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Surface Modification of Silicone EVD Tube by Low Temperature Plasma

D. L. Cho†, and Y. D. Lee
Faculty of Applied Chemical Engineering, Chonnam National University, Kwangju 500-757, Korea
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저온 플라스마를 이용한 실리콘 EVD 튜브의 표면개질

조 동 련† · 이 영 득
전남대학교 응용화학공학부
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ABSTRACT : Surface modification of silicone rubber by low temperature plasma process was investigated to improve quality of silicone EVD tube by reducing tackiness and hydrophobicity. Treatment with nonpolymer-forming plasmas and thin film deposition with polymer-forming plasmas were tried. Tackiness could significantly be reduced, especially by thin film deposition. As a result, the tube became slippery and less vulnerable to contamination in laboratory environment. Inner as well as outer surface of the tube could be changed to be hydrophilic if the plasma contained oxygen. As a result, initial hydrodynamic resistance was reduced. The surface modification did not give any bad influence on mechanical properties of the silicone tube in most cases. Rather, some properties such as Young's modulus, ultimate tensile strength and elongation at break were improved.

요 약 : 점착성과 소수성을 제거함으로써 실리콘 EVD 튜브의 성능을 향상시키기 위하여 저온 플라스마 공정을 이용한 실리콘 고무의 표면개질을 시도하였다. 고분자를 형성하지 않는 플라스마를 이용한 표면처리와 고분자를 형성하는 플라스마를 이용한 박막코팅 방법을 시도하였다. 박막코팅을 할 경우에 점착성이 특히 크게 줄어들었으며, 결과적으로 실험실 환경에서의 오염 정도를 줄일 수 있었다. 산소를 포함한 플라스마를 이용할 경우 튜브의 외부뿐만 아니라 내부의 표면을 친수성으로 개질시킴으로써, 결과적으로 수력학적 초기 저항을 줄일 수 있었다. 대부분의 경우에 있어서, 이러한 표면개질은 실리콘 튜브의 기계적 물성에 아무런 악영향을 끼치지 않았으며 영율, 인장강도, 인장율 등의 물성은 오히려 향상되었다.

Keywords : silicone rubber, surface modification, low temperature plasma process, tackiness, hydrophilic.

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†대표저자(*e-mail : dlcho@chonnam.chonnam.ac.kr*)

I. Introduction

Silicone rubber has a wide variety of applications for commercial products because of its outstanding properties in low-temperature flexibility, heat resistance, chemical resistance, and weathering resistance.[1,2] However, its tacky and hydrophobic nature causes trouble in some applications such as biomedical applications. Tacky surface tends to stick with any material, which causes handling and contamination problems. Hydrophobic surface shows poor wettability and poor adhesion with other materials.

A lot of effort has been made to overcome such drawbacks without affecting bulk properties. Major attention was paid on the development of surface modification technique. The reported techniques are sol-gel modification,[3] laser treatment,[4] plasma treatment,[5-7] and chemical, photochemical, or plasma-induced graft polymerization.[8-13] They were mainly used for the improvement of wettability, adhesion and biocompatibility.

Silicone EVD(Extra Ventricular Drainage) tube is a disposal medical device which is used for sucking out body fluids during brain surgery. Therefore, it is required that outer surface is to be less vulnerable to contamination during handling and inner surface is to be less resistant to the flow of body fluids.

In this study, low temperature plasma process was used for reduction of tackiness and hydrophilic modification of silicone EVD tube, which is suitable for the modification of inner wall of small tube. Both non polymer-forming plasmas and polymer-forming plasmas14 were used and the modification effects were evaluated. Relationships between tackiness and contamination and between hydrophobicity of inner tube wall and resistance to the flow of body fluid were investigated. Effects of the plasma modifications on the mechanical properties of the tube were also investigated.

II. Experimental

Silicone rubbers with shapes of plate(thickness of 1.35mm) and tube(EVD, inner diameter of 2mm) were used as substrates. They were obtained from Yusin Medical and cleaned in a ultrasonic cleaner for 10 minutes before the plasma surface modification process.

Surface modifications were carried out in an RF type of plasma reactor. A glass cylinder with inner diameter of 15cm and length of 30cm was used as a reaction chamber for the modification of plate and outer surface of tube. A glass tube with inner diameter of 4mm and length of 30cm with multiple external electrodes was used as a reaction chamber for the modification of inner surface of tube, as shown in Fig. 1.

Tackiness was determined by measuring sliding angle of silicone rubber on a glass plate. Degree of contamination was determined by observing with a microscope after exposing the samples to laboratory environment at the same condition for 120 hours. Hydrophobicity was determined by measuring water contact angle with a contact angle meter(Erma, G-1) in the case of plate and by measuring capillary rise in the case of inner surface of tube. Chemical structure of the modified surfaces were analyzed with FTIR-ATR(Jasco, FT/IR 430). Mechanical properties of the tubes

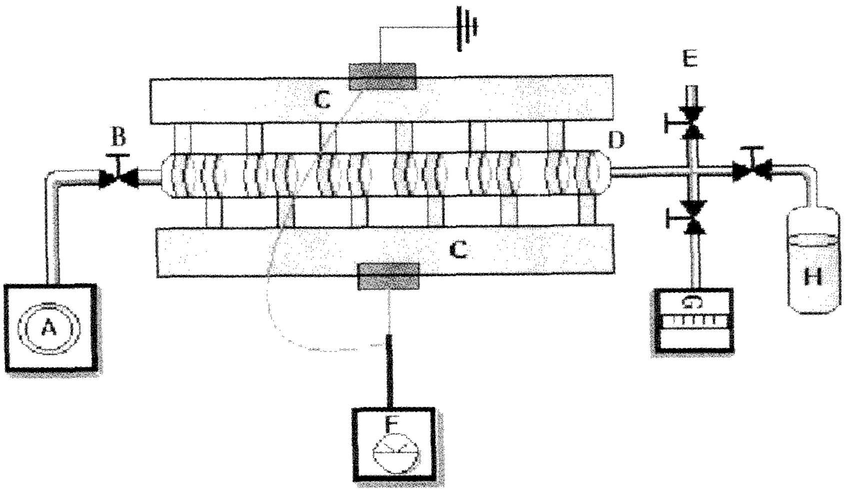

Fig. 1. Schematic diagram of a plasma reactor for treatment of inner surface of tube.
(A: vacuum pump, B: shut-off valve, C: electrodes, D: reaction chamber, E: gas inlet, F: RF power supply, G: pressure gauge, H: liquid monomer).

were measured with UTM(Tira, Tiratest27025).

Ⅲ. Results and Discussion

Silicone rubber plates were treated with some polymer-forming plasmas (hexamethyldisiloxane (HMDSO), HMDSO+O_2, methane, and acetylene plasmas) and nonpolymer-forming plasmas(Ar and O_2 plasmas), and sliding angles on a glass plate were measured to check their tackiness. Values of the sliding angles and plasma conditions for the treatments are listed in Table 1. As shown in Table 1, tackiness could be reduced by any plasma treatment. However, there was difference in the extent of reduction. Sliding angles of plates treated with polymer-forming plasmas were much lower than sliding angles of plates treated with nonpolymer-forming plasmas. Therefore, treatment with polymer-forming plasma seems to be more efficient than treatment with nonpolymer-forming plasma for the reduction of tackiness. In

Table 1. Sliding Angles of Plasma treated Silicone Rubbers on a Glass Plate

Plasma conditions			Treatment time (min)	Sliding angle (deg)
Gases or Monomers	Pressure (mtorr)	Discharge power (Watt)		
-	-	-	0	87
O_2	69	40	2	62
Ar	96	40	10	31
HMDSO	17	40	10	21
HMDSO+O_2	77	40	10	26
methane	187	40	15	25
acetylene	909	10	10	24

case of nonpolymer-forming plasma treatment, Ar plasma treatment reduced the sliding angle more than O_2 plasma treatment.

Tackiness of silicone rubber results from its flexible linear molecular chains. In polymer-forming plasma, tackiness is reduced because highly crosslinked thin film is deposited on the surface of silicone rubber. Ar plasma can induce surface-crosslinking to some extent although no polymer is formed, but O_2 plasma leads to oxidation or removal of some surface molecules of silicone rubber.

Those samples were exposed to laboratory environment for 120 hours, and degree of contamination on the surface was examined with a microscope. The microscopic pictures are shown in Fig. 2. As shown in Fig. 2, the plasma treated surfaces showed more clean surfaces than the untreated one. Therefore, it is judged that tackiness should be reduced to keep clean surface. Among the plasma treated samples, HMDSO+O_2 plasma treated sample showed the cleanest surface.

While tackiness and contamination are problems related to outer surface of EVD tube, hydrophobic nature of silicone rubber is a problem related to inner surface of EVD tube. Since water does not wet well on hydrophobic surface, there will be hydrodynamic resistance while body fluids flow through the tube. Therefore, hydrophilic modification of inner surface is necessary for easy flow of body fluids.

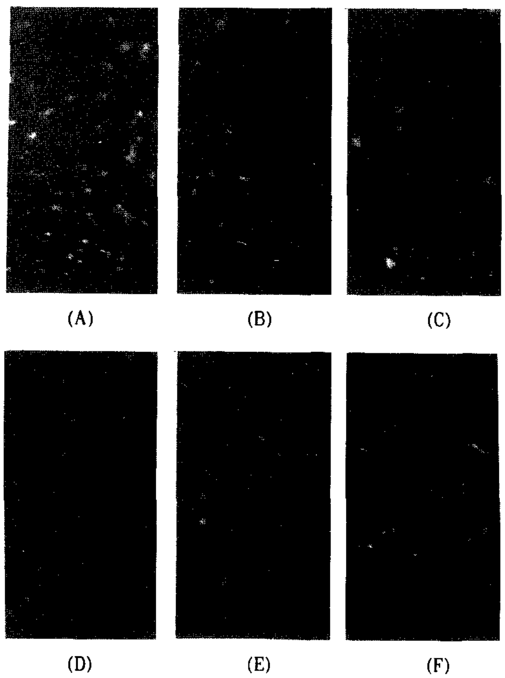

Fig. 2. Microscopic pictures(10×40) of contaminated surfaces of silicone rubbers. (A: untreated, B: O_2 plasma treated, C: HMDSO plasma treated, D: HMDSO+O_2 plasma treated, E: methane plasma treated, E: acetylene plasma treated)

Water contact angles of silicone rubber plates treated with various plasmas were measured to check their hydrophilicity. The results are listed in Table 2. As shown in Table 2, samples treated with oxygen-containing plasmas showed very low values of water contact angle indicating high hydrophillicity, 18° for O_2 plasma treated, 21° for HMDSO/O_2(HMDSO followed by O_2) plasma treated and 33° for HMDSO+O_2(mixture of HMDSO and O_2) plasma treated, while the others showed high values of water contact angle indicating hydrophobicity. Then, inner surface of EVD tube was modified using a plasma reactor shown in Figure 1 and their hydrophilicity was checked by capillary rise method. The results are also listed in Table 2. The same trend was observed. Values of capillary rise are 7mm for O_2 plasma treated, 6mm for HMDSO/O_2 plasma treated, 4mm for HMDSO

Table 2. Water Contact Angles and Capillary Rises of Various Silicone Plates and Tubes

Type of modification	Water contact angles on plate(deg)	Capillary rise in tube (mm)
Untreated	103	0
O_2 plasma treated	18	7
HMDSO plasma treated	98	0
HMDSO/O_2 plasma treated	21	6
HMDSO+O_2 plasma treated	33	4
Methane plasma treated	96	0
Acetylene plasma treated	94	0

$+O_2$ plasma treated, and no capillary rise was observed for the other cases.

Hydrodynamic resistance of the tube was checked by connecting the tube with a coke located at the bottom of a beaker which contained a certain amount of water. The minimum amount of water in the beaker required to make water flow through the tube and the total amount of water which passed through the tube for 10 minutes were measured. The results are listed in Table 3. Initial resistance was quite correlated with the trends in hydrophilicity of the inner surface. Larger amount of water in the beaker, thus higher hydraulic pressure was required to make water flow for hydrophobic surface than hydrophlic surface. However, total amount of water passed through for 10 minutes showed opposite trend. Larger amount of water passed through the tube for hydrophobic surface than for hydrophilic surface in the case of plasma treated tubes. This may be explained by thermodynamics of liquid-solid interface. Hydrophilic surface may be easier to be wet by water than hydrophobic surface in the beginning due to higher surface energy. However, there may be higher shear stress on the hydrophilic surface if it is totally wet at all due to higher work of adhesion. It is not clear why least amount of water passed through untreated tube despite its high hydrophobicity. It may be related to its tackiness.

Table 3. Minimum Amount of Water Required for Initial Flow and Total Amount of Water Passed Through Tubes for 10min

Type of moification	Minimum amount (g)	Total amount (g)	Water contact angles (deg)
Untreated	75.6	76.4	103
O_2 plasma treated	56.5	85.3	18
HMDSO plasma treated	92.2	88.6	98
HMDSO/O_2 plasma treated	60.6	82.3	21
HMDSO+O_2 plasma treated	63.1	81.7	33
Methane plasma treated	88.7	88.1	96
Acetylene plasma treated	79.4	86.5	94

Influence of the surface modification on mechanical properties of the EVD tube was investigated by tensile test. The results are shown in Table 4. The plasma treatments did not give any damage to the bulk properties of EVD tube except for O_2 plasma treatment, rather the mechanical properties were improved. Young's modulus was increased for all samples, tensile strength was either the same or increased, and elongation at break was increased except for the case of methane plasma treated sample. O_2 plasma treatment reduced ultimate tensile strength and Young's modulus.

Fig. 3 shows FTIR-ATR spectra of untreated and some plasma treated silicone rubbers. HMDSO $+O_2$ and HMDSO/O_2 plasma treated samples show chemical structures quite similar to that of ntreated one. Thus, no harmful side effect would be expected in the practical use. In case of methane plasma treated sample, new peak of hydrocabons is observed in the shape of wide shoulder near $3000cm^{-1}$.

Table 4. Mechanical Properties of Plasma Treated Silicone Tubes

Type of modification	Ultimate tensile strength (MPa)	Elongation at break(%)	Young's modulus (MPa)
Untreated	2.82	580	1.05
HMDSO plasma treated	2.78	613	1.62
HMDSO+O_2 plasma treated	3.03	679	1.64
Methane plasma treated	2.83	538	1.67
Acetylene plasma treated	2.98	600	1.68
O_2 plasma treated	2.36	621	1.30

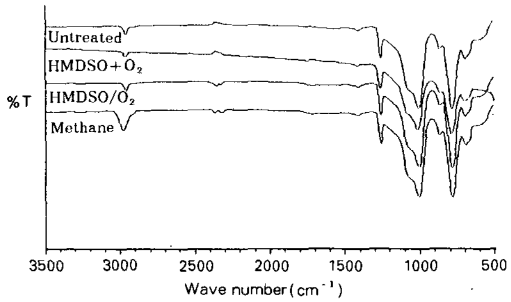

Fig. 3. FTIR-ATR spectra of untreated and $HMDSO+O_2$ plasma treated silicone rubbers.

Considering all the results obtained so far, $HMDSO+O_2$ plasma treatment seems to be the most suitable for the surface modification of EVD tube. $HMDSO/O_2$ plasma treatment is also suitable but it is a double step process while $HMDSO+O_2$ plasma treatment and the other treatments are single step processes.

Ⅳ. Conclusion

Silicone EVD tube has problems of handling, easy contamination, and high initial hydraulic resistance, which results from drawbacks of silicone rubber such as high tackiness and hydropbobicity. Since the drawbacks are related to surface proeprties, they can be overcome by proper surface modification. Low temperature plasma process is a suitable safe process for the surface modification. It is better to use polymer-forming plasma than nonpolymer-forming plasma and $HMDSO+O_2$ plasma may be the most suitable plasma.

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