

ABSTRACT

Purpose: Current methods used to determine advancing contact angles (ACA) have some ambiguity in regards to the interpretation of wettability for lens surfaces. Captive Bubble (CB), Sessile Droplet (SD) and Multiple Attenuated Internal Reflection InfraRed (MAIR-IR) Spectroscopy techniques were used to investigate the means by which novel block copolymers of ethylene oxide and butylene oxide (EOBO) enhance the ability for Silicone Hydrogel (SiH) to be re-wetted by water after short duration air exposures of EOBO-based disinfectant treated contact lenses (PureVision[™] (PV)).

Methods: ACA data were collected from CB videos using OCA20-Beta software. In vitro, SD contact angle data on reference-grade Teflon foil and SiH lenses, supported by MAIR-IR spectra for surfactant residues, were used to study the EOBO-enhanced water wettability.

Results: The apparent mechanism of sustained wettability was embedment of the BO copolymer segments into hydrophobic domains of the SiH lenses, exposing the water-loving EO copolymer segments at the lens/air interface. This was demonstrated by the low ACA's of PV lenses treated with the EOBO formulation in, CB videos: initial ACA of 32° at 160 seconds with liquid surface tension (SFT) at the air bubble of 72.1mN/m; after 10 UNISOL 4[®] rinse cycles, with 90 second air exposure, an ACA of 60° at 160 seconds with SFT at 71.9mN/m. Rinsing demonstrated the substantivity of the EOBO formulations, where EOBO eluted very slowly from the hydrophobic PV lenses.

Conclusion: This mechanism of action supplements simple adsorption, absorption and reservoir/depot effects that can also take place with EOBO block copolymers. The data showed that block copolymers with EOBO's molecular geometry, molecular weight and hydrophilic-lipophilic balance may be effective and efficient to preferentially wet and re-wet hydrophobic contact lenses.

INTRODUCTION

- An important element for improved performance of SiH lenses is enhanced water wettability of the lens surface.^{1,2}
- There have been numerous generations of SiH lenses, where the surface and bulk properties have been improved from technological and manufacturing perspectives. ^{3, 4, 5, 6, 7}
- Many contact lens-care disinfecting solutions contain wetting agents, not specific for SiH lenses, that elute out quickly or are not effectively adsorbed to the surface.
- Exposure to air due to the rotation and migration to the surface of the dimethylsiloxane lens polymer moieties quickly reduces the water wettability of SiH lenses.^{8,9}
- Multiple techniques used to characterize the water wettability of contact lens surfaces include Sessile Drop, Wilhelmy Plate and Captive Bubble methods, ^{10, 11, 12} each with advantages and disadvantages.
- Surface properties of SiH are monitored to characterize sustained wettability. Complementary techniques are needed to understand the dynamic processes at lens/ water interfaces, especially when treated with wetting agents.

OBJECTIVE

The objective of this study was to assess the improved wettability and substantivity of that improvement for SiH lenses treated with a diblock copolymer, poly(ethyleneoxide)-poly(butyleneoxide) (EOBO)solution, for two silicone hydrogel lenses, PV and Acuvue[®] Oasys[™] (AO), monitored through exhaustive saline/air rinse cycles. The EOBO reagent was specifically designed to improve the wettability of SiH lens surfaces. A modified CB method was supplemented with SD measurements and IR spectroscopy to evaluate surface wetting chemistries. ^{13, 14}

MATERIALS AND METHODS

Lens Materials:

Lens	Diameter (mm)	Base Curve (mm)	% Water Content	Manufacturer	Surface Treatment
Pure Vision®	14.0	8.6	36	Bausch & Lomb	Yes
Acuvue® Oasys™	14.0	8.4	38	VISTAKON®	No

The following lens cycling was performed for Captive Bubble:

Lens Cycling Conditions Control

CB technique.

EOBO Test Solution

- measured using CB technique.
- exposure in the eye.

Instrumentation:

Captive Bubble and Sessile Drop

- characterize SiH surfaces.
- equation as follows:

where γ is the interfacial tension between two phases indicated by the subscripts (S: solid, L: liquid, and V: vapor).¹⁵ Additionally all phases are in mutual equilibrium. Increasing γ_{s_1} and/or γ_{1y} increases the contact angle θ .

- surface
- Scientific (N.Y.) was used.

A New Mechanism for Facilitated Re-wetting of Silicone Hydrogel Contact Lenses

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previously. 13, 1614

• Surface Tension measurements during CB studies were taken immediately before, after and with generation of each new air bubble.

Figure 1. The general setup for measuring contact angles via captive bubble method.



Figure 2. Movie sequence of Captive Bubble Pure Vision[®] lens soaked in UNISOL 4[®] for 24hours.



Multiple Attenuated Internal Reflection InfraRed (MAIR-IR) Spectroscopy

- MAIR-IR Spectroscopy is sensitive to monolayer quantities of surfactant deposits.
- MAIR-IR confirmed the continued presence of EOBO in multiple treated-lens rinses using UNISOL 4[®].
- Rinse-off challenges included exposure of the Unisolleached-residual film to an additional 1-Pascal shear stress for 10 seconds.

RESULTS AND DISCUSSION

SD Contact Angle

Figure 3. Sessile Droplet Contact Angles on reference Teflon (PTFE) foil, as measured for UNISOL 4[®] storage solutions containing Pure Vision[®] (PV) and Acuvue[®] Oasys[™] (AO) contact lenses treated with EOBO Test Solution and EOBO Test Solution followed with 10 air-rinse cycles in UNISOL 4[®]. Distilled Water contact angles approach 120 degrees on this referenced surface; lower contact angle values indicate relative presence of surfactant in the storage solutions.

nales of UNISOL 4 ® Storage solutions or



- UNISOL 4 [®] (Control) has a high contact angle on reference Teflon foil of 117°.
- After treatment with the EOBO tests solution, initial rinses showed that both PV and AO lenses did elute some surfactant, producing Unisol rinse fluid contact angles of 94° and 104°, respectively, on the reference Teflon foil.
- More surfactant eluted from the PV lens compared to the AO lens as demonstrated with a lower contact angle.

Table 1: Lens Properties of Silicone Hydrogel Lenses.

• Lenses of each brand were taken from the blister packs and blotted dry with lens tissue paper, then placed in 10mL of UNISOL 4[®] for 24 hours and measured using

 Lenses of each brand were taken from the blister packs and blotted dry with lens tissue paper and placed in 10mL of UNISOL 4[®] for 24 hours, then placed in lens cases with 5mL of EOBO solution for 24 hours and

• Treated lenses were extracted in 10mL of saline (UNISOL 4[®]) for 5 minutes, immediately followed by 90 seconds exposure to air. This in-vitro model mimics an extreme case of dilution of components and air

Contact Angle measurements are commonly used to

• The contact angle, θ , appears in the Young-Dupré

 $\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$

• For SD measurements, a goniometer was used with a 5µL droplet of distilled water, UNISOL 4 [®] rinsing solutions and EOBO solution on reference-grade Teflon foil for which a predetermined Zisman plot was available. The SD experiments confirmed the CB results presented. A platinum wire was used throughout SD technique, meticulously flamed to a dull red heat and cooled before transferring test droplets to the Teflon

• For the CB method, an OCA 20 from Future Digital

• CB technique was modified with this instrument. Methodology and Procedure have been reported

• Additional rinsing demonstrated higher contact angles (about of 111-112°) for PV lens UNISOL 4 [®] aliquots, illustrating a continued slow elution of surfactant.

MAIR

Figure 4. MAIR Spectra overlay of Ge prism (baseline, blue line), EOBO neat (initial application, red line), EOBO postleach with distilled water (green line), and EOBO post-rinse with distilled water (black line).



- The MAIR-IR spectrum for the "Neat" EO-BO copolymer, along with co-plotted spectrum for the same specimens after distilled water leaching and again after distilled water rinsing, with the analytical prism baselines included.
- Comparing these spectra, it is clear that EOBO copolymer is much less susceptible to easy water extraction.
- Residual EOBO-treated lenses-wetting behavior after exhaustive distilled water extraction of the lenses was due to retained EOBO.
- The elimination of all IR spectral traces of both EOBO by distilled water rinsing supports the interpretation that persistent EOBO-treated lens water wetting advantages --after exhaustive water extraction-- must be attributed to EOBO still retained from the lens hydrogel superficial sites.

PureVision[®]

CB Advancing Contact Angle at 160 seconds

Figure 5. Captive Bubble Advancing Contact Angles of Bubble on Pure Vision[®] lens UNISOL 4[®] (control), EOBO Test Solution and EOBO Test Solution followed with 10 air-rinse cycles in UNISOL 4[®].



- In all cases for PV, the lenses treated with the EOBO solution were lower in contact angles relative to the saline soaked lens.
- The saline soaked control lenses had high ACA's, characteristic of hydrophobic lens surfaces, ACA's of 76°±4° at 160sec.
- For the treated PV lenses in the EOBO, the ACA of 30°±8° at 160 seconds was substantially lower compared to the saline control.
- For the PV lenses treated with EOBO and then cycled 10 times with fresh UNISOL 4[®] and exposed to air for 90 seconds, the ACA increased to $58^{\circ}\pm5^{\circ}$ at 160 seconds.
- The low advancing contact angles indicate that the treated lens surfaces become more hydrophilic relative to the saline control lens.

- The treatment with EOBO improves wettability of the PV lens surface, indicated by low advancing contact angles compared to the saline control.
- The rinsing of the treated PV lenses demonstrated the continued ability of the EOBO to better rewet the lens relative to the saline control.
- The rinsing of the treated PV lenses also suggested that the EOBO was slowly being eluted from the lenses, indicated by an increasing ACA.

Acuvue[®] Oasys[™]

CB Contact Angle at 160 seconds Figure 6. Captive Bubble Advancing Contact Angles of Bubble on Acuvue[®] OASYS[™] lens UNISOL 4[®] (control), EOBO Test Solution and EOBO Test Solution followed with 10 air-rinse cycles in UNISOL 4[®].



- In all cases for AO, the lenses treated with the EOBO solution were lower in contact angle relative to the saline soaked lenses.
- The saline soaked lens showed a low ACA, characteristic of hydrophilic lens surfaces; ACA at 160 seconds of 30°±2°.
- For the EOBO-treated AOI enses, before and after cycling, the ACA values at 160 seconds were substantially lower, 9°±8° and 15°±3° respectively. **o** These were statistically different only compared to the control.
- The lower advancing contact angles indicated that the treated lens surfaces had become more hydrophilic relative to the saline control lenses.
- The treatment with EOBO improved water wettability of the AO lens surface, indicated by low advancing contact angles compared to the saline controls.
- The rinsing of the treated AO lens demonstrated the ability of the EOBO to continue to facilitate rewetting of the lenses relative to the saline controls.

CB Surface Tension

Figure 7. Surface Tension at Air Bubble Before and After Captive Bubble Experiment of Pure Vision[®] lens for UNISOL 4[®] (control), EOBO Test Solution and EOBO Test Solution followed with 10 air-rinse cycles in UNISOL 4[®].





Figure 8. Surface Tension at Air Bubble Before and After Captive Bubble Experiment of Acuvue[®] OASYS[™] lens for UNISOL 4[®] (control), EOBO Test Solution and EOBO Test Solution followed with 10 air-rinse cycles in UNISOL 4[®].



- In all cases, for both PV and AO lenses, initial surface tension measurements before all CB experiments were performed and indicated a surfactant-poor environment with all SFT above 72mN/m.
- Foralltreatments, after experimentation measurements indicated that the solution remained surfactant-poor, with a SFT near 72mN/m.

CONCLUSIONS

- Sessile Droplet contact angle results of the UNISOL 4[®] storage solutions on reference-grade Teflon foil confirmed slow elution of EOBO from PV lenses.
- MAI-IR spectroscopy demonstrated the EOBO substantivity even after exhaustive lens rinsing.
- Captive Bubble measurements differentiated saline soaked hydrophobic and hydrophilic lens surfaces from EOBO solution soaked lenses and air-rinse cycling conditions.
- Captive Bubble measurements demonstrated the reservoir/depot effects of the EOBO solution during the rinsing condition.
- EOBO treatment of both SiH lens types lowered advancing water contact angles, providing an improved hydrophilic surface even after rinsing.
- EOBO demonstrated improved hydrophilic and substantive rewetting properties relative to the saline controls, with lower ACA's after rinsing for both lens surface chemistries.

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