Journal of Mechanical Science and Technology 24 (2010) 119~122
www.springerlink.com/content/1738-494x
DOI 10.1007/s12206-009-1180-z

Effect of micro-scale Young's modulus and surface roughness on adhesion property to plasma-treated rubber surface†

Jong-Hyoung Kim[1,*], Noritsugu Umehara[1], Hiroyuki Kousaka[1], Mamoru Shimada[2] and Mitsuru Hasegawa[2]

[1]*Department of Mechanical Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603, Japan*
[2]*Nipro Corporation, Research and Development Laboratory, Nojicho, Kusatsu, Shiga, Japan*

(Manuscript Received May 1, 2009; Revised October 29, 2009; Accepted October 30, 2009)

Abstract

Adhesion between rubbers and metals is often the main cause of machine trouble. Therefore, efficient utilization of rubber in dynamic and static applications requires the modification of the adhesion property of the rubber surface without affecting the bulk characteristics. In this work, we have studied the mechanism of the reduction in adhesion force between medical rubber, chloride-isobutene-isoprene rubber (CIIR), and stainless steel by using surface wave-excited plasma treatment of the rubber surface with oxygen and argon gases. Experimental results showed that surface roughness derivations increased by about 10 times across the treatment, at maximum, corresponding to the increase in time. In addition, the micro-scale Young's modulus of treated CIIR sheet increased by about 6.3 times at maximum from that of the untreated CIIR sheet. These changes in Young's modulus and roughness at the surface of CIIR sheet are considered to be the main reasons for the plasma-assisted reduction of adhesion force between stainless steel ball (SUS 440C, JIS) and CIIR sheet.

Keywords: CIIR rubber; Surface wave excited plasma treatment; Micro-scale Young's modulus; Surface roughness; Adhesion force

1. Introduction

Adhesion, or the sticking of different materials at their interface, is of general interest in many branches of technology, including micro-electronic devices, medical products, and manufacturing. Adhesion between rubbers and metals is often the main source of trouble in a machine. Thus, if molded rubber products easily stick to molds, rollers, and metal "hands", the productivity of the manufacturing line becomes low. Therefore, efficient utilization of rubber sheets demands modifications on certain desirable properties of the rubber surface without affecting the bulk characteristics. Plasma treatment is one of the most employed methods to attain this goal. One of the most significant benefits of the plasma process is it offers the additional advantage that surface modification does not affect the desirable bulk properties of the rubber.

In a previous study, we demonstrated that the surface wave-excited plasma treatment reduces the adhesion force between medical rubber, chloride-isobutene-isoprene rubber (CIIR), and stainless steel ball (SUS440C) by using oxygen and argon gases.

We have also shown a decrease in the real contact area with increasing time and microwave power, and a similar trend in the residual rates of the adhesion force and the real contact area of CIIR rubber. Therefore, it is assumed that the adhesion force is strongly subjected to the real contact area [4]. However, the main reason for the reductions in the real contact area remains unknown. Recent works have shown that plasma treatment increases the roughening of rubber surfaces [5]. The surface roughness may affect the adhesion force, which is largely dependent on the contact geometry and surface topography [6-8].

In this paper, we report our attempts to clarify the factors that reduce the adhesion force during the surface wave-excited plasma treatment process. We also try to determine the Young's modulus behavior in micro-scale; bulk property is measured using a micro-slicer and surface roughness changes are measured by 3D laser scanning microscope.

2. Material and methods

2.1 Material preparation

Chloride-isobutene-isoprene rubber (CIIR) containing 98

† This paper was presented at the ICMDT 2009, Jeju, Korea, June 2009. This paper was recommended for publication in revised form by Guest Editors Sung-Lim Ko, Keiichi Watanuki.
*Corresponding author. Tel.: +8152 789 2788, Fax.: +82 52 789 2788
E-mail address: hotemail@hanmail.net

wt. % of isobutene and 1.3 wt. % of isoprene and a barrier material that is chemical-resistant and has low permeability to gases, vapors, and organic liquids was used. The dimension of the CIIR rubber was 3.5×30×30 mm.

2.2 Surface wave- excited plasma apparatus

Plasma treatment apparatus employing a type of azimuthally symmetric surface wave-excited plasma source was used in this study [3-4]. This source generates high-density columnar plasma along the axis of the quarts tube, where the plasma diffuses to the surface of a CIIR specimen located at r = 50 mm from the quartz tube. Before plasma treatments, the base pressure in the chamber was decreased to 3×10^{-3} Pa using a turbo-molecular pump. Oxygen and argon gases were let into the chamber through a mass flow controller at a flow rate of 20 sccm to get a working pressure of 30 Pa. After plasma treatment, all CIIR specimens were stored in closed dishes at room temperature and humidity.

2.3 Young's modulus measurement in micro-scale

Young's modulus tests (Elionix ENT-1100 of Orionix Co.) involve the contact of an indenter on a CIIR rubber surface and its penetration to a specified penetration depth. In this case, the depth was the displacement into the CIIR rubber starting from its surface. Calculation methods used to determine the modulus were based on the work of Oliver and Pharr [9].

The effective modulus (E_r), which accounts for the deformation of both the indenter and the specimen, is given by

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (1)$$

where E_i (1140 GPa) and ν_i (0.07) are the elastic modulus and Poisson's ratio of the diamond indenter, respectively, and E and ν are elastic modulus and Poisson's ratio of the sample, respectively.

To calculate the elastic modulus of the CIIR rubber, all the specimens were cut in 50-100 μm to avoid the bulk properties of 3 mm thickness by using a microwave slicer (DTK-1000).

2.4 Surface roughness and adhesion measurement

The surface roughness experiments were performed with a Keyence VK-8700.

For measuring the adhesion force, we performed the pull-off force between a SUS 440C (19.05 mm in diameter) adhesively bonded to the CIIR rubber [10]. A compression load of 1 N was applied for 90 s. In all cases, the adhesion tests were performed in an air-conditioned room at 22-24°C and 45-50% RH.

3. Results and discussion

Results of adhesion forces between CIIR rubber and stainless steel ball as a function of plasma treatment time at 200 W are shown in Fig. 1. It is apparent from the figures that the adhesion force dramatically decreased with oxygen plasma treatment according to treatment time. A similar decreasing trend was also observed with argon plasma treatment. However, at 1 min treatment time, the adhesion force was higher with argon treatment than oxygen plasma treatment. After 1 min, argon plasma treatment was more effective than oxygen plasma treatment in decreasing the adhesion force. The adhesion force could not be measured after 10 min because it was lower than the measurable value of 0.001 N. In summary, the figures showed that plasma treatment time is a very important factor in decreasing the adhesion force.

Load-penetration depth curves by using the nano-indenter with 50 μN maximum loads are shown in Fig. 2. The thickness of the prepared CIIR rubber was about 3 mm for the general thickness, and about 50 μm for the cutting thickness, using the microwave slicer. Despite the same conditions, the penetration depth obtained from the 3 mm thickness CIIR rubber was clearly different from that of the 50 μm thickness rubber. In particular, the unloading curve coincided with the

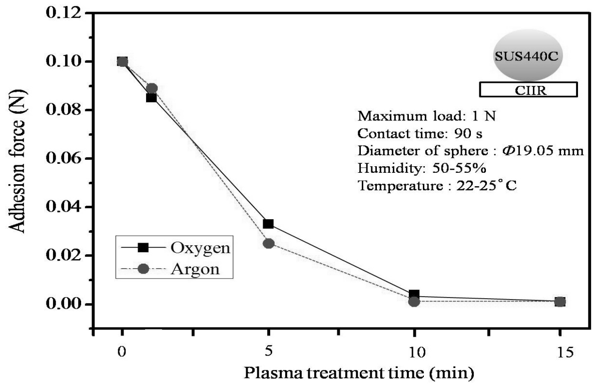

Fig. 1. Adhesion force between CIIR sheet and stainless steel ball after oxygen and argon plasma treatments at a microwave power of 200 W and a gas pressure of 30 Pa, for 0, 1, 5, 10, and 15 min.

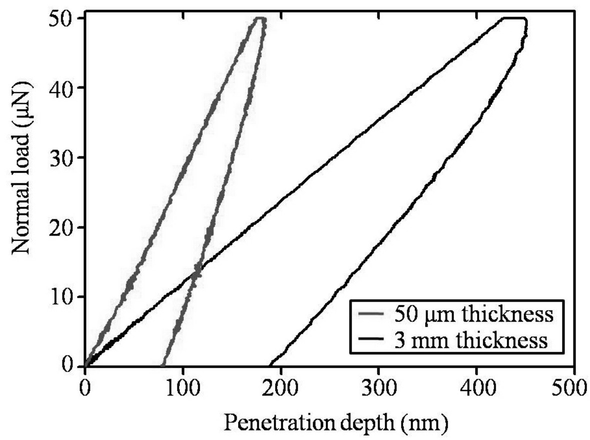

Fig. 2. A sample of load-penetration depth curves obtained using pyramidal indenter for a 50 μN maximum load with different thickness of CIIR rubber.

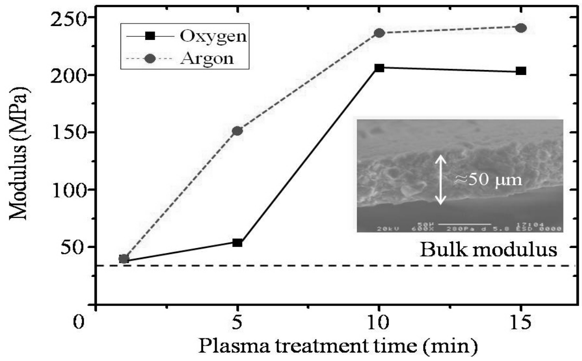

Fig. 3. Effect of plasma treatment time on the elastic modulus of CIIR rubber 50 μm in thickness that was cut from the top surface of treated CIIR sheet. The elastic modulus was measured by nano-indenter for oxygen (black) and argon (red) plasma treated CIIR sheets.

loading curve at a penetration depth of more than 290 nm due to the thickness difference. This indicates that not only has the bulk property greatly affected the Young's modulus, but it has also affected accurate measurement. In other words, a surface wave-excited plasma treatment increased the Young's modulus in μm thickness scale. As a result, we determined that it is possible to develop a clear difference between 3 mm and 50 μm Young's modulus of the CIIR rubber without any influence from the bulk property by using the microwave slicer.

Fig. 3 shows the Young's modulus profile of 50 μm thickness CIIR rubber measured by nano-indenter after oxygen and argon plasma treatment with increasing time. The results are depicted with squares (oxygen plasma treatment) and circles (argon). For the oxygen plasma treatment, Young's modulus was slightly higher (39.8 MPa) than the untreated CIIR rubber (38.0 MPa). However, it increased significantly between 5 min (53.8 MPa) and 10 min treatment time (206.1 MPa), followed by a steady state. A higher Young's modulus (236.4 MPa) was obtained with argon plasma treatment, but only after 15 min treatment with argon gas. As a result, improved Young's modulus, either by the oxygen and argon surface wave-excited plasma treatment, is an important factor that reduces the adhesion force.

The surface roughness deviations of the CIIR rubber were changed by the oxygen and argon plasma treatment. The entire surface roughness factors increased with increasing treatment time.

In particular, the R_z of the argon plasma-treated CIIR rubber (25.78 μm) was rougher than that of oxygen plasma-treated rubber (12.88 μm). These results imply that change in morphology due to surface roughness reduced the real contact area against the SUS440C ball, thus, the adhesion force between stainless steel ball and CIIR was decreased.

Fig. 5 shows the 3D laser scanning microscope photographs of argon plasma-treated CIIR rubber. In the absence of argon plasma treatment at 1 min, the subsurface of the CIIR rubber looks less granular and generally has a smoother shape. However, with 5 min argon plasma treatment at 200 W, changes in

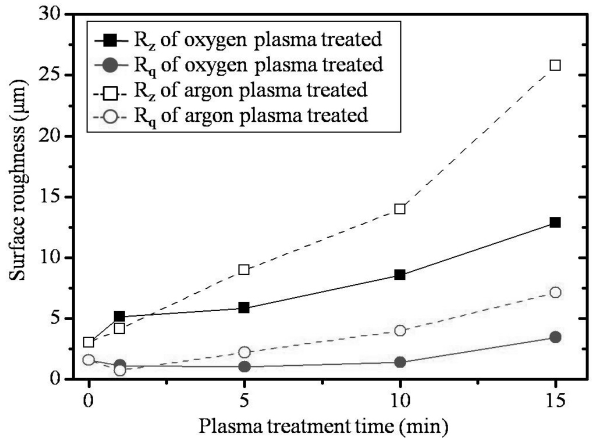

Fig. 4. Surface roughness changes of CIIR sheet as a function of plasma treatment time. The measurements were done for oxygen (dotted line) and argon (solid line) plasma-treated CIIR sheets. The surface roughness parameters, R_z (maximum peak height roughness) and R_q (root mean square roughness) are defined by JIS B 0601 2001.

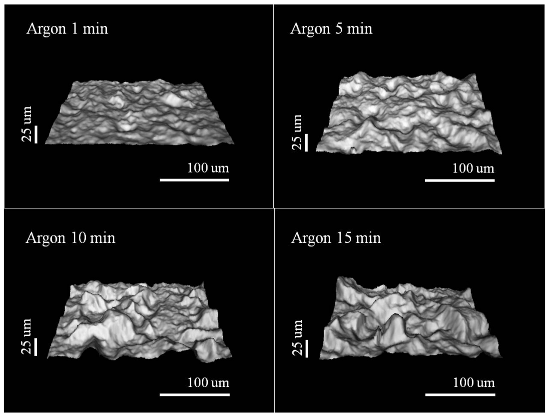

Fig. 5. 3D laser scanning microscope images of CIIR sheets after argon plasma treatment with 200 W at a gas pressure of 30 Pa for treatment times of (a) 1, (b) 5, (c) 10, and (d) 15 min.

the surface were visible. The surface of CIIR rubber pattern was changed compared to the untreated CIIR rubber. The subsurface of the CIIR rubber grew rougher with increasing treatment time (Fig. 5(c)). also In addition, the both width and height of asperities surface increased with treatment time. In this study, the 200 W, 15 min treatment conditions resulted in the roughest surface. As a result, this surface roughness change by etching effect might have affected the adhesion force, which is largely dependent on the contact geometry and surface topography [6].

4. Conclusions

In our previous work, it was demonstrated that the adhesion force between chloride-isobutene-isoprene rubber (CIIR) and stainless steel is drastically decreased by surface wave-excited plasma treatment of CIIR surface with oxygen and argon gases [4]. In this work, we tried to clarify the change in surface mechanical properties of CIIR sheet after the plasma treatments. In order to evaluate the change in Young's modulus of CIIR sheet surface, the top 50 μm thickness of a plasma-treated CIIR sheet was cut away to avoid the bulk property.

The Young's modulus measurements with nano-indenter showed the clear difference between the surface and bulk elastic modulus of CIIR rubber after plasma treatment, indicating the success of surface modification without changing bulk property. In addition, it was shown that the plasma treatment with Ar gas increased the Young's modulus of CIIR sheet surface from 38 MPa to 236.4 MPa. Surface roughness of CIIR rubber also became rougher with both oxygen and argon gas plasma treatments. These changes in Young's modulus and roughness at the surface of CIIR sheet are considered to be the main reasons for the plasma-assisted reduction of adhesion force between stainless steel ball (SUS 440C, JIS) and CIIR sheet.

References

[1] M. Tuda and K. Ono, New-type microwave plasma source excited by azimuthally surface waves with magnetic multi-cusp fields, *J. Vac. Sci. Technol.,* 16 (5) (1998) 2832-2839.

[2] H. Kousaka and K Ono, Numerical Analysis of the Electromagnetic Fields in a Microwave Plasma Source Excited by Azimuthally Symmetric Surface Waves, *Jpn. J. Appl. Phys.,* 41 (1) (2002) 2199-2206.

[3] H. Kousaka, S. Kishine and N. Umehara, High-speed and uniform deposition of amorphous carbon on inner surface of metal tube with microwave-excited high-density plasma column, *Proc. of Micro Nanomechatronics and Human Science,* (2007) 490-493.

[4] J. H. Kim, I. Nitta, N. Umehara, H. Kousaka, M. Shimada and M. Hasegawa, Relationship between Real Contact Area and Adhesion Force of Plasma-Treated Rubber Sheets Against Stainless-Steel Ball, *Tribology Online*, 4 (1) (2008) 361-365.

[5] K. F. Grythe and F. K. Hansen, Surface Modification of EPDM Rubber by Plasma Treatment, *Langmuir*, 22 (14) (2006) 6109-6124.

[6] N. A. Burnham and A. J. Kulik, *Handbook of Micro/Nanotribology*, B. Bhusan, ed., 2nd edition, CRC Press, Boca Raton, FL, USA (1998).

[7] G. Briggs, B. Briscoe, Surface roughness and the friction and adhesion of elastomers, *Wear,* 57 (1979) 269-280.

[8] K. Maeda, A. Bismarck, B. Briscoe, Effect of bulk deformation on rubber adhesion", Wear, 263 (2007) 1016-1022.

[9] W. C. Oliver and G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.,* 7 (6) (1992) 1564-1583.

[10] J. H. Kim H. Kousaka, N. Umehara, M. Shimada and M. Hasegawa, Study of the decrease in adhesion force between chloride-isobutene rubber and stainless-steel by plasma treated on the rubber surface, *Adv. Mater. Res.,* 48 (2008) 459-462.

Jong-Hyoung Kim received his B.S. degree at the School of Mechanical Engineering from Yeungnam University, Korea, in 2006. He then received his M.S. in Mechanical Engineering from Kyungpook National University, Korea. He is currently Ph.D. candidate at the school of Mechanical Science and Engineering, Nagoya University, Japan. His research interests include tribology, polymer, and plasma treatment.

Noritsugu Umehara received his Doctorate in Engineering from Tohoku University, Japan in 1988. After his academic career as a Research associate and an Associate Professor in Tohoku University, he became Professor at the Mechanical Engineering Department of Nagoya Institute of Technology, Japan, in 2002. He is currently Professor of Mechanical Science and Engineering department in Nagoya University, Japan. His research interests include tribology and green-manufacturing.

Hiroyuki Kousaka received his Doctorate in Engineering from Kyoto University, Japan, in 2003. After his academic career as a Research associate in Nagoya Institute of Technology, he became a Research Associate in 2004 and Lecturer in 2006 in Nagoya University, Japan. He is currently Associate Professor of Mechanical Science and Engineering Department in Nagoya University, Japan. His research interests include plasma, tribology, and advanced surface manufacturing.