Characterization of Plasma-Induced Graft Polymerization of 2-Hydroxyethyl Methacrylate onto Silicone Rubber

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SYNOPSIS

Graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) as attempted onto the surface of silicone rubber membrane, which was pretreated by Ar-plasma, then exposed in oxygen to introduce a peroxide group. The effect of the amount of HEMA grafted on Ar-plasma-treated and graft copolymerization was examined for various parameters of power, pressure, time, reaction time, and concentration of HEMA aqueous solution. The surfaces were characterized by ATR–FTIR, ESCA, contact angle, and SEM. PHEMA was indicated by ATR–FTIR and ESCA analysis to be present successfully onto the grafted surface of silicone rubber membrane. The stable wettability, as demonstrated once the PHEMA grafted films, indicated contact with a hydrated environment by the study of contact angle. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Surface properties of polymers are often as important as their bulk properties. Low-temperature plasma has been studied to modify the surface properties of polymer membranes.[1,2] Silicone rubber, used in my study, has been primarily used as a soft-tissue substitute because of its excellent softness, stability, and bioinertness. However, silicone rubber is also a hydrophobic substrate in the study; it possesses properties of water-soluble monomers onto the surface of hydrophobic substrates having produced permanent hydrophilic surface, which consequently enhances the adhesion of protein and the attachment of cells as biomaterial.[3,4]

Polymer grafting has also been employed for the surface modification for the function of polymers. The methods investigated for the surface grafting have involved either immobilization of polymer chains onto a polymer surface by coupling reactions,[5,6] or graft polymerization of monomers via plasma,[7–9] corona discharge,[10] UV irradiation,[11,12] gamma-ray irradiation,[13–15] or ozone exposure.[16]

The advantage of plasma-induced graft polymerization is that the location of grafting is definitely limited to the surface region of the polymer material.[8] The result of surface modification of HEMA being obtained by plasma-induced graft copolymerization is described in this article. The inspection with an attenuated total reflection ourier transform infrared spectrophotometer (ATR–FTIR), electron spectroscopy for chemical analysis (ESCA), contact angle, and scanning electron microscopy (SEM) is used for making a characterization regarding these surfaces during each stage of modification.

EXPERIMENTAL

Materials

The polymer used for grafted polymerization is composed of silicone rubber films (MDX4-4210, medical grad elastomers, Dow Corning, Midland, MI). The thickness of silicone rubber film was 340 μm to 360 μm by hot compression molding (250 psig, 75°C) and the diameter was 9.5 mm by trephine. The HEMA monomer (supplied by Merck Chemical Company, Inc.) was redistilled under vacuum (3–5 torr, 52°C) to make it free from the inhibitor. All other solutions used were of reagent analytical grade.
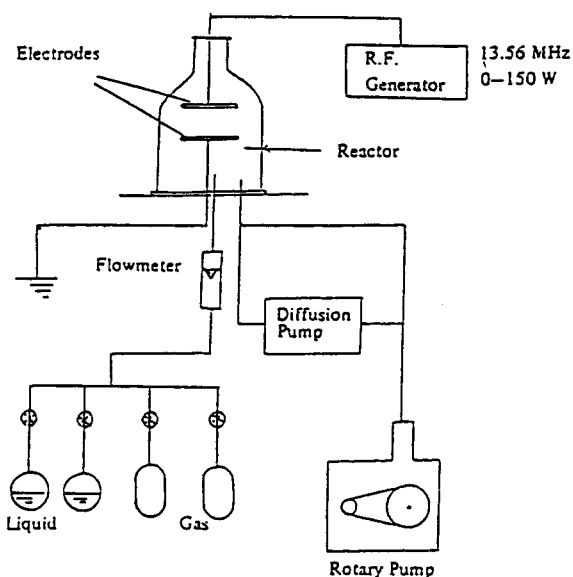
Figure 1   Schematic diagram of the glow discharge apparatus.

Plasma Treatment

A schematic diagram of the main part of the plasma reactor used in this work is illustrated in Figure 1. This apparatus is equipped with a bell-jar type reaction called a Samco model PD-2. The frequency applies 13.56 MHz and consequently requires an impedance-matching unit. Glow discharge treatment is carried out onto the silicone rubber as follows. Silicone rubber membranes are placed between the two electrodes. The pressure in the bell-jar is reduced to 10 mtorr, followed by introduction of Ar-gas into the bell-jar at flow rate of 5 L/min for 1 min three times. Current was supplied to produce plasma state at a given electric power and the film was exposed to plasma for a predetermined time. Oxygen gas was used in the reactor to form a peroxide group on the silicone rubber membrane.[8] Y. Ikada et al. reported that graft copolymerization must be performed immediately.[17] Table I shows the interval of various parameters used in this study.

Graft Copolymerization

The membranes exposed to oxygen gas after Ar-plasma treatment were immersed in a HEMA aqueous solution in glass ampules. Following vigorous degassing three times, the ampules were sealed and kept in a water bath (60°C) for a predetermined time. Grafted films were taken out of glass ampule and washed with 95% ethanol at 40°C overnight three times under ultrasonics and then dried by vacuum. The amount of grafted PHEMA was deter-

mined with the microbalance (Sartorius RC system) to weigh as shown in the following equation:

$$\text{Grafted amount } (\mu g/cm^2) = \frac{W_1 - W_0}{A} \quad (1)$$

where W_1 is the dry weight of the grafted film, W_0 is the dry weight of the original film, and A is area of the silicone rubber film ($2 \times 0.702 \text{ cm}^{-2}$).

Apparatus

ATR–FTIR

ATR–FTIR was recorded using a Bomem DA 3.002. KRS-5 (Harrick) of IR crystal cell on Fourier transform infrared spectrophotometer. Scanning was carried out from 4,000 cm^{-1} (2.5 μm) to 650 cm^{-1} (15.4 μm) for the sake of confirming the formation of the graft copolymerization.

ESCA Study

A spectrometer model ESCA 850 manufactured by Shimadzu Corp., Japan, was used. The ESCA data analyses were processed with a model ESPAC 210-S, Kyoto: 250 W was supplied for the current of analysis; take-off angle of 60°, was employed for carrying out the electron spectroscopy for chemical analysis measurement of control, Ar-plasma-treated, and PHEMA-grafted film at a pass energy of 1253.6 ev with a Mg Kα X-ray source.

Contact Angle Measure

Static contact angle of water on plasma-treated and PHEMA-grafted membranes were maintained by

Table I   Interval of Various Parameters Used in the Experiment

Power (W)	Time (sec)	Pressure (mtorr)	HEMA (Conc) Aqueous Soln (%)	Reaction Time (min)
20	10	100	1	15
40	30	200	3	30
60	60	300	5	60
80	120	600	10	120
100	180	908	25	180
	240	1,280	50	240
			75	300
				360

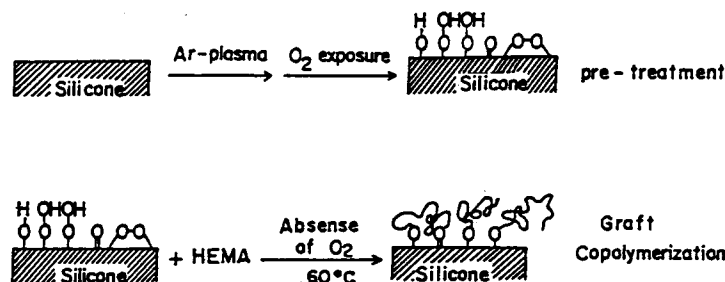Conc, concentration; Soln, solution.

Figure 2 Schematic representation of the surface modification of silicone rubber film.

relative humidity meter (Today) in an air-conditioned room. There were wet and dry methods for storage of treated silicone rubber membranes. Identification of wet and dry methods for the membranes which were placed into a sample cell included deioned water; they were placed into desiccator by vacuum. The treated membranes were measured at 25°C and 65% relative humidity with the sessile drop method[17] using a contact angle goniometer (Emra model G-1). A 2 μL deionized water bubble was placed on the polymer surface using a micropipette. Ten separate drops were recorded and averaged for each ampule.

SEM Study

A SEM (Hitachi-570), 20 KV, was used for examining the morphology of control, Ar-plasma, and PHEMA-grafted silicone rubber membranes.

RESULTS AND DISCUSSION

Graft Polymerization

PHEMA was graft copolymerized onto the Ar-plasma-treated film in HEMA aqueous solution at 60°C without any additive. The reaction paths of plasma-induced graft copolymerization of the surface modification are shown in Figure 2. The first step produced the peroxide group by Ar-plasma pretreatment in the presence of oxygen exposure to the surface region of silicone rubber films. The second step, graft copolymerization, was carried out at 60°C by the thermal decomposition of the peroxide group. The influence of the Ar-plasma-treated condition on the grafted amount was investigated.

The amount of PHEMA per square centimeter of film was found to be obtainable under the experimental conditions used, which were sensitively affected by Ar-pressure in the bell-jar (Fig. 3). The grafted amount decreased after passing a maximum at 200 mtorr. The amount of PHEMA grafted per

square centimeter of film is plotted in Figure 4 as a function of the plasma-treated power. The higher the power supplied, the larger the amount of PHEMA grafted onto the surface of silicone rubber. The relationship between the PHEMA-grafted amount and plasma-treated time is shown in Figure 5. The grafted amount did not monotonously *increase* with the increasing plasma-treated time, but *decreased* after passing a maximum at 120 sec. The effect of a concentration of HEMA aqueous solution on the amount of PHEMA grafted onto silicone rubber films is shown in Figure 6. The grafted amount of PHEMA increased from 0% to 25%, then decreased, reaching a maximum of 1,585 μg/cm^2. Increasing the amount of grafted PHEMA decreased
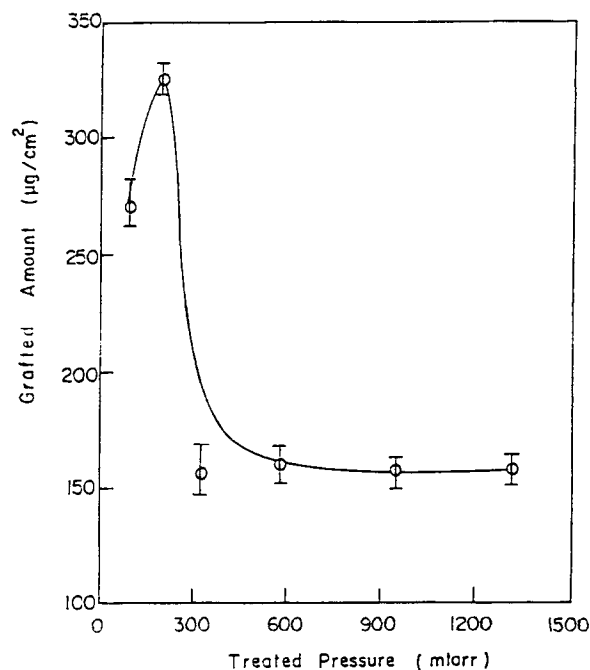

Figure 3 The effect of the amounts of grafted PHEMA on Ar-plasma treated from 100 to 1,300 mtorr of pressure (60 W, 60 sec).
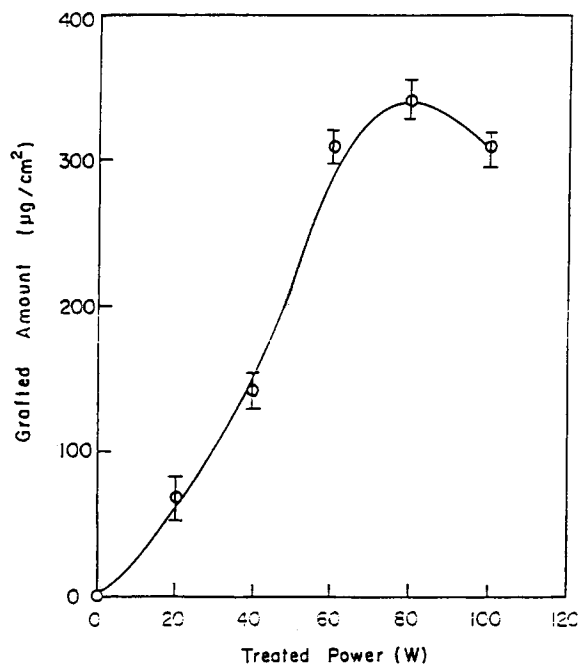
Figure 4   The effect of the amounts of grafted PHEMA on Ar-plasma treated from 0 to 110 W of power (200 mtorr, 60 sec).
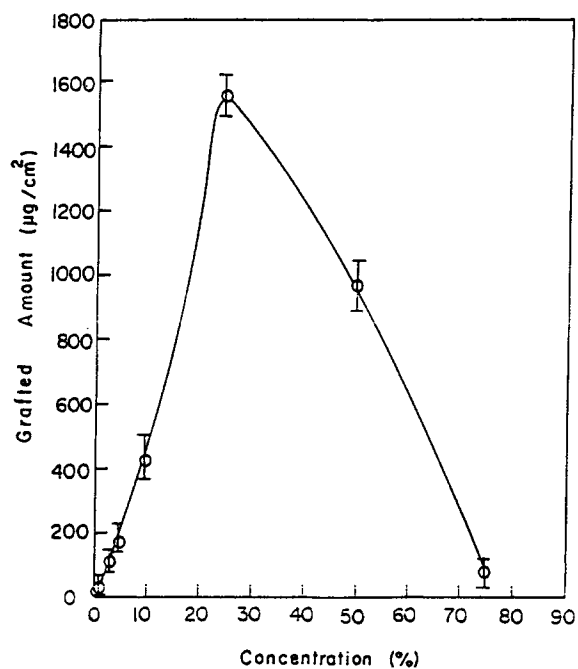

Figure 6   The effect of PHEMA grafted amount on the concentration of solution (60 W, 90 sec; reaction temperature 60°C, reaction time 60 min).
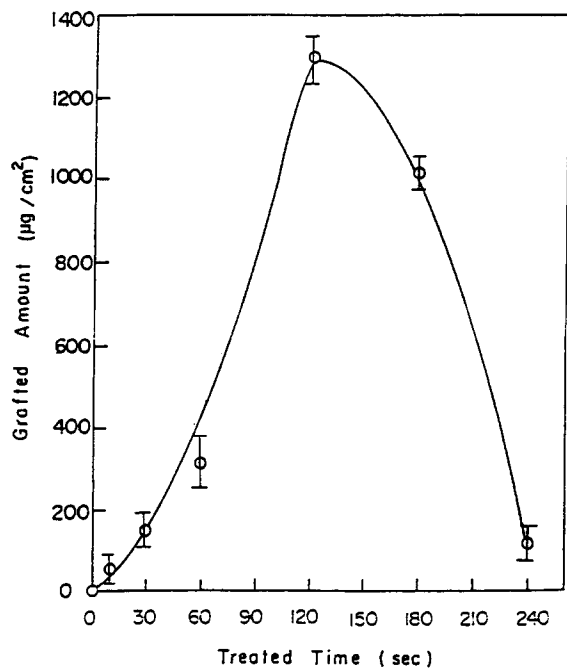

Figure 5   The effect of the amounts of grafted PHEMA on Ar-plasma treated from 0 to 240 sec of treated time (60 W, 200 mtorr).
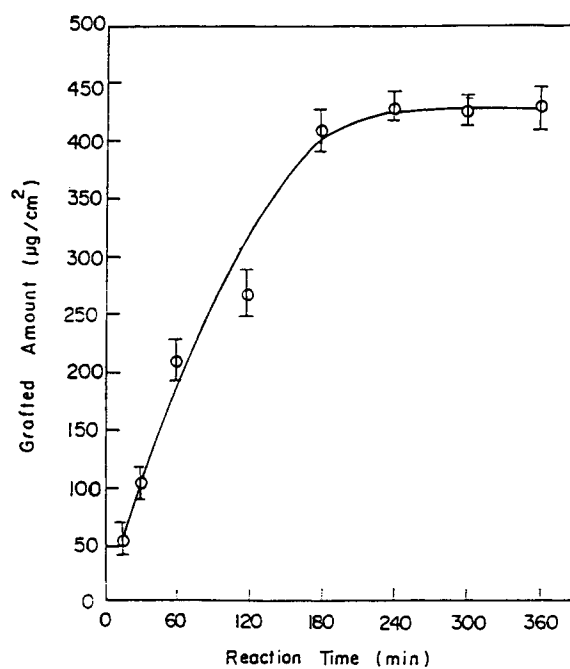

Figure 7   The effect of PHEMA grafted on graft copolymerization reaction time (200 mtorr, 1 min; 10% HEMA aqueous solution, reaction temperature 60°C).
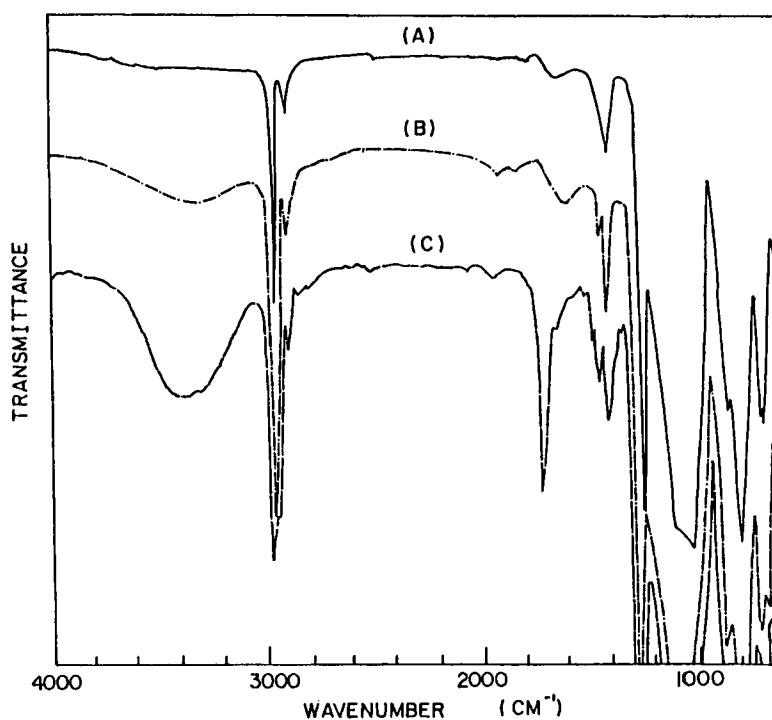
Figure 8 ATR–FTIR spectra for (a) control, (b) Ar-plasma-treated, and (c) PHEMA-grafted.

the transparency, which consequently limited its application in biomaterials. This event was a consequence of the increasing extent of initiation and propagation of graft polymerization reactions with concentration. Above 25%, however, the grafted amount decreased progressively. The decrease in the grafted amount showed that a correspondingly higher homopolymer formation also occurs, many precipitates of PHEMA were observed, and the viscosity of the solution rose in the glass ampule, leading to the lowering of the graft yield at a higher monomer concentration. Hence, 10% (v/v) HEMA concentration was thought to have been apparently used for other parameters of the experiment. The effect of reaction time on the amount of PHEMA grafted onto silicone rubber film is shown in Figure 7. The grafted amount increased with an increasing

reaction time, up to 180 min, beyond which the grafted amounts began leveling off.

Surface Analysis Characterization

ATR–FTIR Study

The respective Fourier transform ATR spectra of (a) control, (b) Ar-plasma-treated, and (c) PHEMA -grafted silicone rubber film are shown in Figure 8. The spectra of control and Ar-plasma-treated films exhibited similar bands. Silicone rubber membranes which were grafted with PHEMA exhibited a strong band of approximately $1,718.8$ cm^{-1} corresponding to a C$=$O group. A peak was also observed at approximately $3,300$ cm^{-1}, which was indicative of an

Table II Positions of Differential Peak on Surface of Silicone Rubber Membrane by Various Plasma Treatments (cm^{-1})

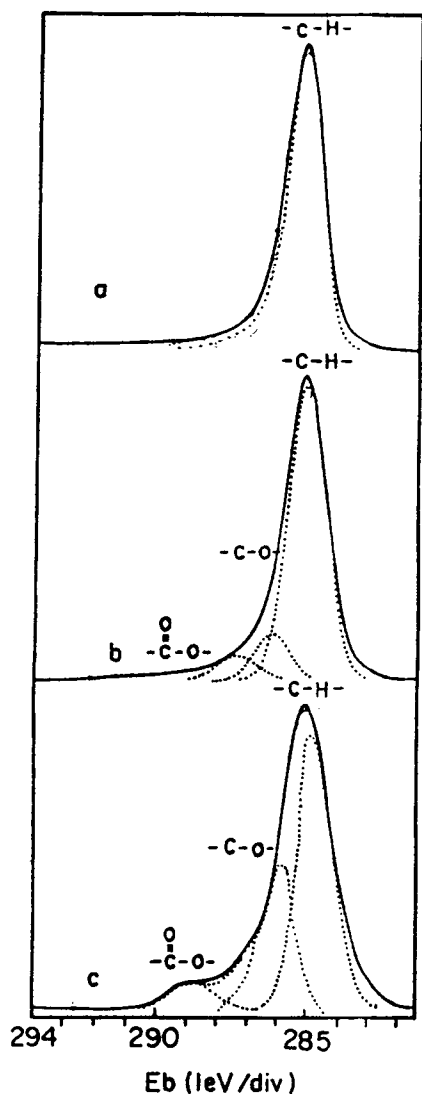|	—OH	C$=$O	Si—CH$_3$	Si—O—Si	CH$_3$
Control	—	—	1,245	1,020	802
Ar-plasma	3,302.5	—	1,245	1,020	802
PHEMA-grafted	3,347.1	1718.8	1,245	1,020	802

Figure 9 C1s curve fitting spectra for (a) control, (b) Ar-plasma-treated (60 W, 200 mtorr, 60 sec), and (c) PHEMA-grafted 56 $\mu g/cm^2$.

OH stretch. PHEMA was clearly demonstrated by the evidence of the spectra to have grafted onto silicone rubber films by covalent bonding with each other. Some varieties in the position of these peaks occurred for each path of modified silicone rubber film (Table II).

ESCA Study

ESCA was used for examining the bonding state and the elemental abundance of silicone rubber films. This is probably the most powerful technique available for the analysis of grafting polymer films.[18] The C1s curve fitting spectra of control, Ar-plasma-treated and PHEMA-grafted are shown Figure 9.

Table III   Percent (%) of Carbon Function by C1s High Resolution of ESCA

	Sample Number		
	C—H	C—O	O—C—O
Control	100	—	—
Ar-plasma	77.81	15.21	6.98
PHEMA-grafted	53.01	33.37	13.63

The main peak at 285.75 ev is attributed to all the carbon atoms bound to hydrogen for control, Ar-plasma-treated, and PHEMA-grafted silicone membranes. Figure 9b,c showed that the shoulders which occurred at 286.70 ev and 290.00 ev are a result of the carbon bound to oxygen as C — O, and O — C = O groups, in which the C1s spectrum exhibited a higher binding energy. This event indicated the information of carbon–oxygen functionalities.[19,20] Table III showed the surface elemental composition expressed as %, which indicated that the number of functional groups have increased by each stage of the treated silicone membrane at higher bonding energy.

Contact Angle Measurement

Figure 10 showed the effect of grafted amounts of PHEMA on contact angle onto silicone rubber film.
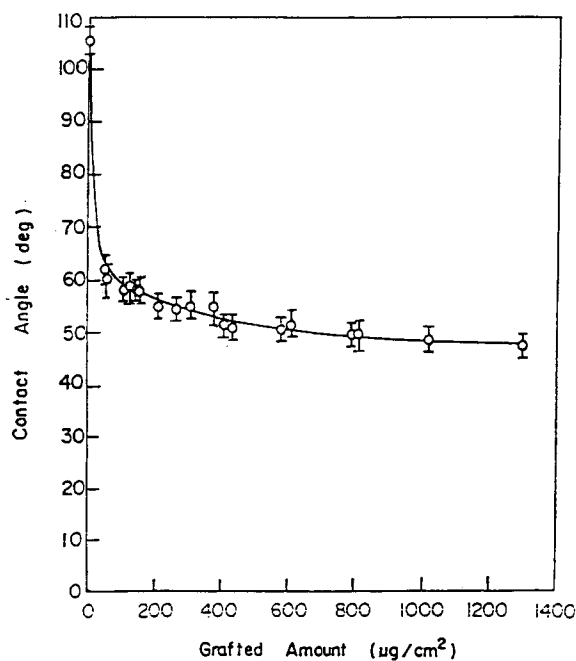

Figure 10 The effect of contact angle (degree) with PHEMA-grafted amount.
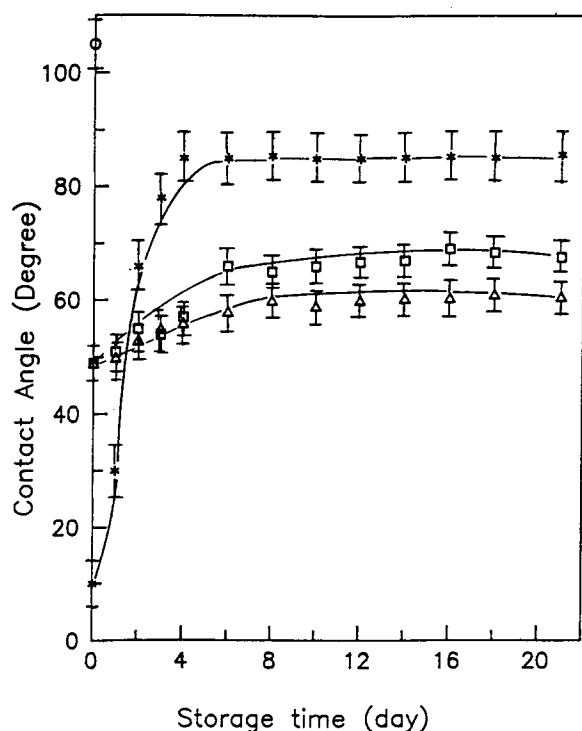
Figure 11 The effect of contact angle (degree) on storage time: (O) control, (*) Ar-plasma-treated (60 W, 200 mtorr, 60 sec), (□) storage by dry method PHEMA-grafted, (△) storage by wet method for PHEMA-grafted; grafted amount 210 $\mu g/cm^2$.

The PHEMA grafted onto the surface; this decreased the values of contact angle which were equaled to an increase in the wettability of the polymer. Given the values of 50° to 60° with an increasing grafted amount of PHEMA, the region of change was not relatively large. Grafting with PHEMA for silicone film then became a hydrophilic polymer film.

Figure 11 shows the effect of water contact angles on each stage of treated silicone rubber film, which was stored wet and dry, respectively. Using Ar-treated plasma, grafting with PHEMA took place in a thin layer onto silicone, which consequently increased the wettability of the polymers. The contact angles were measured for different membranes of storage with wet and dry methods. The membrane treated by Ar-plasma, grafted PHEMA, exhibited a gradual increase in contact angle with time, when these membranes were stored by the dry method; but the contact angle of treated silicone rubber films was a level-off valve following about 4 days of storage.

The event explained that oxidized surface attained by Ar-plasma treatment contained only oxygen polar groups because individual groups would

become buried into the bulk surface with time because of the small size of polar groups. That is, *if* the surrounding environment is of low interfacial energy.[21,22] The contact angles of the surface of PHEMA grafted attained a differential state from each other by respective storage methods of wet and dry. This phenomenon occurred because of the surface, demonstrating a variable orientation which could be strongly influenced by the properties of the surface contact on the different environments. This reversible orientation implemented to minimize interfacial energy is schematically shown in Figure 12. When these membranes contacted with air, occurring at a low-energy surface, polar groups were buried away from the polymer/air interface. Meanwhile, polar groups which came into contact with water at a high-energy surface remained at the polymer/water interface.[23]

SEM Study

The SEM of control, Ar-plasma-treated, and PHEMA-grafted silicone rubber films, respectively, are shown in Figure 13. The surfaces between the control and Ar-plasma-treated films were apparently similar. The surface, however, became rough homogeneously after PHEMA was grafted onto the surface. The surface, observed by SEM, was very uniform.
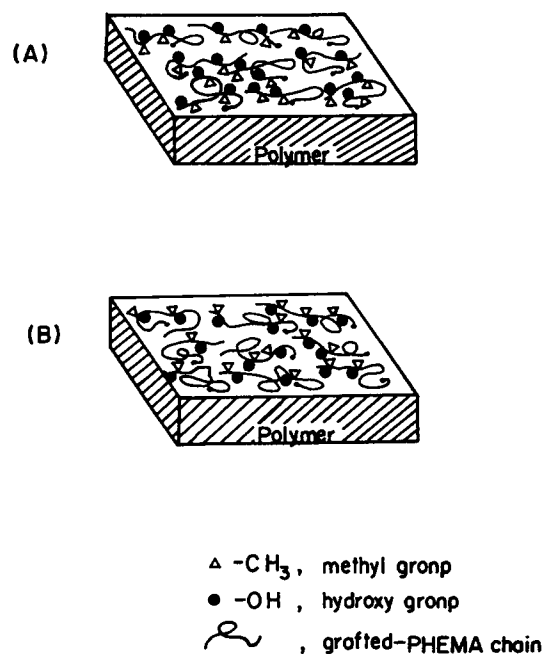

△ -CH₃ , methyl group
● -OH , hydroxy group
⌒ , grafted-PHEMA chain

Figure 12 Schematic demonstration of the reorientation of the function group by PHEMA grafted onto silicone rubber film.

(A)

x2.0k 0026 20kV 20μm

(B)

x2.0k 0003 20kV 20μm

(C)
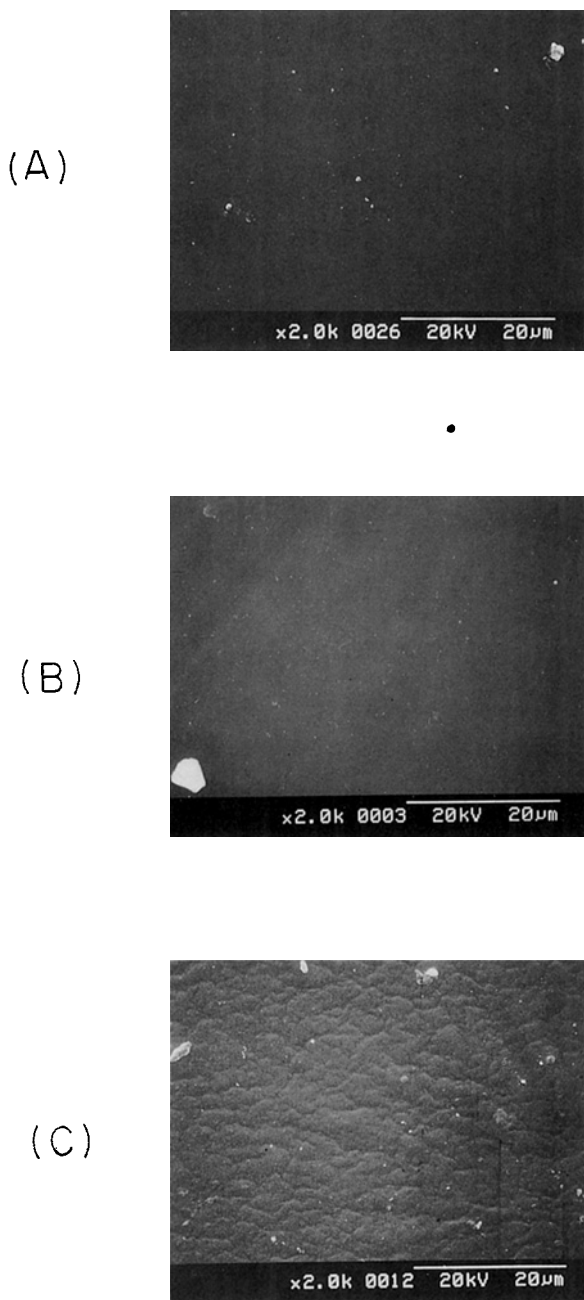
x2.0k 0012 20kV 20μm

Figure 13 SEM photographs of (a) control, (b) Ar-plasma-treated, and (c) PHEMA-grafted silicone rubber membrane.

CONCLUSION

Following the formation of peroxide group, the silicone film was modified with plasma-induced graft polymerization with HEMA onto the silicone rubber film. The effect of the amount of PHEMA grafted

on plasma-treated and graft copolymerized for various parameters were not similar, but most had a maximum value. Moreover, HEMA concentration affects transparency of silicone rubber membranes significantly. This phenomenon accounted for the optimization of the plasma parameters and graft copolymerization.

ATR–FTIR and ESCA have provided an adequate qualitative analysis for the presentation of these groups. The value of the contact angle was obtained to maintain 50° to 60° for different amounts of PHEMA graft. The effect of change of contact angle on PHEMA-grafted films was obtained for different methods of storage in wet or dry. This occurrence could possibly be a result of the surface contact on the different environments.

The potential use of properties of wettability for silicone films, with PHEMA applied as biomaterials, could be a direction of future research.

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