer of HEMA-grafted rubber. The grafting yield was enhanced more at higher HEMA concentration and dose. The composition ratios could be controlled in the range from 0.29 to 0.93 by HEMA concentrations from 30 to 70% and dose from 10 to 20 kGy.

The changes in the physical properties of the surface hardness and the dry friction were investigated

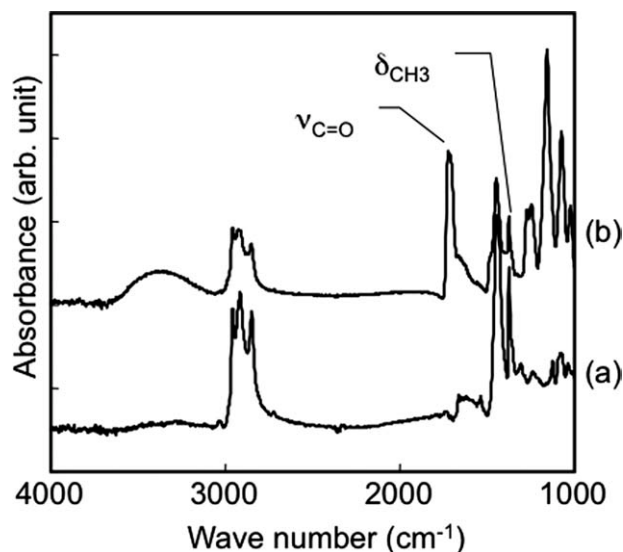


Figure 1 ATR-FT/IR spectra of (a) trunk rubber, and (b) HEMA-grafted rubber prepared by irradiating electron beam of 20 kGy in 70% HEMA aqueous solution.

using resulted HEMA-grafted rubbers. Effect of composition ratios on the surface hardness and the coefficient of dry friction are shown in Figure 3. The surface hardness of the HEMA-grafted rubber increased slightly in composition ratio up to 0.7 and then it went up dramatically from 68 to 74. As a result, the surface hardness can be changed from 64 to 74 by HEMA grafting. On the contrary, the coefficient of dry friction decreased significantly when the composition ratio exceeds around 0.7. This composition ratio at tuning points was achieved by grafting conditions in the area of 70% HEMA aqua solution with 10 kGy, 50% and higher with 15 kGy, and 30% and

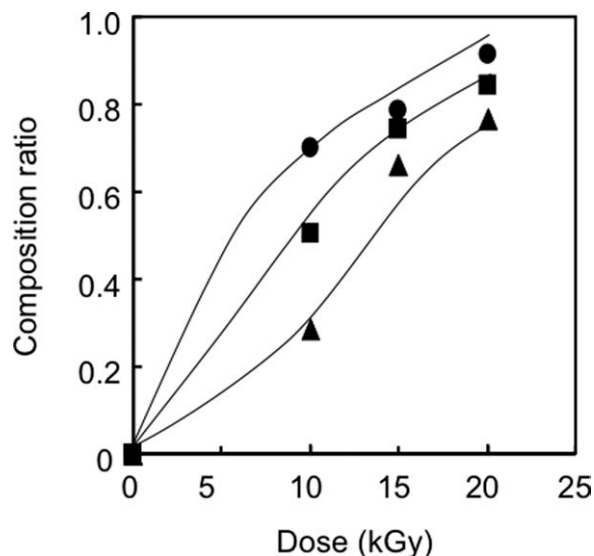


Figure 2 Effect of dose on composition ratios in various concentrations of HEMA; (▲) 30% HEMA, (■) 50% HEMA, and (●) 70% HEMA.

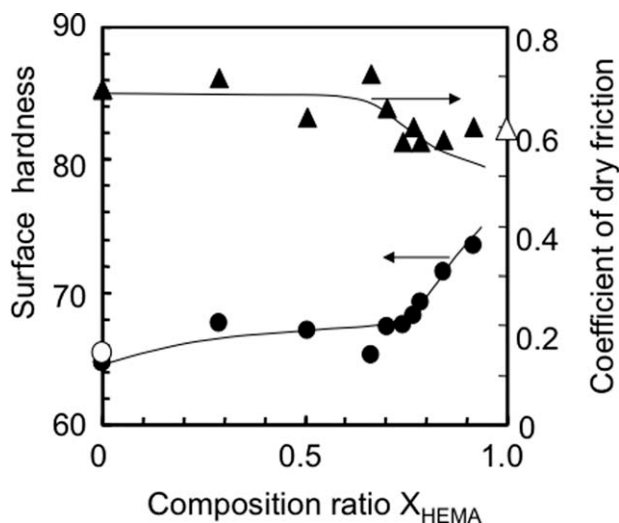


Figure 3 Effect of composition ratio on surface hardness and coefficient of dry friction of HEMA-grafted rubbers: (●) surface hardness and (▲) coefficient of dry friction. Open symbols in the corresponding vertical axes indicate surface hardness and coefficient of dry friction for chlorinated rubber.

higher with 20 kGy. The surface hardness and the coefficient of dry friction of the chlorinated rubber were 66 and 0.60, respectively. Accordingly, the composition ratio of 0.8 and higher satisfied both properties of surface hardness and the coefficient of dry friction in the HEMA-grafted rubber. This result indicates that the graft polymerization of HEMA onto the rubber surface is a promising technique to increase the surface hardness and reduce the dry friction without producing the waste chlorine and acid wastewater which are produced in chlorination process for surface modification of rubber.

Surface hardness is deeply related with wiping performance when the rubber is applied to a wiper material for car window. Figure 4 shows the change in the surface hardness of the grafted rubbers having the composition ratio of 0.77, 0.84, and 0.91 with wiping time. In this graph, 0 min represents the "completely wet" condition and 3 min the "completely dry" condition. In the wet condition, the surface hardnesses for the composition ratio of 0.77, 0.84 were close to 64.7 of the untreated rubber. In the case of the composition ratio of 0.91, the surface hardness was 62.5 in the wet state. After 3 min of wiping time, the surface hardnesses went up to 74, 71, and 67 for the composition ratio of 0.91, 0.84, and 0.77. The increase degrees of surface hardness were higher in the larger composition ratios. This is because the surface of the HEMA-grafted rubber is swelled and softens in the wet state. As the passing of wiping time, the surface changed from wet to dry states and the each surface hardness was close to the value of the dry state. These results indicate the possibility that the soft surface of the HEMA-grafted

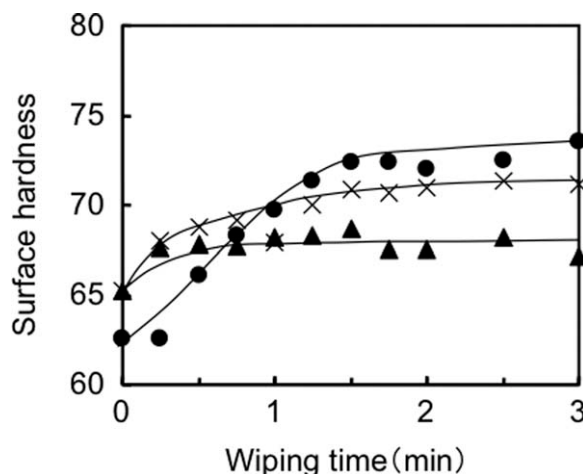


Figure 4 Changes of surface hardness in the transition time of 3 min from the wet to dry states; (\blacktriangle) composition ratio of 0.77, (\times) 0.84, and (\bullet) 0.91.

rubber in the wet condition improves the wiping performance on the curved glass surface during raining. On the other hand, the grafting of HEMA hardened the rubber surface in the dry state and decrease the dry friction.

We focused on this point to realize the compatibility between high wiping performance in the wet state and low friction due to high surface hardness in dry state. Figure 5 shows the relationship between wiping performance and coefficients of dry friction. In the HEMA-grafted rubber, the wiping performance was maintained the level more than 95% till the coefficient of dry friction decreased down to 0.55. This phenomenon was caused by surface hardness change between wet and dry states. The surface of HEMA-grafted rubber became soft and better contact with the surface of wet glass. The friction in wet condition is principally quite low and it is not essential for

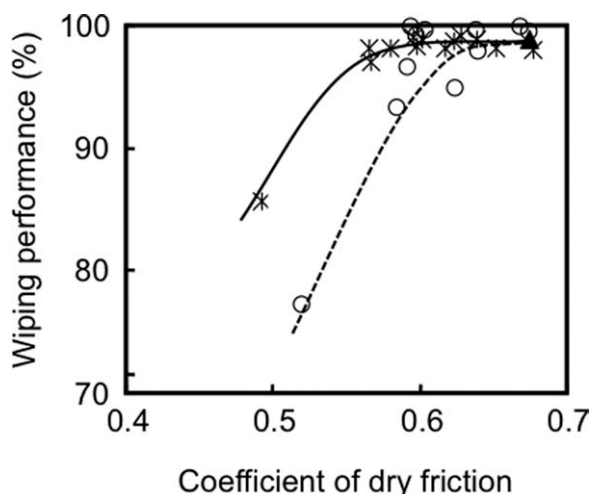


Figure 5 Relationship between coefficient of dry friction and wiping performance; (\times) HEMA-grafted rubber, (\circ) Chlorinated rubber, and (\blacktriangle) trunk rubber.

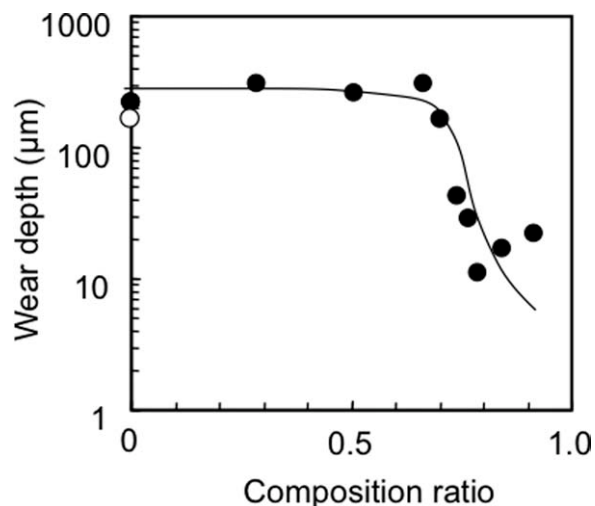


Figure 6 Effect of composition ratio on wear depth of HEMA-grafted rubber. Wear depth of the chlorinated rubber was pointed out by open circle.

design of wiper system. After wipe of water on the glass surface, the surface of grafted rubber becomes harder and reduces the coefficients of dry friction. In the case of chlorinated rubber, the wiping performance went down around the coefficient of dry friction of 0.62. The trunk rubber showed high wiping performance of 99.9%. However, the coefficient of dry friction was high, 0.68, without any response of surface hardness to the wet state. This result clarified that the grafting of HEMA onto the rubber solved the general contradiction of the both high wiping performance and low coefficient of dry friction.

Duration of wiper rubber is important factor for industrialization of the HEMA-grafted rubber.

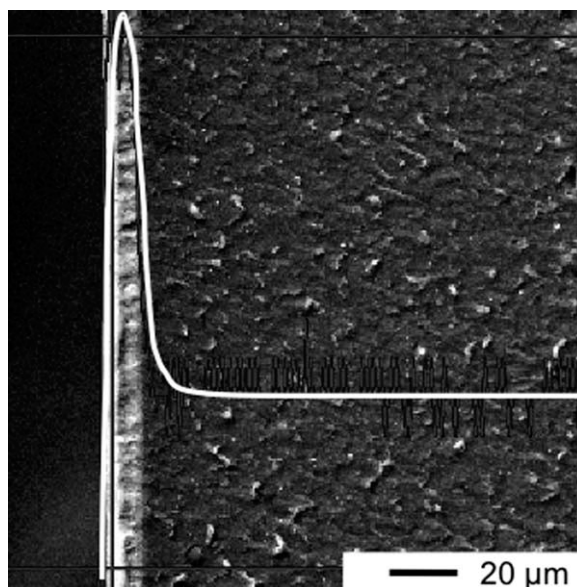


Figure 7 Depth profile of HEMA-grafted layer at composition ratio of 0.84.

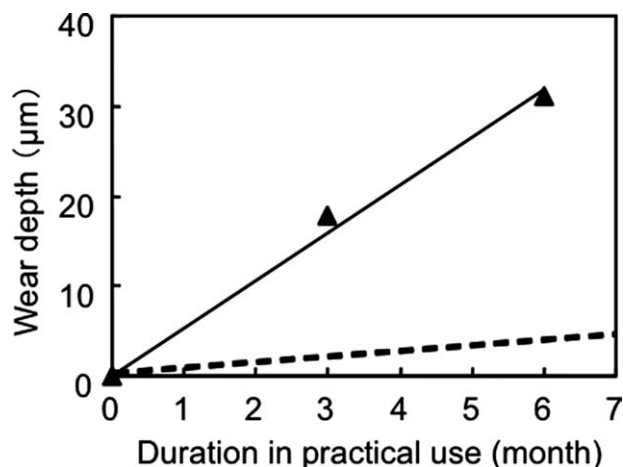


Figure 8 Relationship between wear depth and duration in the practical use; solid line shows wear depth of chlorinated wiper rubber and broken line for HEMA-grafted rubber with composition ratio of 0.84.

Degradation of performance in wiping rubber was caused by various factors such as oxidation of ozone, UV irradiation, and deformation and so on. In the case of modification of the surface grafting, the disappearance of the grafted layer on the rubber surface by wear is considered to determine the wiper life. Figure 6 shows the relationship between the wear depth and the composition ratio of grafted rubber. The wear depth started decreasing when the composition ratio was around 0.7. This reducing of wear depth was due to the increment of surface hardness of the HEMA-grafted rubber. The wear depth was 17 μm at the range of composition ratio at 0.84 which satisfied the high wiping performance and low coefficient of dry friction for practical application as a wiper rubber. The wear depth of the chlorinated rubber was around 140 μm . These results indicate that the wear depth of the HEMA-grafted rubber was roughly one eighth of that of the chlorinated rubber and the substantial improvement in the wear resistance was achieved by HEMA grafting on the wiper rubber. Figure 7 shows the depth of the HEMA-graft layer near the surface of grafted rubber in the composition ratio of 0.84. Grafted-HEMA was located in the surface layer of 20 μm . The reason why the grafted layer was located in the surface layer of the rubber is the limited diffusion of HEMA into the rubber since the graft polymerization was carried out by simultaneous method using high dose rate of EB radiation.

The wiper life of the HEMA-grafted rubber was estimated by the empirical wear depth of the commercialized product of chlorinated wiper rubber. Figure 8 shows the wear depth of the commercialized chlorinated wiper rubber and the estimated value of the grafted rubber. After six months, the wear depth of the commercialized chlorinated wiper rubber

reached 30 μm in the practical usage. However, only 4 μm of the grafted layer will be worn off during six months since the wear depth in the surface layer of the HEMA-grafted rubber at the composition ratio of 0.84 was one eighth of that of the chlorinated rubber as shown in Figure 6. It means that the wear rate of the grafted rubber is 8 μm per year. Therefore, the wiper life of the HEMA-grafted rubber at the composition ratio of 0.84 was assumed to be two years since the thickness of grafted layer was 17 μm .

CONCLUSIONS

HEMA-grafted natural rubber was evaluated by surface hardness, dry friction, wiping performance, and wear duration on the viewpoint of the practical usage for car wiper. When the composition ratio of HEMA to natural rubber near the surface layer of the HEMA-grafted rubber was higher than 0.7, the coefficient of dry friction was lower than that of commercially available chlorinated-rubber. Additionally, the wiping performance was more than 95%. These results indicate that the graft polymerization of HEMA on rubber surface provides sufficient characteristics as the wiper rubber and is promising surface treatment for the novel wiper rubber which can achieve both the reduction of dry friction and the holding of high wiping performance. The wear resistance of HEMA-grafted rubber was eight times higher than chlorinated rubber. This high performance of wear resistance gives the life of two years in the practical use as wiper rubber. It is concluded that the HEMA-grafted rubber is promising material for wiper rubber instead of the chlorinated rubber currently used.

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