Improving Silicone Elastomer Hydrophilicity

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Statement of Purpose: Silicones have found a myriad of uses in healthcare due to their extreme hydrophobicity and favorable mechanical properties. However, applications such as ocular lenses would benefit from a more hydrophilic surface. Incorporation of a biological polymer such as hyaluronan (HA) would increase surface hydrophilicity and might also make the surface more hemocompatible for blood contacting applications such flexible heart valve leaflets. Therefore, this study sought to produce a hydrophilic, non-hydrogel silicone elastomeric material by incorporating HA into silicone to form an interpenetrating polymer network (IPN) between the HA and the silicone at the silicone surface.

Materials and Methods: Sodium hyaluronan (Lifecore Biomedical) with a 740 kDa molecular weight was silylated as described elsewhere [1]. Commercially available two-part PDMS (polydimethyl siloxane) kits (Silicones Inc. and Momentive) were used. Four different formulations, representing a range of mechanical properties relevant to ophthalmic and HV applications, were investigated.

Table 1: Summary of silicone kits used and example properties as reported by the manufacturers.

Kit	P-125	XP-536	XP-565	LSR 7030
Durometer, Shore A	40	22±2	16±2	30
Tear Strength [N/mm]	15.8 ±2.6	15.8 ±2.6	7 ±1.8	3

Elastomer synthesis was carried out as directed by the manufacturers. Post-cure treatment of the elastomers consisted of a series of overnight baths in xylenes to wash out the majority of the lower molecular weight, unbound components. The samples were formed into 2 cm^2 square slabs 0.45 cm thick for testing. A 300µL of a solution of 2 wt% silylated HA in xylenes was eluted onto the surface of the silicone. This solution was allowed to fully adsorb into the silicone. Then 300 µL of a 4% v/v cross-linking solution, hexamethylene diisocyanate in xylenes, was eluted onto the same surface and allowed to fully adsorb, resulting in swelling of the samples. The swollen samples were allowed to dry and cure in a vacuum oven at -25 mmHg and 50°C for one hour. The samples then underwent a hydrolysis procedure to return the silylated HA to its native form. Hydrophilicity was measured using captive bubble contact angles. Samples were submerged in DI water and approximately 1µL of air was dispensed from below. The angle between the bubble and the sample was measured (larger contact angle indicates greater hydrophilicity). Surface presence of hyaluronan was confirmed with FTIR/ATR. Toluidine Blue-O stain was used to visually map the presence of HA on the sample surfaces.

Results: Increases of 30 to 40 degrees in captive bubble contact angles indicated improved hydrophilicity of HA-treated samples compared to untreated controls for nearly all kits. However, not all kits saw equal improvements. The P-125 kit (Figure 1) saw the greatest increase in contact angle while the XP-565 kit saw the least.

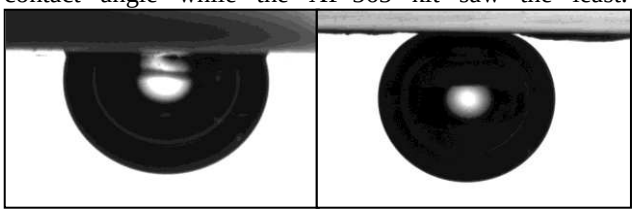
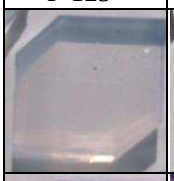
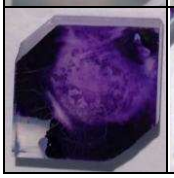
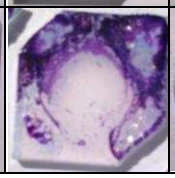
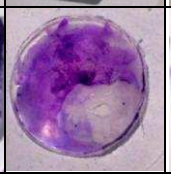
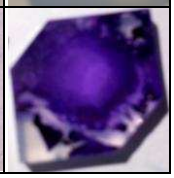


Figure 1: Images of captive bubble contact angles on an untreated sample (left) and an HA-treated sample (right) made with the P-125 kit.

Differences in the IR spectra of the treated and untreated samples confirmed the presence of HA. IR spectra of treated samples showed a peak around 3400 cm^{-1} (-OH bonds) and a series of peaks around 1600 (-NH bonds) through 1320 cm^{-1} (carboxyl groups and C-N bonds) that were not present in the spectra of plain PDMS, indicating the presence of HA. TBO staining showed HA on the surface of the treated surfaces, but not on the untreated controls or in the middle of the bulk silicone in the treated samples.

Table 2: TBO staining on untreated controls (top row), by kit, and HA-treated samples (bottom row). Inconsistency of stain on treated samples indicates that HA modification is limited to the near surface region.

P-125	XP-536	XP-565	LSR 7030
			
			

Treatment resulted in slight surface irregularities (e.g., opaqueness, roughness) in some samples that seemed to vary with kit.

Conclusions: HA was successfully incorporated into the surface of the silicones resulting in increased hydrophilicity. Future work will optimize treatment approaches and test hemocompatibility, oxygen permeability, optical clarity, cytotoxicity, protein deposition, and anti-inflammatory and anti-infective characteristics.

References

1. M. Zhang and S. James. Silylation of hyaluronan to improve hydrophobicity and reactivity for improved processing and derivatization. Polymer **2005** 46, 3639-3618

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