



# Improvement of the surface wettability of silicone hydrogel contact lenses via layer-by-layer self-assembly technique



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## ABSTRACT

The surface wettability and anti-protein adsorption of a silicone-based hydrogel that was synthesized by a block copolymer of polydimethylsiloxane (PDMS) and poly (ethylene glycol) methacrylate (PEGMA) was improved via polyelectrolyte multilayer (PEM) immobilization. Polysaccharide PEMs of chitosan (CS, as a positive-charged agent) and hyaluronic acid (HA, as a negative-charged and anti-adhesive agent) were successfully assembled on the PDMS-PU-PEGMA silicone hydrogel in a layer-by-layer (LBL) self-assembly manner. Atomic force microscopy (AFM) and dyeing data verified the progressive buildup of the PEM silicone hydrogel. The results showed that the contact angle of the silicone hydrogel decreased with an increase in the number of PEM grafting layers. Furthermore, after immobilizing five layers of CS/HA, the protein adsorption decreased from  $78 \pm 11$  to  $26 \pm 4 \mu\text{g}/\text{cm}^2$  for HSA and from  $55 \pm 10$  to  $20 \pm 4 \mu\text{g}/\text{cm}^2$  for lysozymes. This indicates that CS/HA PEM-immobilized silicone hydrogels can resist protein adsorption. Furthermore, these hydrogels were non-cytotoxic according to an *in vitro* L929 fibroblast assay. Overall, the results demonstrated that the modified silicone hydrogels exhibited hydrophilicity and anti-protein adsorption, as well as relatively high oxygen permeability and optical transparency. Therefore, they would be applicable as a contact lens material.

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## 1. Introduction

In a conventional soft contact lens, the oxygen permeability through the polymer phase is lower than for the water phase. As a result, oxygen transport is via the water phase. Thus, the oxygen permeability of these contact lenses is limited by the oxygen permeability (Dk) in water which is only 80 barrers. The way that oxygen is transported through silicone hydrogels is different and not dependent on water content alone. In silicone hydrogels, with the incorporation of oxygen-permeable silicone domains, the path of least resistance is through the silicone component, which allows more oxygen to permeate via the lens and results in fewer hypoxia-related complications as compared to conventional hydrogel contact lenses [1]. Silicone hydrogels have been specifically developed for contact lenses in order to dramatically improve corneal oxygen supply [2–8], which is 4–6 times greater than that available with traditional hydrogels.

The main problem of silicone-based contact lenses is the inherent hydrophobicity of siloxane groups, which significantly impedes the development of silicone hydrogel lenses. Hydrophobicity leads to problems such as decreased surface wettability, increased lipid interaction, and accentuated lens-binding, problems that are historically seen in silicone-based materials [9–17].

In order to make the surfaces of silicone hydrogel lens materials hydrophilic and more wettable, techniques incorporating plasma into the surface processing of lenses have been developed [18–19]. More recent techniques have involved incorporating hydrophilic monomers into the lens material, which “migrate” to the surface of the lens and aid wettability [20–22]. The purpose of these surface treatments is to mask the hydrophobic silicone from the tear film, which increases the surface wettability of the materials and reduces lipid deposition [23,24].

Balafilcon A lenses are surface treated in a reactive gas plasma chamber, which transforms the silicone components on the surface of the lens into hydrophilic silicate compounds [18,25]. This process results in glassy, discontinuous silicate “islands” [23–27], and the hydrophilicity of the transformed surface areas “bridge” over the underlying balafilcon A material. These do not completely cover the surface and hence do not affect the permeability of the material.

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However, these islands are sufficiently large and well distributed enough to allow good lens wettability. Lotrafilcon A and lotrafilcon B lenses use a gas plasma technique to apply an extremely thin, uniform, high-refractive-index, 25 nm-thick hydrophilic plasma coating on the lens surface after manufacturing [23–27]; this coating is significantly more wettable than the underlying material. Asmofilcon A uses a combined approach that uses plasma polymerization and a plasma coating to improve wettability [28].

The layer-by-layer (LBL) self-assembly of polycations and polyanions into multilayers has emerged as an efficient, versatile, and easy technique for developing biologically active surfaces. The method depends on the sequential charge inversion of a polymeric surface upon successive immersion of this surface in solutions of oppositely charged polyelectrolytes. Recently, application of the electrostatic LBL self-assembly technique in biomedical engineering was widely developed in artificial tissues [29–36]. Herein, we describe the preparation and properties of a new bioactively immobilized polyelectrolyte multilayer (PEM) on a silicone hydrogel for ophthalmic devices based on the LBL self-assembly of chitosan (CS) and hyaluronic acid (HA).

In the literature, most past efforts to increase the hydrophilicity or reduce the protein adsorption of ophthalmic materials were conducted by surface modification. However, van Beek et al. [37] developed model lens materials based on poly(2-hydroxyethyl methacrylate) (pHEMA) that physically entrapped hyaluronic acid (HA) as a wetting agent. They showed that adsorption of all the proteins studied was considerably decreased by the presence of a small amount of crosslinked HA. The impact of the addition of HA to silicone hydrogel materials on the adsorption of tear film proteins was examined and compared to that of commercially available lens materials. HA, being hydrophilic, is hypothesized to decrease protein adsorption, possibly by the same mechanism as poly(ethylene oxide) (PEO). Thus, most of the protein molecules would deposit on the PEO layer and lead to reversible fouling, which can be easily removed by washing with water. Bozukova et al. [38] developed a poly(ethylene glycol) (PEG) chemical coating on the surface of a hydrogel intraocular lens. The PEG coils effectively excluded from the space they occupied proteins of a comparable or greater size. They showed that a strong decrease of protein adsorption and cell adhesion depended on the molar mass of the grafted PEG. Chen et al. [39] showed that significant reductions in the adsorption of fibrinogen, albumin, and lysozymes were observed on mono- and bifunctional poly(ethylene oxide) (PEO)-modified surfaces of silicone-based polymers. The magnitude of protein adsorption was found to decrease with increasing surface hydrophilicity of the polymer. Yao et al. [40] reported that after tethering water-soluble 2-methacryloyloxyethyl phosphorylcholine (MPC), which is a hydrophilic layer, onto the surface of hydrophobic silicone intraocular lenses (IOLs), the platelet, macrophage, and lens epithelial cell adhesion on the IOL surface was significantly suppressed, which indicates the enhancement of surface biocompatibility.

The PDMS-PU-PEGMA silicone hydrogel should be modified to have reactive groups for PEM immobilization because the hydrogel has no functional groups on its surface. Surface O<sub>2</sub> plasma oxidation has been widely employed for surface modification because it allows for the uniform introduction of peroxides onto the polymer surface and offers an easy-to-handle, inexpensive technique.

This study investigates the surface wettability and biocompatibility of PDMS-PU-PEGMA silicone hydrogels as prepared in our previous study [1]. The deposition of CS/HA self-assembled multilayers on silicone hydrogels were prepared by the LBL self-assembly technique and characterized by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and hydrophilicity measurements. Additionally, the mechanical properties, protein

adsorption, and ophthalmic characterization, as well as the *in vitro* cytotoxicity, were also investigated.

## 2. Materials and methods

### 2.1. Materials

Poly(dimethylsiloxane) dialkanol (KF-6001, viscosity = 45 mm<sup>2</sup>/s) was purchased from Shin-Etsu Chemical Co. Ltd., Tokyo, Japan. Poly(ethylene glycol) methacrylate (PEGMA,  $M_n = 360$ ), 2-hydroxyethyl methacrylate (HEMA, 99%), isophorone diisocyanate (IPDI, 99%), acrylic acid (AA, 99%), chitosan (with a molecular mass of approximately 160 kDa and a degree of deacetylation of 85.3% was obtained from Taiwan Textile Research Institute, Taipei, Taiwan), hyaluronic acid (HA, sodium salt, 757 kDa), and ethylene glycol dimethacrylate (EGDMA, 99%) were purchased from Sigma, USA. Diethoxyacetophenone (DEAP, 99%) as the photoinitiator was purchased from Fluka Chemical Corp., USA. All the compounds and solvents were used as received.

### 2.2. Silicone hydrogel preparation

As described in our previous study [1], the silicone hydrogels were obtained from the synthesis of PDMS-PU-PEGMA hydrogels via UV photopolymerization. The reacting solution was prepared by mixing 20 g of a PDMS-PU macromer/tetrahydrofuran (THF) solution, 3 g of PEGMA, 0.5 g of DEAP as the initiator, and 0.5 g of EGDMA as the crosslinking agent. The mixture was poured into Petrie dishes and then exposed to ultraviolet (UV) light (365 nm) at 5 mW/cm<sup>2</sup> for 30 min, thus providing the silicone hydrogel. After the reaction was completed, the silicone hydrogel was immersed in ethanol for one day to leach out the photoinitiator, unreacted monomers, and THF. Afterwards, the hydrogel was immersed in water to remove the residual ethanol and dried in a vacuum oven at 60 °C for one day. The thickness of the hydrogel was 80 ± 10 μm.

### 2.3. Surface modification

Fig. 1 shows the chemical scheme for immobilizing CS/HA self-assembled multilayers on the silicone hydrogel. The silicone hydrogel was ultrasonically cleaned in ethanol for 15 min prior to surface grafting. Subsequently, the as-cleaned silicone hydrogel was cut into 1 × 1 cm pieces and treated with 100 W of O<sub>2</sub> plasma for 30–150 s. The flow rate of the oxygen was kept constant at 25 L/min. The hydrogens on the methacrylate (MA) unit were easily attacked by the plasma. Afterwards, the hydrogel was immersed in 10 mL of 30 wt% AA in a glass tube purged with nitrogen. 0.1 mL of 0.015 M FeSO<sub>4</sub>/0.005 M H<sub>2</sub>SO<sub>4</sub> was added to carry out graft polymerization at 60 °C for 120 min. The carboxylic-grafted silicone hydrogel (SiH-A) was rinsed with phosphate buffer saline (PBS, pH 7.4) and double-distilled water to remove the unreacted monomers and homopolymers.

Solutions of HA (2 mg/mL in 0.14 M aqueous NaCl) and CS (1.5 mg/mL in 0.1 M acetic acid containing 0.14 M NaCl) were prepared separately. Ultrapure water was used in all experiments (Milli-Q system, Millipore). The multilayer build-up was accomplished by sequential dipping of the SiH-A substrate into the polysaccharide solution (alternating between CS and AA), followed by 15 min adsorption and washing with a 0.14 M NaCl solution. Finally, the samples were extensively cleaned with ultrapure water and freeze-dried at –52 °C using a freeze-dryer (model ZDG, Vacuum Freeze Drier, China) for 24 h. The silicone hydrogel modified with CS/HA polyelectrolyte multilayers (PEMs) are denoted as SiH-A(CS-HA) *n*, where *n* represents the number of PEMs.

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