

Surface Wettability Improvement of Silicone Elastomers Synthesized with Water-Soluble Polyacrylic Acid Molds

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Received 20 August 2002; accepted 28 December 2002

ABSTRACT: The aim of this work was to evaluate the use of water-soluble hydrophilic plastic molds for preparing siloxane based random copolymers and for enhancing the surface wettability of resultant polymers, with a view for contact lens manufacture. The random copolymer consisted of silicone monomers and a small amount of N-vinyl-2-pyrrolidone (NVP) along with vinyl acetate and diethyleneglycoldiallylether as a crosslinker. The surface of this copolymer, which faced against a polyacrylic acid (PAA) mold, showed a higher degree of wettability compared to that obtained against a hydrophobic polypropylene (PP) mold. After heating at 80°C for 4 h, the surface of this copolymer became hydrophobic. When it was immersed in

water, however, the high degree of surface wettability regained within 30 s, whereas no significant change in wettability was observed for the PP-facing surface. The results obtained from X-ray photoelectron spectroscopy indicated that the polar fraction, which is attributed to NVP fractions of the copolymer, concentrated at the vicinity of the PAA facing surface and, in consequence, improved the surface wettability. This surface also showed a dynamic rearrangement of the wettability in response to changes of the surrounding environment. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3786–3789, 2003

Key words: surfaces; molding; hydrophilic polymers; silicones

INTRODUCTION

In the last 3 decades the number of contact lens wearers has risen from 10 to 80 million because the safety of contact lens materials has been significantly improved.¹ The cornea normally receives oxygen and other nutrition from the tears. Wearing contact lenses disturbs this supply and reduces the oxygen level available to the anterior corneal surface, resulting in an abnormal metabolism.¹ The oxygen availability to the cornea depends primarily on the oxygen permeability (Dk) of the contact lens material and is supplemented from the oxygen in the tear film between the lens and the cornea. In this sense, Dk is of a paramount concern for the contact lens property. Several clinical studies have showed that the use of low Dk contact lenses on an extended wear basis causes relatively high levels of ocular complications.^{2,3} To increase Dk of lenses, silicone and/or fluorocarbon monomers have been widely utilized in contact lens manufacture.^{4,5} Increasing silicone content has brought the benefit of increased Dk , but this benefit is compensated by the disadvantage of decreased surface wettability and poor biocompatibility.

Numerous strategies to increase the surface wettability of silicone contact lens materials have been attempted via surface modification, such as polymer

grafting, plasma oxidation, chemical treatment, or polymer coating.^{6–9} Although the surface wettability has been improved to some extent, durability, complicated procedures, and increased manufacturing cost accompanied these modifications limit their practical use in the contact lens industry.

Theoretical and experimental studies have shown that the surface properties of polymers change in accordance with the nature of the surrounding environment.^{10–12} Lai et al. reported that when siloxane-based hydrogels were manufactured with hydrophilic plastic molds, such as those fabricated from polyacrylonitrile-*co*-polymethylacrylate, the surface of the hydrogel lenses were wettable.¹³ If a hydrophilic mold is used, the hydrophilic monomer would be attracted to the mold surface. After the monomer mixture is fully cured, the hydrophilic fractions would remain near the surface and the mobility of siloxane moieties to migrate to and aggregate at the lens surface would be reduced. The surface wettability of the lens in the above study was improved to some extent; this hydrophilic plastic mold, however, has a fundamental drawback. Some physical interactions may occur at the interface between the polar fractions of a silicone lens and the mold, causing difficulties to remove the lens from the mold. This may reduce the possibility of applying this method in contact lens manufacture due to a large number of defected lenses.

In this study, we attempted to minimize this drawback by using water-soluble hydrophilic molds fabricated from polyacrylic acid (PAA) rather than water-insoluble hydrophilic plastics used in previous

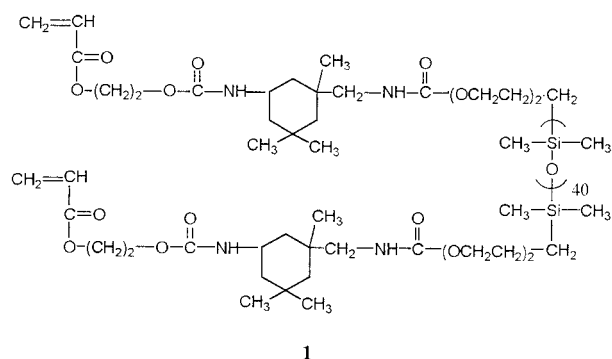
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study.¹³ A silicone elastomer composed of two kinds of siloxanyl monomers and a small amount of N-vinyl-2-pyrrolidone (NVP) was synthesized. The water content of this random copolymer was below 10%, which is classified as nonhydrogel contact lenses.¹⁴ The complex of NVP and acrylic acid can be expected due to electrostatic interaction and/or hydrogen bonding.¹⁵ To achieve such a complex at the interface, the monomer mixture was polymerized with the PAA mold. After polymerization, the mold adhered to the elastomer was immersed in water instead of being forced to remove. The efficiency of the PAA mold for surface wettability enhancement of the silicone elastomer was evaluated. The dynamics of surface rearrangement of the elastomer in response to the surrounding environment was also investigated.

MATERIALS AND METHODS

Monomers

Methacrylate-capped polydimethylsiloxane based polyurethane prepolymer 1, Tris(trimethylsiloxy)silil-propylacrylate (TRIS), N-vinyl-2-pyrrolidone (NVP), and Vinyl acetate (VAC) were purchased from Tomey Co., Ltd (Nagoya, Japan). Diethyleneglycoldiallylether (DEGDA) was purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan). 2-Hydroxy-2-methyl-1-phenylpropane-1-one (Darocur) was obtained from Merck (Darmstadt, Germany). These monomers were all purified by extraction or distillation prior to usage.



Plastic molds

Polyacrylic acid (PAA, M_n : 23,500, Wako Pure Chemical Industries, Ltd, Osaka, Japan), Polyvinylpyrrolidone (PVP, M_n : 40,000, Nacalai Tesque Inc., Kyoto, Japan), Polyethylene glycol (PEG, M_n : 2,000,000, Wako Pure Chemical Industries, Ltd, Osaka, Japan), and Polypropylene (PP, Chisso Co., Tokyo, Japan) were utilized as plastic resins for molds.

Preparation of the plastic molds

PAA, PVP, and PEG molds were fabricated by compression molding at 200–250°C for 5 min using a

compression molding machine (37TON heating-cooling two-step compression molding, Miura Press Co. Ltd., Osaka, Japan). All the plastic molds had good mechanical strength and were soluble in water. The PP mold, which is the most common material for a plastic mold, was made by injection molding. The plasma treated PP mold was prepared by a plasma asher (PA-102AT, Kyoto Denshi Kesoku INC, Kyoto, Japan) at approximately 107 Pa of O₂ and 40 W for 3 min.

Preparation of silicone elastomers

Methacrylate-capped polydimethylsiloxane based polyurethane prepolymer (5 g, 50 wt %), TRIS (1.4 g, 14 wt %), VAC (2.5 g, 25 wt %), NVP (1.0 g, 10 wt %), DEGDA (0.08 g, 0.8 wt %), and Darocur (0.02 g, 0.2 wt %) were mixed thoroughly. Aliquots of the mixture (0.1 mL) were withdrawn and injected between two different plastic molds (20 mm diameter, 0.3 mm thickness), one fabricated from PP, the other one from the hydrophilic molds shown in the previous section. The monomer mixture was kept in the molds for different periods (0, 30, and 60 min). Then free radical polymerization was initiated with UV irradiation at an intensity of 10 mW/cm² at 365 nm for 60 min at room temperature. After polymerization, the PP mold was removed, and then the water-soluble mold adhered to the elastomer was immersed in a large amount of distilled water to dissolve the mold. After dissolving the mold, the elastomer obtained was washed successively with water, 0.9% NaCl, water, propanol, methanol, and water at room temperature. Each type of washing lasted for at least 2 day, during which the respective washing solution was replaced every 12 h, encompassing a total washing period of 14 days.

Static contact angle measurements

Influence of the duration that the monomer mixture in contact with the molds prior to polymerization

The monomer mixture was injected in the molds, kept in stand for a given period (0, 30, and 60 min), and then polymerized. After removing the molds and washing the silicone elastomer, the static contact angle of the elastomer was measured by the captive bubble method in distilled water at 25°C using a goniometer (G-1, Erma optic, Tokyo, Japan). The elastomer was kept in water for at least 24 h prior to measurement.

Influence of water immersion on contact angle of the silicone elastomer

After heating the silicone elastomer at 80°C for 4 h and cooling it down to room temperature, the elastomer was immersed in distilled water and the static contact angle was measured by the captive bubble method at 25°C at different time intervals (15, 30, 60, 90, and 120 s).

Surface characterization of dried silicone elastomers

The silicone elastomer was dried *in vacuo* at room temperature. Surface of the dried plates were characterized by X-ray photoelectron spectroscopy (XPS) (JPS-9000MX, JEOL Ltd., Tokyo, Japan). The X-ray source utilized an AlK α operated at 10 kV and 10 mA, and the operating pressure was under 10^{-6} Pa. The sample depth is approximately 10 nm. To analyze the residual surface element distribution with respect to depth, the depth profiling was conducted by argon ion sputtering at 400 V and 6.4 mA for 30 s, which corresponds to a 10 nm depth.

RESULTS AND DISCUSSION

Preparation of silicone elastomers

The silicone elastomer was easily removed from the PP mold, while it was adhered to all the other hydrophilic molds (PAA, PVP, PEG, and plasma treated PP), due to a certain degree of attractive interaction at the interface. It was impossible to remove the elastomer from these molds without damage. When they were immersed in water, the PAA, PVP, and PEG molds were dissolved. Nonetheless, we obtained intact silicone elastomers only from the PAA mold. The elastomers obtained from the PVP and PEG molds were swollen by water and too fragile to handle. This is because PVP and PEG partially penetrated into the monomers mixture prior to polymerization, resulted in interpenetrating polymer networks. In addition, the elastomer on the plasma treated PP mold, which is water insoluble, was not able to be removed without damage. As a result, the PAA mold was being used in further experiments with the PP mold as the control.

The silicone elastomers obtained from the PP and PAA molds were all optically transparent and mechanically strong. The water content of the silicone elastomer was 9.0%, indicating that it is classified as a non hydrogel material.¹⁴

Influence of the duration that the monomer mixture in contact with the molds prior to polymerization

As shown in Figure 1, surface contact angle of the silicone elastomer obtained from the PP mold was almost constant regardless of the duration that the monomer mixture was in contact with the mold prior to polymerization. When the monomer mixture was polymerized immediately after injecting in the molds, the contact angle of the elastomer obtained from the PAA mold showed similar contact angle compared to that from the PP mold. However, increasing the time that the monomer mixture was in contact with the PAA mold resulted in a decrease in contact angle. These results can be explained as follows: when contacted with the PP mold, the hydrophobic fraction of

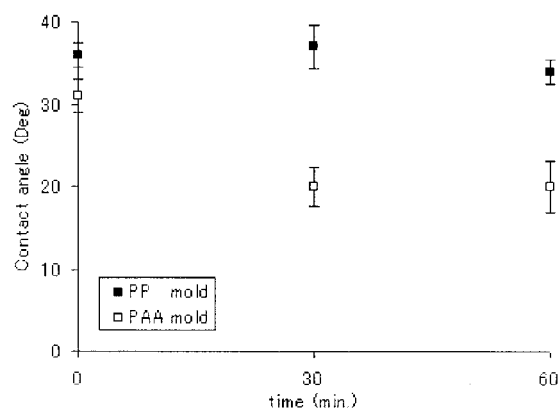


Figure 1 Influence of the duration that the monomer mixture in contact with the mold prior to polymerization on the surface contact angle of the silicone elastomer. The contact angle was measured by the captive bubble method. Data are expressed as mean \pm SD ($n = 5$).

the monomer mixture, silicone monomers, was prone to be distributed at the interface. Even after cured and immersed in water, this fraction was still rich at the vicinity of the surface due to the crosslinking constraints. For the PAA mold, it was likely that the hydrophilic monomers rather than hydrophobic silicone monomers concentrated at the interface due to the polar interaction with the PAA mold. However, when the monomer mixture was polymerized immediately after injection, the hydrophilic monomers such as NVP did not have enough time to diffuse to the interface, and thus their existence at the surface was negligible, resulting in a high contact angle that is similar to that with the PP mold. This result indicated that the residual PAA remained on the surface of the elastomer would not be significant, otherwise, the surface contact angle at the time 0 min should be lower (Fig. 1). Our result also suggested that it took maximum 30 min for the monomer mixture to reach its equilibrium before polymerization, because the contact angles of the PAA case at 30 and 60 min were virtually the same. In addition, only elastomers with 30-min in contact with the mold are used in the following discussions.

Influence of the mold materials on surface chemical composition of the silicone elastomer

The chemical composition on both surfaces of the silicone elastomer were investigated and compared by XPS. As shown in Table I, the surface obtained from the PAA mold showed a higher level of nitrogen, which is attributed to a higher NVP content compared to that from the PP mold. When 10 nm of the polymer was etched away by argon ions, no significant difference in chemical composition was seen on both surfaces, indicating that NVP was present almost exclusively within the top 10 nm layer in the case of the PAA mold.

Influence of water immersion on contact angle of the silicone elastomer

For some block copolymers and polymer blends, hydrophobic functional groups are rich on the surface to minimize the surface free energy at the interface.^{16–18} For silicone contact lenses, the dynamics of surface rearrangement is very important. When silicone lenses are stored in the air, their surfaces are hydrophobic. As they are placed onto the cornea, it is important that the surface of the lens becomes hydrophilic instantaneously to avoid any uncomfortable feeling for the patient. As shown in Figure 2, after drying at 80°C for 4 h followed by water immersion, the surface contact angle of the elastomer obtained from the PP mold showed no significant change within a relatively short time scale (120 s). In the case of the PAA mold, on the other hand, the contact angle decreased significantly within 30 s and became constant after that. The surface obtained from the PP mold consisted mostly of hydrophobic moieties (Table I). Due to the crosslinking constraints, it would be unlikely that the polar fraction in the random copolymer network reoriented itself towards the outermost surface. On the contrary, after a 30-min contact, NVP already existed in the vicinity of the PAA surface and was fixed there upon polymerization. Even though surface wettability decreased by heating, it would be likely from the thermodynamic point of view that rearrangement of the polar fraction may occur according to change of the environment. The decreased contact angle was similar to the value that measured at equilibrium condition in water shown in Figure 1, indicating that the surface rearrangement occurred and reached its equilibrium within 30 s after immersing in water.

CONCLUSION

The silicone elastomer with high surface wettability can be prepared when the water-soluble PAA mold was used for fabrication. The degree of the surface wettability was higher compared to that obtained from the conventional PP mold. The silicone elastomer could rapidly alter its surface wettability depending

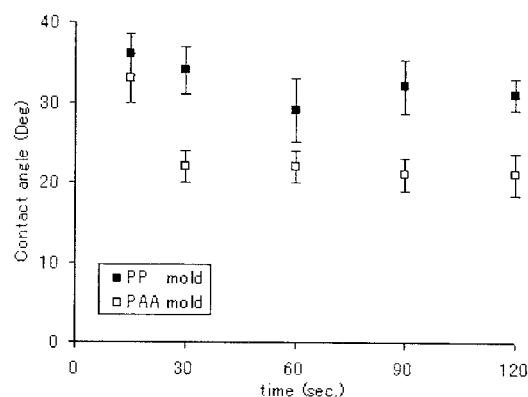


Figure 2 The dynamics of the surface rearrangement of the silicone elastomers synthesized from the PAA and PP molds. After drying the elastomers at 80°C for 4 h, they were immersed in distilled water and the contact angle were measured by the captive bubble method at different time intervals. Data are expressed as mean \pm SD ($n = 5$).

on the surrounding environment. We believe that the silicone elastomer fabricated from the water-soluble PAA mold is suitable for contact lens. Furthermore, this PAA mold has the advantages in (1) enhancing the surface wettability of silicone elastomer, (2) environmental impact (reduced pollution by organic solvent), (3) reducing manufacturing costs for a surface modification of hydrophobic lenses, and (4) reusability after dissolving in water.

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TABLE I
Atomic Composition of Silicone Elastomer Obtained from PP and PAA Molds

Depth (nm)	Mold materials	Element (%)			
		O	N	C	Si
0–10	PP	24.9	3.7	50.2	21.2
	PAA	23.9	7.2	53.9	14.9
10–20	PP	21.4	4.0	55.7	18.9
	PAA	19.4	3.4	53.6	23.6
20–30	PP	22.9	4.5	51.7	20.8
	PAA	19.9	4.0	53.1	23.0