Surface Graft Polymerization onto Silicone

HIROO IWATA* and SHUJI ISOZAKI†

National Cardiovascular Center Research Institute, Fujishiro-dai, Suita, Osaka 565 Japan

SYNOPSIS

A method was developed for surface graft polymerization onto silicone. A silicone prepolymer carrying vinyl groups, which can be cured by a free-radical mechanism, was used. Acrylamide can be easily graft polymerized by simply heating the films made of a mixture of the silicone prepolymer and peroxide in an acrylamide monomer solution using an autoclave. Any complicated procedures, such as thorough degassing of the silicone films and the monomer solution, and sealing them into a glass ampoule, are not necessary. The grafted layer uniformly covered the silicone surface. The surface properties of the silicone become hydrophilic and slippery after grafting of the poly(acrylamide). © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Surface properties of polymeric materials are important in various applications.[1] Many methods, such as corona and glow discharge treatments, flame flashing, and a chromic acid mixture treatment, have been used to increase the wettability of polymers. Surface graft polymerization of hydrophilic monomers has also been carried out after activation of polymers by discharge treatments and irradiation with high energy radiation.[2-4] Few studies, however, have been done on the surface modification of silicone because hydrophobicity and inertness are some of the most important properties of the silicone surface and/or the activation of chemically inert silicone is difficult. In the past few years, serious problems have been recognized when biomedical devices made of silicone have been implanted long term. Ikada et al.[5] attempted to graft polymerize hydrophilic monomers on the surface of the silicone activated by a corona discharge treatment to increase the biocompatibility of silicone. However, they mentioned that it is critical to exclude oxygen from the silicone interior in order to produce effective graft polymerization. The other limitation of their method is that it may be only applicable to thin silicone films because only these films can be uniformly treated by corona discharge and extensive removal of oxygen is difficult from a silicone object having a complicated shape.

The aim of this work was to develop an easy method for the surface graft polymerization onto silicone.

MATERIALS AND EXPERIMENTS

Graft Polymerization

The silicone compound (MDF-0209, Dow Corning K. K. Kanagawa, Japan) was a mixture of 100 parts silicone prepolymer [poly(dimethylsiloxane-co-methyvinylsiloxane)] with a molecular weight of 1,500,000 Da carrying 0.142 mol % vinyl groups, 70 parts silica as a filler, and 10 parts silicone oil with a molecular weight of 480 Da as a plasticizer. The peroxide, 2,4-dichloro benzoyl peroxide (DCBPO, RC-2, Dow Corning Toray Silicone Co., Ltd., Tokyo, Japan), was added to the compound at various concentrations. These were well mixed using a roller mixer. The mixture was pressed to a 1-mm thickness on a glass plate for 12 h using a cold press to remove air voids. Electrophoresis grade acrylamide (AAm) was purchased (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and used without further purification.

Graft polymerization of AAm (a silicone prepolymer film), which was pressed on a glass plate, was immersed in a 10% AAm aqueous solution. Air dissolved in the film and the monomer solution were removed under reduced pressure using a vacuum

---

* To whom correspondence should be addressed.
† Currently at Dow Corning K.K., Yamakita Kanagawa 259-01, Japan.

pump for 30 min. The silicone prepolymer film im-
mersed in the AAm aqueous solution was heated to
and kept at 121°C for different times using an au-
toclave to produce polymerization. After polymer-
ization, the obtained films were washed with distilled
water and then heated at 150°C for 5 h to allow a
second curing of the silicone and to remove any 2,4-
dichloro benzoic acid formed as a degradation prod-
uct of DCBPO. The films were immersed and agi-
tated in distilled water for 24 h to thoroughly remove
the homopolymer. The amount of polyacrylamide
(PAAm) grafted was determined from liberated NH_2
by the ninhydrin method after hydrolysis of the
PAAm-grafted silicone in 2.5 N NaOH at 121°C for
20 min in an autoclave.[2]

### Surface Properties of PAAm-Grafted Silicone

For staining the grafted layer, the grafted PAAm
was first hydrolyzed in 0.5 N NaOH at 50°C for 30
min to poly(acrylic acid) and then immersed in an
aqueous solution of toluidine blue-O for 15 min. Its
cross section on a glass slide was observed using an
optical microscope (Optiphot-104, Nikon Corp.,
Tokyo, Japan). The static contact angles of water
on the silicone films were measured by a sessile drop
method using a contact angle meter (CA-S, Kyouwa
Kagaku Corp., Tokyo, Japan). A 10 μL water droplet
was placed on the dry films and the contact angle
was measured after 1 min. The reading was repeated
10 times and averaged. Dynamic friction coefficients
of the surfaces of the wet films against a stainless
steel ball were measured using a HEIDON-14
(Shinto Scientific Corp., Tokyo, Japan). X-ray
photoelectron spectroscopy (XPS) analyses were
performed using an ESCA 750 spectrophotometer
(Shimadzu Corp., Kyoto, Japan).

RESULTS AND DISCUSSION

The reactions expected to occur in this system are
schematically shown in Figure 1. Radicals produced
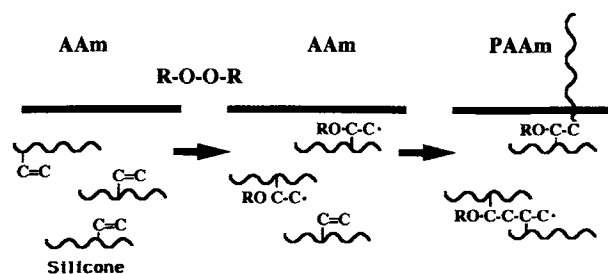
Figure 1   Schematic representation of the reactions that
occurred during graft polymerization onto the silicone.
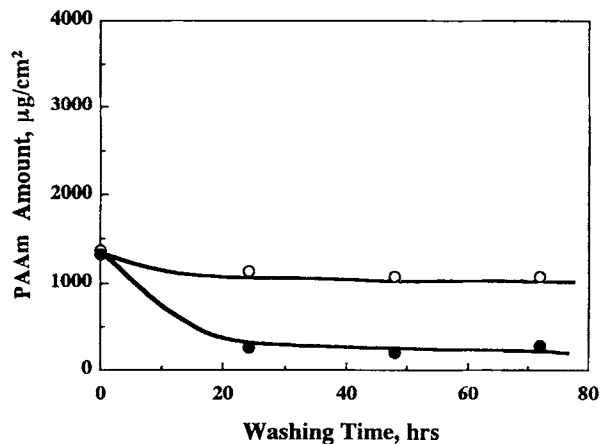
Figure 2   Effect of washing at 70°C on the amount
of poly(acrylamide) on the silicone films: (O)
poly(dimethylsiloxane-co-methyvinylsiloxane); (●)
poly(dimethylsiloxane).

by the decomposition of DCBPO react with pendant
vinyl groups of silicone prepolymer and yield sec-
ondary radicals. Crosslinks are formed by successive
addition of the radicals to vinyl groups of other sil-
icone prepolymers. A three dimensional network is
formed and the silicone prepolymer is cured by these
reactions. When the AAm monomer solution con-
tacts the surface of the silicone film, the vinyl rad-
icals formed on the film surface react with AAm in
the aqueous solution. Graft polymerization of AAm
may be expected to proceed on the film's surface.

To clarify the grafting mechanism, two different
types of silicone prepolymers were used. In one ex-
periment the silicone prepolymer having vinyl
groups, that is, poly(dimethylsiloxane-co-methyl-
vinylsiloxane), was used as mentioned in Materials
and Experiments. In the comparative experiment,
poly(dimethylsiloxane) was used instead of poly-
(dimethylsiloxane-co-methyvinylsiloxane). The
same amounts of DCBPO was added to it and was
cured by the terminal OH groups with added poly-
functional silicate by the catalytic reaction of di-n-
butyltin dilaurate. These two silicone films im-
mersed in the AAm solution were kept at 121°C for
1 min in both experiments. The amount of PAAm
on the films were then compared. Figure 2 shows
the effect of washing on the removal of PAAm
formed on the silicone films. The amount of PAAm
on the silicone carrying vinyl groups was almost
constant in spite of washing in deionized water. On
the other hand, PAAm on the silicone without hav-
ing pendant vinyl groups was easily removed by
washing, that is, that produced by the direct reaction
between AAm and radicals from DCBPO. Vinyl

groups on the silicone prepolymer play a key role in the graft polymerization on the silicone surface (Fig. 1).
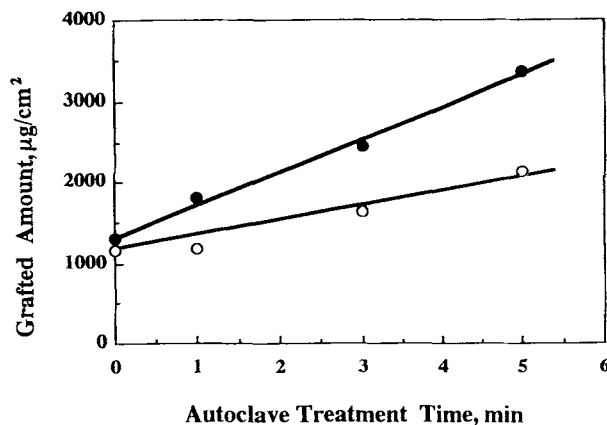
Figure 3 shows the dependence of the grafted amount of PAAm on the concentration of DCBPO mixed on the silicone prepolymer. The amount grafted was increased with increasing concentration of DCBPO. The dependence of the amount of PAAm grafted with time at 121°C is shown in Figure 4. The longer the heating time, the greater the amount of graft. Even when the residence time at 121°C was zero, plenty of PAAm was grafted on the film. The decomposition temperature of DCBPO is 95°C. Radicals produced from DCBPO while the reaction system was being heated to 121°C initiated graft polymerization.

Figure 5 is a photo of the cross section of a stained silicone film with 164 μg cm^{-2} of grafted PAAm. It is clearly seen that the location where the graft polymerization proceeds is restricted to the film surface. Radicals are formed not only on the surface, but also inside the silicone film. But the hydrophilic monomer, AAm, cannot penetrate into the silicone film. Hence graft polymerization was restricted to the surface. The thickness of the hydrated grafted layer in Figure 5 seems to be 30 μm. The graft layer is much thicker than expected from the PAAm grafted model shown in Figure 1. More complicated reactions apparently occur, such as chain transfers and crosslinking between the polymer radicals and previously formed graft polymers. Thus, a thicker hydrogel layer forms on the silicone film.

When the surface of the silicone was grafted with a large amount of PAAm, the hydrophobic surface may be expected to become very slippery in the wet
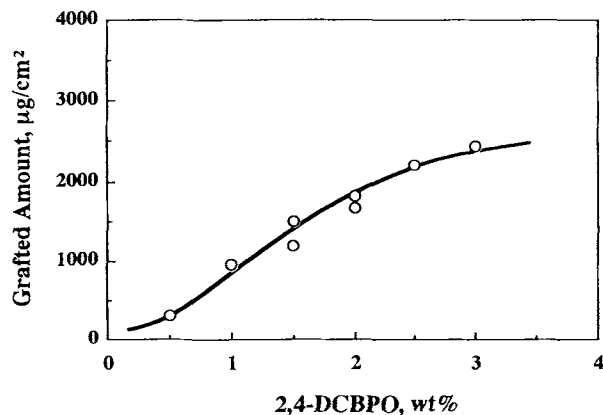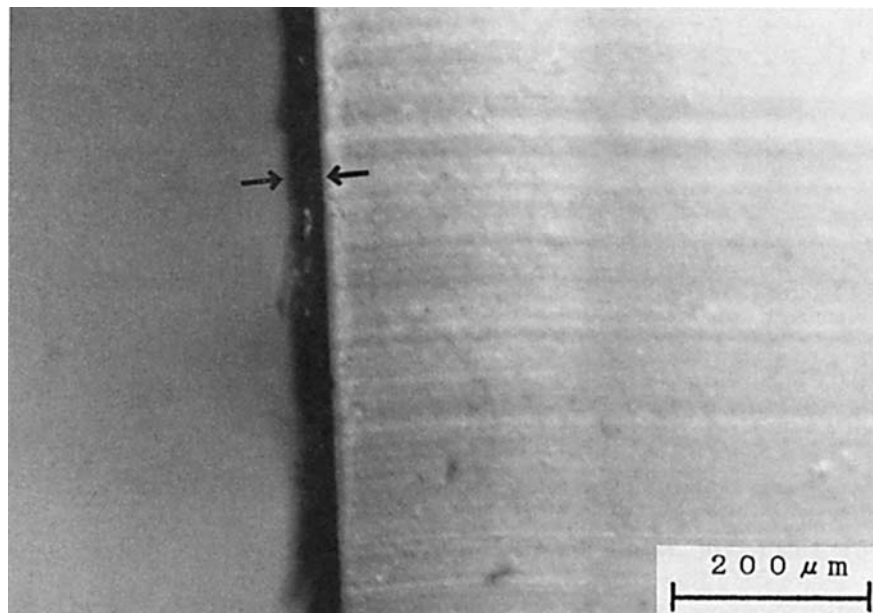

Figure 4 Dependence of the grafted amount of poly(acrylamide) on time while the reaction system was maintained at 121°C. Concentration of 2,4-dichlorobenzoyl peroxide: (O) 1.5 wt %; (●) 2.0 wt %.
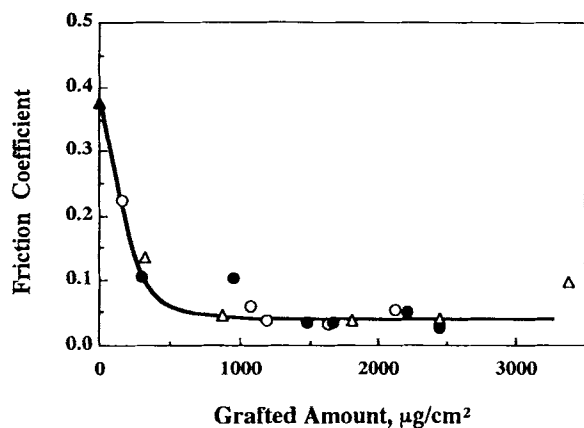
state. Friction coefficients of the surfaces are shown in Figure 6. They are drastically decreased when the surfaces of the silicone films are covered by a small amount of grafted PAAm. The friction coefficient became less than 0.05 when the grafted amount was larger than 500 μg cm^{-2}.

Silicone is one of the most hydrophobic of polymers. On the other hand, PAAm is water soluble and highly hydrated in water. It is anticipated that the hydrophobicity of the silicone surface should be drastically changed by PAAm grafting. Contact angles of water on the films, which were determined by the sessile drop method, are shown in Figure 7. The contact angle of the silicone film without a grafted PAAm layer was about 100 degrees reflecting its hydrophobicity. The contact angle on the surface decreased with increasing grafted amount of PAAm. But, the decrease in contact angles was not as large as expected. Even when the grafted amount was more than 1000 μg cm^{-2}, it leveled off around 40 degrees. In our previous study,[2] PAAm was grafted on the polyethylene (PE) surfaces activated by a glow discharge treatment. The contact angle of water drastically decreased from 90 degrees for the native PE surface to 10 degrees when 90 μg cm^{-2} of PAAm was grafted. This curious discrepancy observed between these materials can be explained by migration of the silicone oil from the silicone film through the grafted PAAm layer to the surface in the dry state as discussed in the following section.

The compositions of the surfaces were characterized by XPS analysis. The XPS can analyze a thin surface layer having a thickness less than 50 Å. Even when a small amount of PAAm is grafted, the XPS spectra should be drastically changed. The

Figure 3 Dependence of the grafted amount of poly(acrylamide) on the concentration of 2,4-dichlorobenzoyl peroxide mixed in the silicone prepolymer. The reaction systems were maintained at 121°C for 1 min.

Figure 5 Optical photomicrograph of a cross section of the poly(acrylamide) grafted silicone film stained by toluidine blue-O. Arrows indicate the grafted layer.

Grafted Amount, μg/cm²

Grafted Amount, μg/cm²

Figure 6 Changes in the friction coefficients of the grafted silicone films as a function of the poly(acrylamide) grafted amounts. (○) Films were obtained from the prepolymer containing 1.5 wt % of DCBPO by being heated to 104°C and 112°C and by being maintained at 121°C for 1, 3, and 5 min. (△) Films were obtained from the prepolymer containing 2.0 wt % of DCBPO by being heated to 104°C and 112°C, and by being maintained at 121°C for 1, 3, and 5 min. (●) Films were obtained from the prepolymer containing 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt % of DCBPO by being maintained at 121°C for 1 min. (▲) A film was obtained from the prepolymer containing 1.5 wt % of DCBPO by being maintained at 121°C for 1 min without acrylamide.
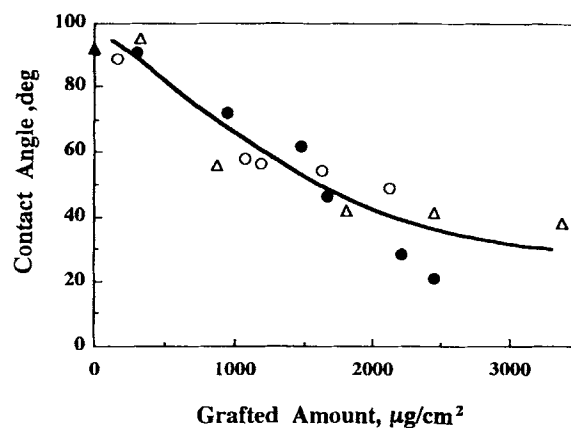
Figure 7 Changes in the contact angles of the grafted silicone films as a function of the poly(acrylamide) grafted amount. (○) Films were obtained from the prepolymer containing 1.5 wt % of DCBPO by being heated to 104°C and 112°C and by being maintained at 121°C for 1, 3, and 5 min. (△) Films were obtained from the prepolymer containing 2.0 wt % of DCBPO by being heated to 104°C and 112°C, and by being maintained at 121°C for 1, 3, and 5 min. (●) Films were obtained from the prepolymer containing 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt % of DCBPO by being maintained at 121°C for 1 min. (▲) A film was obtained from the prepolymer containing 1.5 wt % of DCBPO by being maintained at 121°C for 1 min without acrylamide.
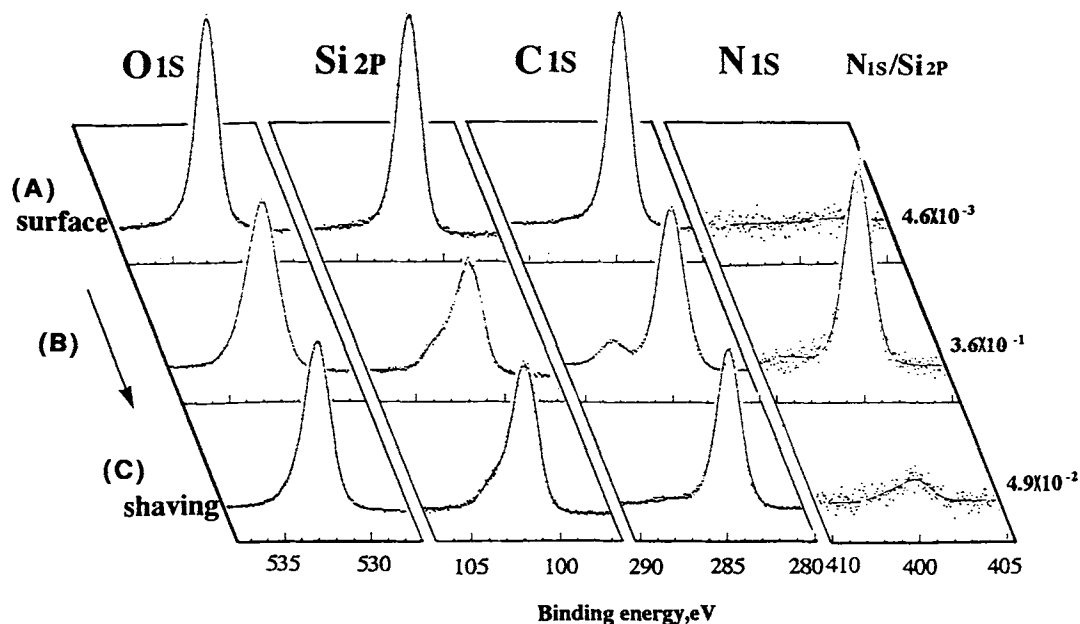
Figure 8   XPS spectra of the silicone films. (A) The silicone films grafted with 1500 μg cm^{-2} of poly(acrylamide); (B) the outer surface layer was removed using sandpaper; and (C) the grafted layer was further removed.

spectra are shown in Figure 8. Even after 1500 μg cm^{-2} of PAAm are grafted, the XPS spectra closely resemble that of poly(dimethylsiloxane). The intensity of the Si$_{2P}$ spectrum was high. The spectrum of N$_{1S}$ is hard to detect or was not seen as the peak of the C$_{1S}$ spectra at a binding energy of 287 eV that corresponds to a carbonyl carbon of PAAm. They demonstrate that the outermost surface of PAAm-grafted silicone is silicone. The surface of the film with 1500 μg cm^{-2} of PAAm grafted was removed using sandpaper. After the outer surface was removed, the intensity of the Si$_{2P}$ peak decreased, the signal of N$_{1P}$ apparently appeared, and the C$_{1S}$ peak corresponding to a carbonyl carbon was also detected. The PAAm-grafted layer appeared by removing the outermost surface. When a further amount of surface layer was removed, the XPS spectra looked like that of poly(dimethylsiloxane) again. The base silicone appeared.

These curious results of the XPS spectra and the contact angles may be explained by migration of low molecular-weight silicone oil added to the silicone prepolymer as a plasticizer. The silicone oil migrated from the cured silicone through the PAAm-grafted layer to the interface between the grafted layer and air to reduce the interfacial tension during the dry condition. The PAAm-grafted layer was covered by a thin silicone oil layer. It gave an XPS spectra like

pure silicone because the thickness, which can be analyzed by the XPS measurement, was less than 50 Å. The properties of the grafted layer characterized during the dry condition, the contact angle, and the XPS spectra are affected by the silicone oil migration. The contact angle could not be reduced to less than 40 degrees thus reflecting the presence of a silicone oil layer on the grafted surface. Such dynamic properties of the polymer surfaces and mobility of the additives in polymers have been observed in various other polymers.[6,7] On the other hand, the properties examined under wet conditions, such as friction coefficient, are not influenced very much by the addition of silicone oil (Fig. 6), because silicone oil penetrates into the bulk to produce the lowest interfacial tension between the grafted PAAm layer and water.

In the system described herein, hydrophilic monomers can be easily graft polymerized by simply heating the silicone prepolymers in the monomer solution using an autoclave. Complicated procedures, such as thorough degassing and sealing in a glass ampoule, are not necessary. The grafted layer uniformly covers the silicone. The surface of the silicone becomes hydrophilic and slippery.

REFERENCES

1. K. L. Mittal, Ed., *Physicochemical Aspects of Polymer Surfaces*, Plenum Press, New York, 1983.
2. M. Suzuki, A. Kishida, H. Iwata, and Y. Ikada, *Macromolecules,* **19,** 1804 (1986).
3. H. Iwata, A. Kishida, M. Suzuki, Y. Hata, and Y. Ikada, *J. Polym. Sci. A, Polym. Chem.,* **26,** 3309 (1988).
4. A. Chapiro, *Radiation Chemistry of Polymeric Systems,* Interscience Publishers, New York, 1962.
5. T. Okada and Y. Ikada, *Macromol. Chem.,* **192,** 1705 (1991).
6. M. J. Owen, T. M. Gentle, T. Orbeck, and D. E. Williams, in *Polymer Surface Dynamics,* J. D. Andrade, Ed., Plenum Press, New York, 1988, pp. 101–110.
7. B. D. Ratner and S. C. Yoon, in *Polymer Surface Dynamics,* J. D. Andrade, Ed., Plenum Press, New York, 1988, pp. 137–152.