

Surface Modification of Automobile Rubber by Various Plasma Treatments

Seung-hun Lee¹ and Seock-sam Kim^{2†}

¹Department of Mechanical Engineering, Graduate School, Kyungpook National University, Daegu, Korea

²School of Mechanical Engineering, Kyungpook National University, Daegu, Korea

Abstract: This study examined the surface modification characteristics of NBR using sealing in automobile. Surfaces of NBR were modified by RF power Ar plasma treatment. In experiment, pressure, flux, temperature were fixed and RF bias voltage. Treatment time was changed. In friction test, we used PTFE grease. After modification, surfaces of NBR showed many grooves, hydrophilic functional groups, and lipophilic functional groups. As increasing treating voltage and time, the amount of them was increased. And wetting angle and friction coefficient was decreased with increasing treating voltage and time. However, the pattern of changing friction coefficient was not fixed.

Keywords: Ar plasma, NBR, molecular structure, wetting angle, friction coefficient

1. Introduction

Rubbers in automobile have some very useful properties such as low Young's modulus, large elongation-to-break and high value of Poisson's ratio, which make them suitable for many sealing applications. J. A. Btydson and Andrew Ciesielski[1, 2] reported that seal is a component that prevents the leakage of fluids or gas from the machine and contaminants entering the machine. Most seals operate in the presence of oils during their service life. Friction and wear are two important factors for seal performance and the overall efficiency of the machine. Therefore, the interaction between oils and elastometric, and its influence on friction and wear behavior of elastometric have an important role in seal performance. The use of permanent lubrication by oil for lowering the coefficient of kinetic friction and reducing the wear of rubber seals in pneumatic devices is a common practice.[3-9] However, it has become imperative to restrict this method to some extent due to the associated health hazards. This problem can be solved by surface treatment. Surface treatment of polymers is an ideal way to improve their tribological properties, especially in the dry operating conditions. On the other hand, surface modification can lead to changes in the surface energy and other properties. Modification can be performed separately by chemical or physical processes such as plasma treatment.

General methods of surface modification for durability use sulfuric acid. After dilution of the acid, NBR is soaked in it and dried. After surface treatment of the rubber, the acid should be refined and removed to avoid environmental pollution. This is a costly practice. Moreover, the effect of the

surface treatment is dependent on the dilution rate. For surface treatment, intricate plant is a necessity because of manpower, cost and environment factors. Physical surface modification uses alloy and rolling process for changing roughness. But the change in the roughness is not regular because rubber has viscoelasticity and network structure [8].

Surface modification of rubber, especially the one using plasma treatment, has been investigated extensively. Surface roughness can be controlled under micrometer by plasma treatment. Plasma has high energy that can change molecular structures and functional groups on surface.[10-16] However, the correlation between rubber and plasma is not adequately investigated because rubber has intricate molecular structure and changeable chemical characteristic, and plasma is not easily available.[17,18]

In this study, we examined the effect of Ar plasma treatment on NBR. The surface of NBR is treated by RF Ar ion plasma various bias voltage and treatment time, as both of them are very important parameters during plasma surface treatment. After treatment, we conducted different analysis to find out the interaction mechanisms between parameters and surface characteristics. Using friction test, we compared tribological characteristics of original and treated NBR. We examined the mechanisms of changing characteristics of NBR and its effects on tribological characteristics.

2. Experimental Detail

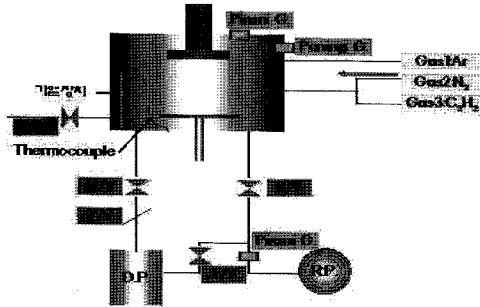
2.1. RF Ar plasma etching process

In this experiment, we used RF Ar plasma for treating surface of NBR. The NBR, which contains 25% ACN (Acrylonitrile) was supplied by Pyunghwa Oil seal company. Table 1 shows properties of specimen. Hybrid RF-power sputtering system was used for generating RF Ar plasma. Hybrid RF-power

†Corresponding author; sskim@knu.ac.kr
Tel: +82-53-950-5577, Fax : +82-53-950-6588

Table 1. Properties of specimen.

Specimen	Viscosity [N · s/m ²]	Strength [kg/cm]	Expansion ratio[%]	JISA Hardness [Hs]	Temp. [°C]
T4531	1.15	100	30	20	-30~120

**Fig. 1. The schematic diagram of hybrid RF-power sputtering system.**

sputtering system consists of vacuum chamber, vacuum pump, MFC, ion generator, power supply etc. vacuum pump is consisted of rotary pump and diffusion pump. The vacuum chamber is cylindrical shape, with 650 mm diameter and 600 mm height. Plate is connected above the spindle gear and bias power supply device. Gas flux is controlled by MFC (Mass flow controller). Figure 1 shows the schematic diagram of hybrid RF-power sputtering system. We controlled bias voltage and treatment time. Working pressure and treatment temperature were fixed. Bias voltage was supported under the range that surface of NBR doesn't burn or melt. Table 2 shows experimental conditions of RF Ar plasma etching treatment.

3. Surface analysis

3.1. Molecular structure & wetting angle

ATR-IR was used for analyzing change of molecular structure of surface. Because change of molecular structure, that is, change in functional group has effect on surface energy. Functional groups that affect the surface energy are hydrophilic groups and lipophilic groups. Hydrophilic groups

Table 2. Experimental conditions of RF Ar plasma etching treatment.

No	Temp. [°C]	Bias voltage [V]	Time [min]	Flux [sccm]	W/P [torr]	U/P [torr]
1	R/T	100	30	20	8.0×10^{-3}	2.0×10^{-6}
2	R/T	200	30	20	8.0×10^{-3}	2.0×10^{-6}
3	R/T	300	30	20	8.0×10^{-3}	2.0×10^{-6}
4	R/T	400	30	20	8.0×10^{-3}	2.0×10^{-6}
5	R/T	400	60	20	8.0×10^{-3}	2.0×10^{-6}
6	R/T	400	90	20	8.0×10^{-3}	2.0×10^{-6}
7	R/T	400	120	20	8.0×10^{-3}	2.0×10^{-6}

(R/T : Room temperature, W/P : Working pressure, U/P : Ultimate vacuum pressure)

Table 3. Condition of friction test

Counter body	Load[N]	Velocity[rpm]	Cycle[n]	Temp.[°C]
100Cr6	0.1	200	10000	R/T

are carboxyl group, amino group etc. and lipophilic groups are hydrophobic carboxyl group, ester group, acrylonitrile group etc. ATR-IR device is Spectrum GX & Auto Image made by Perkin-Elmer corporation in America. And through measuring wetting angle, we can know changing surface energy.

3.2. Microscopic observation & friction test

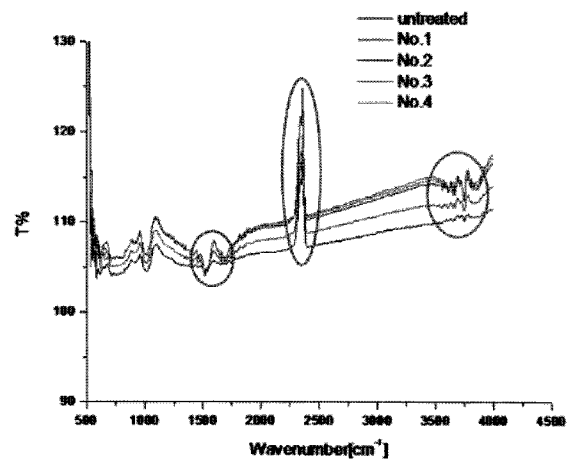
As we know, surface profile and friction coefficient are have a functional relation. So we used SEM and tribo-meter, which is ball on disk type. Counter body was bearing steel(100Cr6) ball. Because NBR is generally used for sealing with bearing steel in motormobile. And PTFE(Polytetrafluoroethylene, Teflon series lubricant oil) was used as lubricant oil, as it is generally used at high temperature situation such as in engine. Table 3 is condition of friction test.

4. Results and discussion

4.1. Molecular structure & wetting angle

After plasma treatment, we analyzed the changes in molecular structure. We found changes in the analyzing transmission rate of molecular monomer by ATR-IR.

In Figure 2 we compared original NBR with treated NBR modified from different bias voltage. Change in the transmission rate was observed. Result showed that change in area and the biggest one was 2410 cm^{-1} , COOH carboxyl group area. Carboxyl group was typical hydrophilic functional group, and C-O group (2300 cm^{-1}) increased. NH group(1530 cm^{-1}) and NH_2 group(1770 cm^{-1}) also increased. NH and NH_2 were typical lipophilic functional groups. $\text{C}\equiv\text{N}$ group(1680 cm^{-1}), C-H group(3450 cm^{-1}) and C-C group(3810 cm^{-1}) also increased. But the amount of increase was minimal. The amount of molecular changes increased

**Fig. 2. ATR-IR spectra with changing bias voltage(-100~400 V / 30 min).**

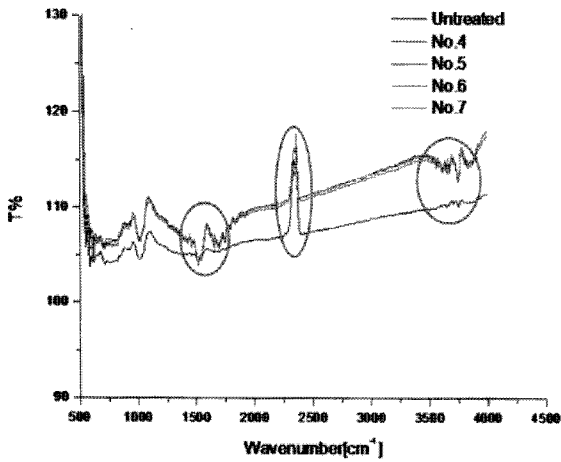


Fig. 3. ATR-IR spectra with changing treatment time(-400 V / 30 ~ 120 min).

with increasing bias voltage.

Figure 3 also shows that the comparison between original NBR and treated NBR with changing treatment time. As seen in Figure 3, the bonding area was the same. Increasing treatment time had an increasing effect on the amount of molecular changes, although this effect was less than the one due to changing bias voltage.

Almost rubbers were not transparent in the IR range, since their ingredients and fillers cause strong scattering in this spectral region. In this connection, most investigators limit themselves to studying the interaction of gas-discharge plasma with raw elastomers. [19,20].

It was undoubted that the chemical nature of an unvulcanized elastomer as the base rubber component exerts a determining effect on the character and direction of plasma-induced processes in surface layers.

Distilled water was used for measurement of wetting angle, and we took the average of five independent observations. Figure 4 shows wetting angle with changing bias voltage. As the bias voltage increased, wetting angle greatly decreased. However, as the treatment time was changed, the degree of

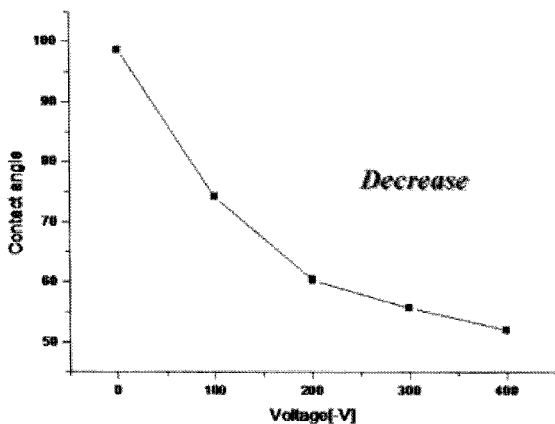


Fig. 4. Wetting angle with changing bias voltage(-100~ -400 V / 30 min).

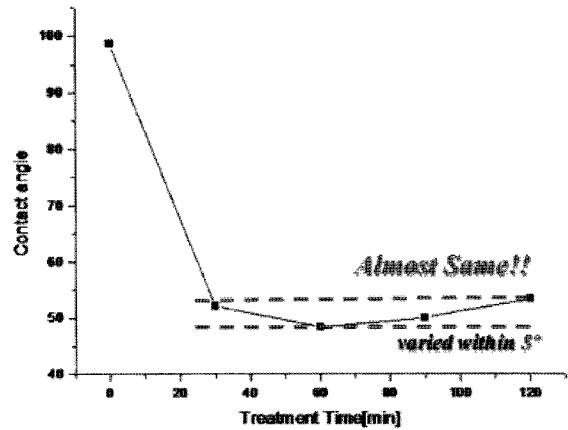


Fig. 5. Wetting angle with changing treatment time(-400 V / 30 ~ 120 min).

change of wetting angle was very small as shown in Figure 5. The degree was in error range so they were almost same.

5. Microscopic observation & friction test

Figure 6 shows surface profile of non-treated NBR. It looked

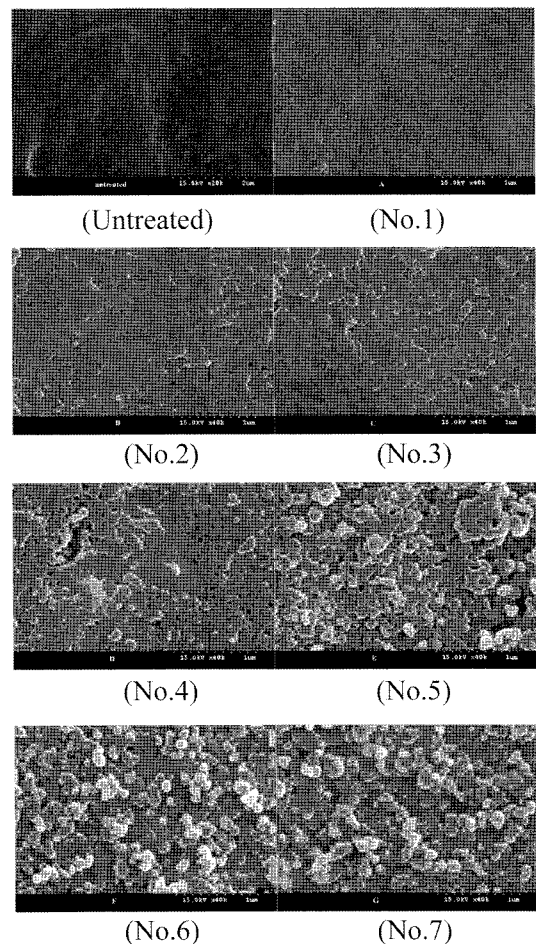


Fig. 6. Surface images of untreated and RF Ar plasma treated NBR.

very smooth. However, after RF Ar plasma treatment, waves, asperities and dimples existed. Figure 6 are surface profiles after RF Ar plasma treatment. When the bias voltage increased, surface profiles became rougher. And after 90min treatment time, waves turned asperities and dimples became deeper.

U. Cvelbar and S. Pejovnik[17] reported that the thermal effects caused by ion and atom interactions from long time plasma discharge together with the etching effects may be responsible for the dramatic changes of surface roughness.

In the friction test, we controlled bias voltage, treatment time and also the lubrication condition. Because NBR is sensitive under lubricated condition. Figure 7 and Figure 8 show friction coefficients under unlubricated conditions. As seen in Figure 7, the friction coefficient was decreasing with increasing bias voltage. It was also decreasing, though at a minimal level, with increasing treatment time as Figure 8. Figure 9 and Figure 10 show the result of friction coefficient under lubricated condition. The friction coefficient showed more decreasing tendency under lubricated condition than unlubricated condition, although the tendency of this effect

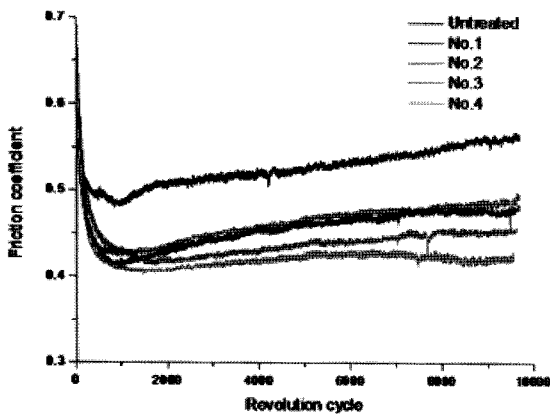


Fig. 7. Friction coefficient graph with changing bias voltage in unlubricated condition.

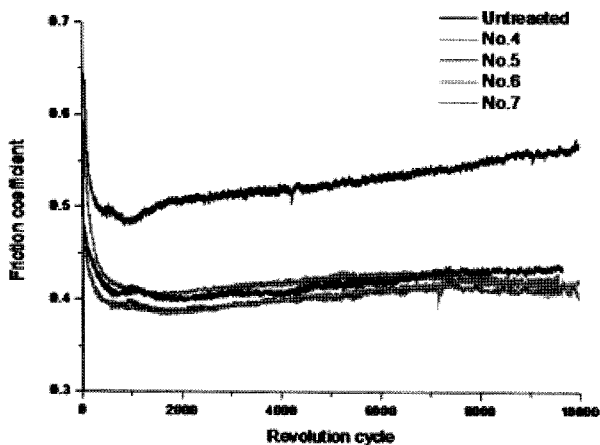


Fig. 8. Friction coefficient graph with changing treatment time in unlubricated condition.

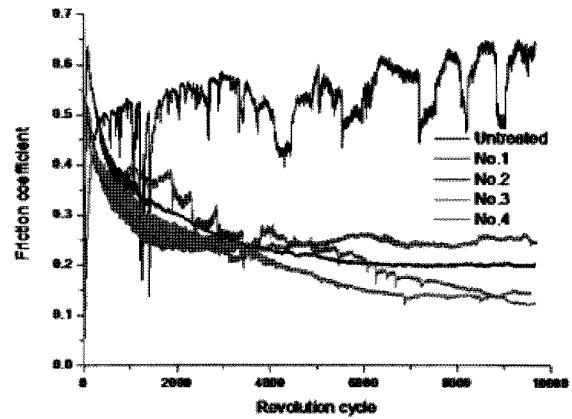


Fig. 9. Friction coefficient graph with changing bias voltage in lubricated condition.

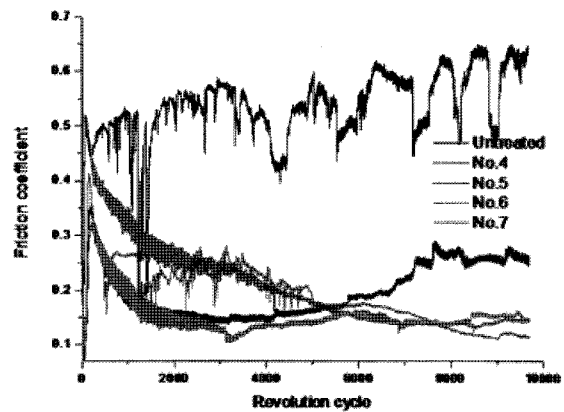


Fig. 10. Friction coefficient graph with changing treatment time in lubricated condition.

was not regular.

6. Conclusions

In this study, we modified the surface of NBR by RF Ar plasma etching in order to examine surface characteristics. Based on the surface analysis and micro-scopic observations, obtained conclusions are as follows.

1. Molecular structure and amount are changed by RF Ar plasma etching. Hydrophilic groups and lipophilic groups are generated. Changing and generating amount of functional groups are increasing with bias voltage and treatment time.
2. Surface energy of NBR modified by RF Ar plasma treatment also increases with increasing bias voltage and treatment time.
3. Geometric irregularity of modified NBR surface becomes roughly with increasing bias voltage and treatment time.
4. Under lubricated friction, friction coefficient becomes lower with increasing bias voltage and treatment time.

Acknowledgment

This paper was supported by Korea Research

Foundation(2007) and BK21 in Kyungpook National University.

References

1. J.A. Brydson, *Rubbery materials and their compounds*, Elsevier Applied Science, 1988.
2. Andrew Ciesielski, (An) *Introduction to Rubber Technology*, Rapra Technology Limited, Shropshire(UK), 2000.
3. Moore DF., *The friction and lubrication of elastomers*, Pergamon Press, 1972
4. Persson BNJ, on the theory of rubber friction, *Surf. Sci.*, Vol. 401, p445-454, 1998.
5. Persson BNJ, Albohr O, Tartaglino U, Volokitin Al. Tosatti E, On the nature of surface roughness with application to contact mechanics, sealing rubber friction and adhesion, *T Phys Condens Matter*, Vol. 7, No. 1, p1-62, 2005.
7. Greenwood JA, Tabor D., The friction of hard sliders on lubricated rubber: the importance of deformation losses, *Proc Phys Soc*, Vol.71, p989-p1001, 1958.
8. Hofmann W, *Rubber technology handbook*, Munich: Hanser, 2001
9. Torbacke M, Johnsson A, Seal material and base fluid compatibility: an overview, *J Synth Lubr*, Vol. 22, No. 2, p123-42, 2005.
10. Papiya Sen Majumder, Anil K. Bhowmick, Friction behavior of eletron beam modified ethylene-propylene diene monomer rubber surface, *Wear*, Vol. 221, p15-p23, 1998.
11. Kyung Kyoong Kim, Jeong Suk Kim, Myeong Chang Kang, Studies on Improvement in the Coefficient of Friction on Oil Seal rubber by Ino Implantation, *KSMTE Autm. proc.*,p166-p171, 2007
12. Alfred Grill, *Cold Plasma in Materials Fabrication-From Fundamentals to Application*, John Wiley & Sons, p181-p189, 1994.
13. Hoffman, A. S., In *Plasma Polymerization and Plasma Interactions with Polymeric Materials*, ed. H. K. Yasuda, p341. New York: John Wiley & Sons, 1990.
14. Hoffman, A. S., In *Plasma Polymerization and Plasma Interactions with Polymeric Materials*, ed. H. K. Yasuda, p339. New York: John Wiley & Sons, 1990.
15. Hoffman, A. S., In *Plasma Polymerization and Plasma Interactions with Polymeric Materials*, ed. H. K. Yasuda, p153. New York: John Wiley & Sons, 1990.
16. M. Sugawara, *Plasma Etching-Fundamentals and Application*, Oxford Science Publication, 1998.
17. E. F. Abdrashitov and A. N. Ponomarev, *Plasma Modification of Elastomers*, *High Energy Chemistry*, Vol. 37, No. 5, p279-p285, 2003.
18. L. Martinez, L. Alvarez, Y. Huttel, J. Mendez, E. Roman, A. Vanhulsel, B. Verheyde, R. Jacobs, Surface analysis of NBR and HNBR elastomers modifaied with different plasma treatments, *VACUUM*, Vol. 81, p1489-p1492, 2007.
19. Tikhomirov, L.A., *Khim. Vys. Energ.*, Vol. 24, No. 2, p171, 1990.
20. Chichagova, Zh.S. and Tikhomirov, L.A., *Khim. Vys. Energ.*, Vol. 25, No. 2, p176, 1991.
21. Krylova, S.N., Ural'skii, M.L., and Gorelik, R.A, *Trenie Iznos*, Vol. 7, No. 3, p542, 1986.
22. Ratway, R.J and Balik, C.M., *J. polym. Sci., Part B*, Vol. 35, No. 11, p1651, 1997
23. Cho, D.L. and Yasuda, H., *J. Appl. Polym. Sci. Symp.*, Vol. 23, No. 1, p64, 1988.