Abrasion Resistant Anti-Reflective Sol-Gel Coatings

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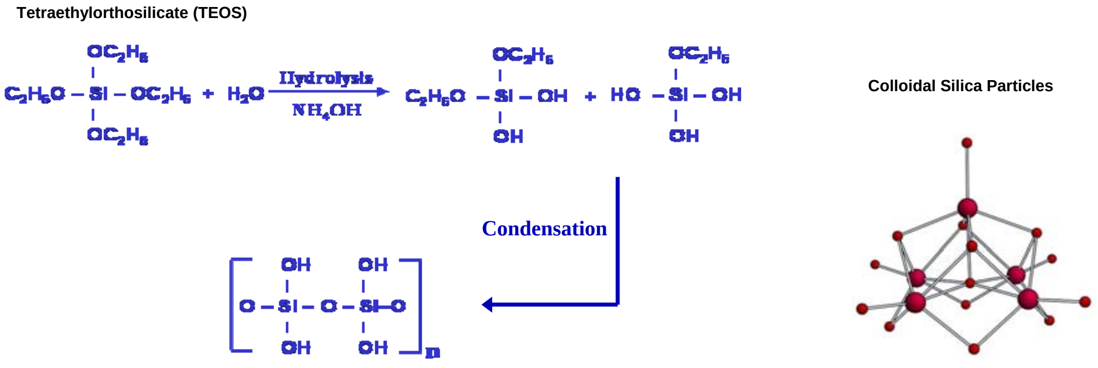
1. Abstract

Many optics in both the OMEGA and OMEGA EP lasers are coated with anti-reflective (AR) silane sol-gel to maximize their transmittance. Although these coatings are highly resistant to both airborne contaminants and laser damage, they are susceptible to mechanical damage by abrasion, and thus require extra care during the handling, installation and alignment of sol-gel optics. Previous "hardened" sol-gel AR formulations achieved physical robustness through exposure to ammonia, but were highly susceptible to degradation by atmospheric contaminants. In this work, alternate cross-linking agents for improving both mechanical robustness and contamination resistance were studied. The effectiveness of acryloyl chloride and glyoxal as "hardening" agents was evaluated through both solution and vapor-phase exposure. A drag-wipe testing protocol was developed for these chemically modified sol-gel AR coatings to determine their abrasion resistance as a function of hardening agent and exposure time. Results showed that glyoxal modification of AR coatings is effective in improving abrasion resistance, while contamination resistance and laser damage resistance need to be explored further.

2. Introduction

Silane modified sol-gel coatings are deposited on many optics in the OMEGA laser. The surface of every optic has a potential loss in transmission due to the difference between its refractive index and that of air (Fresnel loss). Sol-gel coatings function as an anti-reflective (AR) layer by minimizing this difference in refractive index. The sol-gel is synthesized from tetraethylorthosilicate (TEOS), an alokxysilane compound, by a base-catalyzed condensation reaction.[1] In this process TEOS reacts with ethanol in the presence of ammonia. The alkoxy groups (OR) on the TEOS are replaced with hydroxyl groups, with an alcohol as a byproduct (OHR). The hydroxyl groups bond together to form silicon-oxygen bonds through a condensation reaction. Over time these siloxane chains condense in three dimensions to form colloidal particles. After the sol-gel colloidal suspension is deposited onto the surface of an optic, the loss of solvent increases the rate of condensation and the particle network tightens, forming a “xerogel”. [2,3] Figure 1 shows this reaction schematically.



(a) (b)

Fig.1: Formation of sol-gel particles. (a) Base-catalyzed condensation of TEOS with ethanol forms siloxane chains; (b) with time, the chains extend in three dimensions to form a network of colloidal silica particles. Further treatment of the colloidal silica particles with a reactive silane increases their contamination resistance.

Because of the presence of volatile and semi-volatile contaminants (organic compounds, water) in the laser-bay air, standard TEOS based sol-gel AR coatings lose their transmission efficiency over periods of several months.[4] The current silane modified TEOS based sol-gels used in OMEGA have extended working lifetimes due to their excellent contamination and laser damage resistance,[4] but are very sensitive to abrasion. Previously, sol-gel AR coatings were treated through cross-linking of hydroxyl groups with ammonia vapor for 24 hours to increase their physical robustness. Although this method is very effective in improving abrasion resistance without decreasing transmission significantly, the contamination resistance of these ”ammonia-hardened” sol-gels is not significantly better than standard TEOS sol-gel AR coatings.

In this study TEOS based sol-gel solutions were modified using a series of organic cross-linking agents, including glyoxal, acryloyl chloride and triethoxyvinylsilane with ethylene glycol dimethycrylate.[5] Figures 2-4 show how these materials react with the OH groups on the surface of the sol-gel coating to improve its abrasion resistance.

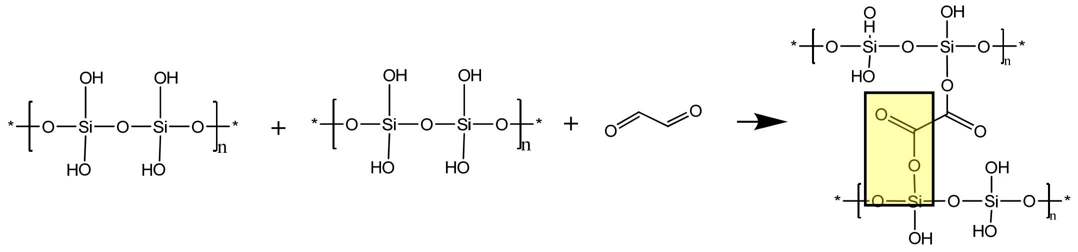


Fig.2: Cross-linking reaction of glyoxal with the siloxane surface of the sol-gel particle. The yellow box shows the cross-link point between siloxane chains.

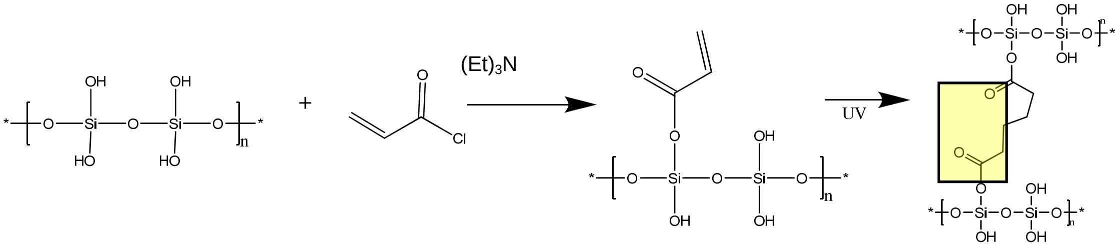


Fig.3: Cross-linking reaction of acryloyl chloride with the siloxane surface of the sol-gel particle. The yellow box shows the cross-link point between the siloxane chains.

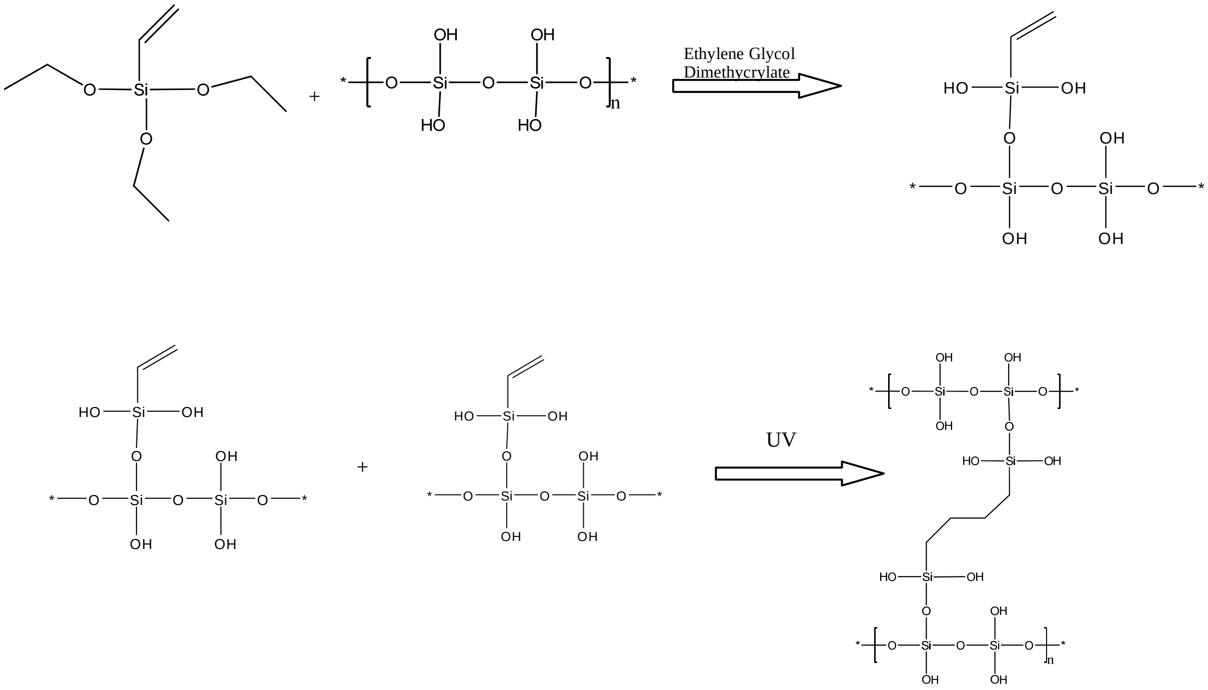


Fig. 4: Cross-linking reaction of triethoxyvinylsilane with the siloxane surface of the sol-gel particle. This reaction differs from those shown in Figs 2 and 3 in that it utilizes a free-radical mechanism initiated by UV light.

For both the acryloyl chloride and glyoxal cross-linking agents, studies of cross-linking efficiency and abrasion resistance were conducted by exposure of the sol-gel-coated substrate to a saturated vapor-phase environment of the cross-linking agent as well as cross-linking directly in the coating solution. Experiments with triethoxyvinyl silane were conducted only in the solution phase.

The effectiveness of these cross-linking agents in terms of improving abrasion resistance was measured using a drag-wiping protocol. Preliminary testing of contamination resistance was also conducted. The goal of this project was to find a cross linking agent that would achieve both abrasion resistance and contamination resistance without affecting the transmission of the AR coating.

3. Experimental Data

The un-modified TEOS based AR coating was prepared using 22.0425 L of ethanol, 2.320 L of TEOS, and 717.5 ml of ammonium hydroxide (NH_4OH). For glyoxal and acryloyl chloride vapor saturation trials, a previously prepared TEOS based sol-gel "stock" solution was spin-coated onto substrates in a Class 100 laminar flow hood housed in a Class 10,000 clean room. The substrate surface was first completely flooded with sol-gel solution with the spin-coater at rest. The substrate was then spun at 2000 RPM for 40 sec, which removed excess coating material and distributed the remaining solution evenly over the substrate surface. Both the spin time and speed affect the thickness of the AR coating, which in turn affects the transmission efficiency of the coating as a function of wavelength. After spin coating the substrates were allowed to dry for 24 hours.

The optical transmission of the substrates both before and after sol gel AR coating was tested using a Perkin Elmer Lambda 900 UV-VIS-NIR spectrophotometer over a wavelength range of 300 nm to 1500 nm. Over the area where the coating acted as an AR layer (500 nm to 800 nm) the transmittance of the substrate after coating was increased by an average of 5.5% .

Vapor-phase crosslinking experiments were conducted by exposing the substrates to a vapor-saturated environment of the cross-linking agent in a sealed container for 24 hours. The optical transmission of the exposed coatings was then measured again to determine any changes in transmission caused by the cross-linking reaction.

For solution-phase cross-linking experiments, solutions of acryloyl chloride (5% and 10% wt/wt) and glyoxal (2%, 4%, 6%, 8% and 10% wt/wt) in the stock TEOS sol-gel solutions were prepared. Triethylamine was added to the acryloyl chloride solutions as a catalyst. The glyoxal and acryloyl chloride modified sol-gel solutions were spin coated and dried for 24 hours in a Class 100 laminar flow hood housed in a Class 10,000 clean room. Subsequently, the acryloyl chloride substrates were irradiated under a UV lamp for 90 minutes, to promote cross-linking. Then the coatings' abrasion resistance and optical clarity were tested.

Abrasion resistance was tested qualitatively by means of a drag-wiping protocol developed specifically for this measurement. Figure 5 illustrates the testing process. The sol-gel AR coated substrate was placed on a clean dry surface and a clean room wipe was placed on the AR coated surface. Additional substrates (each with a mass of 7.4 grams) were placed on top of the wipe and the wipe was dragged across the surface of the sol-gel coated substrate. The substrate was then examined by optical microscopy in reflection to assess the amount of coating abrasion. The process was repeated with an increasing mass load (more substrates) until significant coating damage was observed.

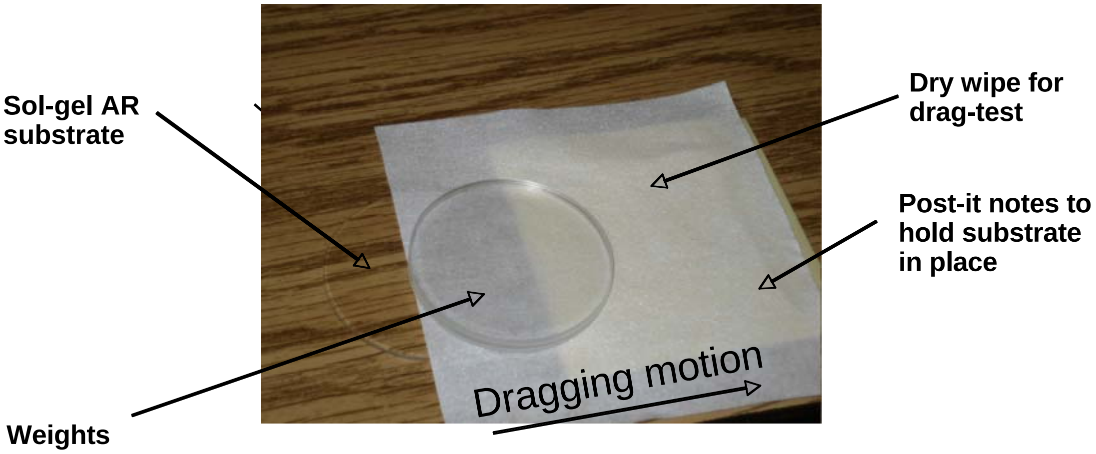


Fig. 5: Abrasion resistance drag-wipe testing process for modified sol-gel coatings. Additional mass in the form of substrates is added to the wipe until significant sol-gel coating damage is observed.

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After the initial testing of transmission and abrasion resistance, the modified sol-gel coatings were left to age for four weeks. The abrasion resistance of the glyoxal-modified coatings substantially increased after this aging period, in some cases by a factor of 6. Figure 6 presents the abrasion resistance values for these four-week aged coating samples. All cross-linking agents demonstrated an increase in abrasion resistance over the standard TEOS based sol-gel. The glyoxal-modified AR coatings prepared by solution deposition demonstrated the highest abrasion resistance, with the 8% glyoxal modified coating showing no damage under the highest mass loads tested. The photomicrographs in Fig. 6 compare the abrasive damage sustained by a standard TEOS sol-gel coating and a glyoxal-modified coating after drag-wiping with the maximum sustainable load for each coating. The TEOS coating shows severe abrasion with only 7.4 g load, whereas the glyoxal-modified coating is able to withstand a 21x greater drag-wipe load while showing only minimal damage.

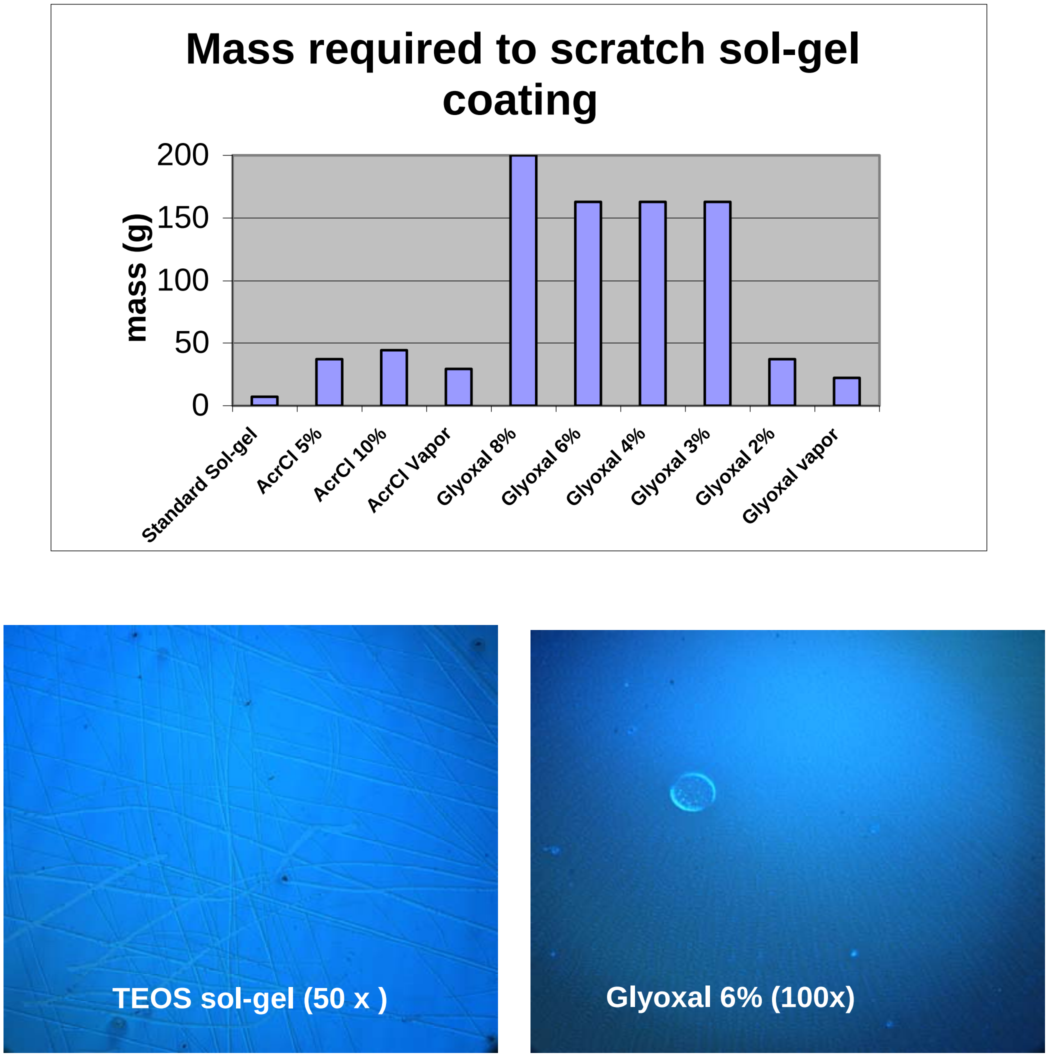
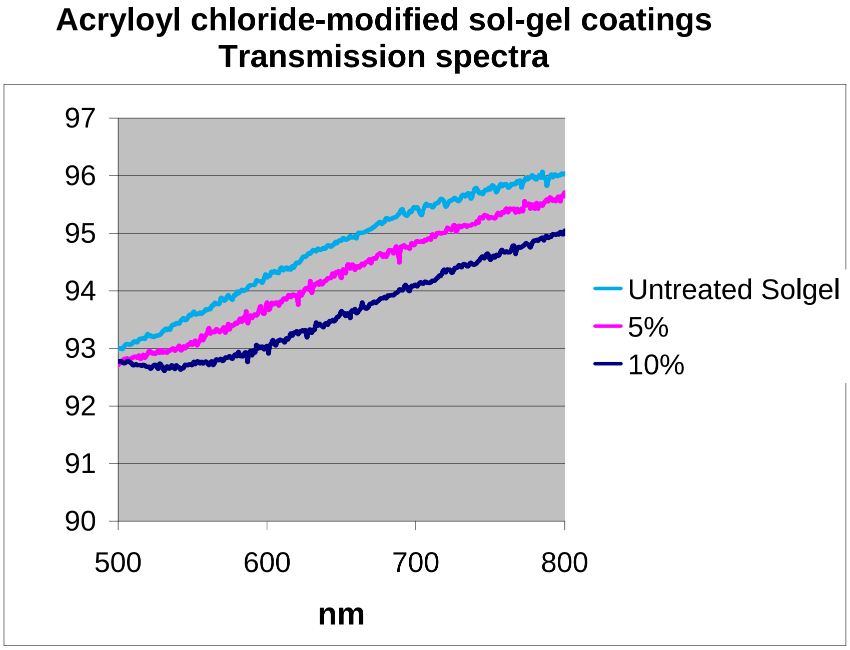


Fig. 6: *Top*: Abrasion resistance data for modified sol-gel coatings aged for 4 weeks. *Bottom*: Photomicrographs of standard TEOS sol-gel AR and 6% glyoxal-modified sol-gel AR after drag-wiping with 7.4 g and 160 g mass loads, respectively.

Figure 7 shows optical transmission data for both acryloyl chloride-modified and glyoxal- modified sol-gel AR coatings as a function of cross-linking agent concentration. Overall, the glyoxal modified coatings showed higher abrasion resistance than the acryloyl chloride modified coatings.



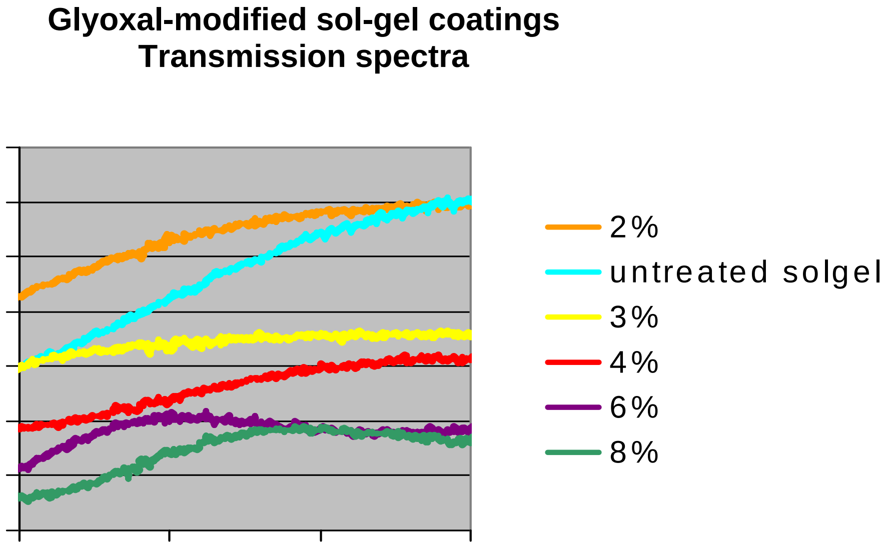


Fig. 7: Transmission spectra of modified sol-gel coatings as a function of cross-linking agent concentration. *Top*: Transmission spectra for acryloyl chloride-modified sol-gel coatings. *Bottom:* Transmission spectra for glyoxal-modified sol-gel coatings. Included with both sets of transmission spectra are a transmission profile for a standard (non-modified) sol-gel coating as a reference.

A change in transmission of the cross-linked sol-gel AR coatings was observed as a function of time after preparation. Figure 8 shows this change in optical transmission for two representative glyoxal-modified coatings at two different cross-linker concentrations. The 4.4% glyoxal-modified coating demonstrated an increase in optical transmission, while the 8% glyoxal-modified coating demonstrated a decrease in transmission. This change in transmission may be due to either loss of volatiles (solvent) or a very slow change in coating morphology due to extended cross-linking occurring at a very slow rate. Loss of solvent could produce either an increase or decrease in transmission, depending on whether the refractive index of the coating is increased or decreased by the solvent loss. Extended slow cross-linking may be causing an increase in sol-gel particle size (a change in surface morphology), with a concurrent increase in forward (or backward) scattering- either of which would result in transmission loss. Further work needs to be done to understand the full nature of this time-based change in optical and mechanical properties.

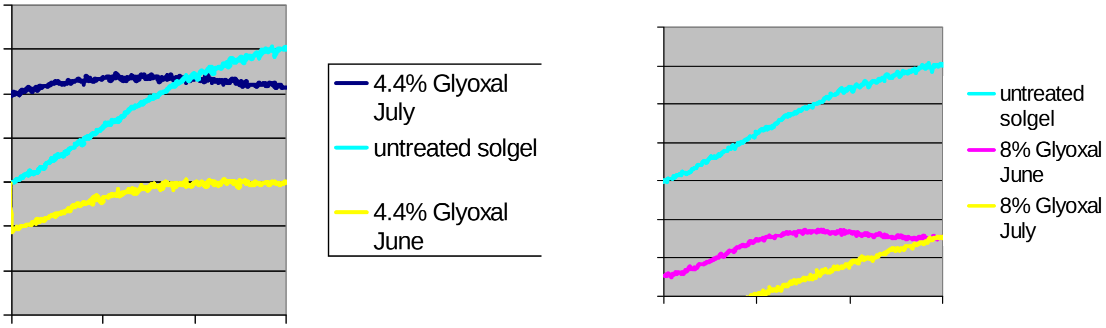


Fig. 8: Optical transmission of glyoxal-modified coatings as a function of aging time. *Left:* Coating modified with 4.4% wt glyoxal. *Right:* Coating modified with 8 wt% glyoxal. Transmission curves for a standard (non-crosslinked) sol-gel coating are included for reference.

Preliminary testing was done with triethoxyvinylsilane (TEVS) combined with ethylene glycol dimethacrylate. The procedure was adapted from that used to prepare the silane-modified sol-gels currently in use in OMEGA. The standard TEOS-based sol-gel stock solution was added to a light-proof flask and stirred for 3 hours. Ammonium hydroxide was added and the mixture was stirred for another two hours. The solution was sealed and left to sit for three days. The solution was then refluxed to evaporate off excess ammonia. The TEVS was then added at 10%, 20%, and 30% wt/wt to three 25 ml portions of the sol-gel solution. A few drops of ethylene glycol dimethyacrylate were also added to each portion as a free radical catalyst. Sixty ppm of hydroquinone was added to prevent the TEVS from undergoing intra-molecular cross-linking. These solutions were sealed in light-proof containers and left to react for 3 days. The modified sol-gel solution was then filtered to remove the hydroquinone prior to spin-coating. After spin-deposition, the coating was irradiated while still wet to prevent the evaporation of ethylene glycol dimethycrylate. The TEVS-modified coating at a cross-linking concentration of 30% shows improved transmission as compared to a standard sol-gel coating (Fig 9). In terms of abrasion resistance, the 30% TEVS coating scored a “6” on the abrasion index test, which corresponds to a drag load of 44.4 grams- roughly equivalent to the abrasion resistance shown by the 2% glyoxal modified coating or any of the acryloyl chloride-modified coatings.

Preliminary experiments were conducted on both glyoxal-modified and TEVS-modified sol-gel AR coatings using iso-octane to test the effectiveness of these coatings to contamination by an organic vapor. Figure 10 shows that the transmission for a glyoxal- modified coating after exposure to iso-octane vapor is comparable to that of an unmodified TEOS based sol-gel, while the TEVS-modified coating had excellent contamination resistance. This enhanced contamination resistance is believed to be due to the same mechanism responsible for producing the high contamination resistance in earlier silane-modified sol-gel coatings- the presence of bulky, hydrophobic silane functional groups on the sol-gel particle.

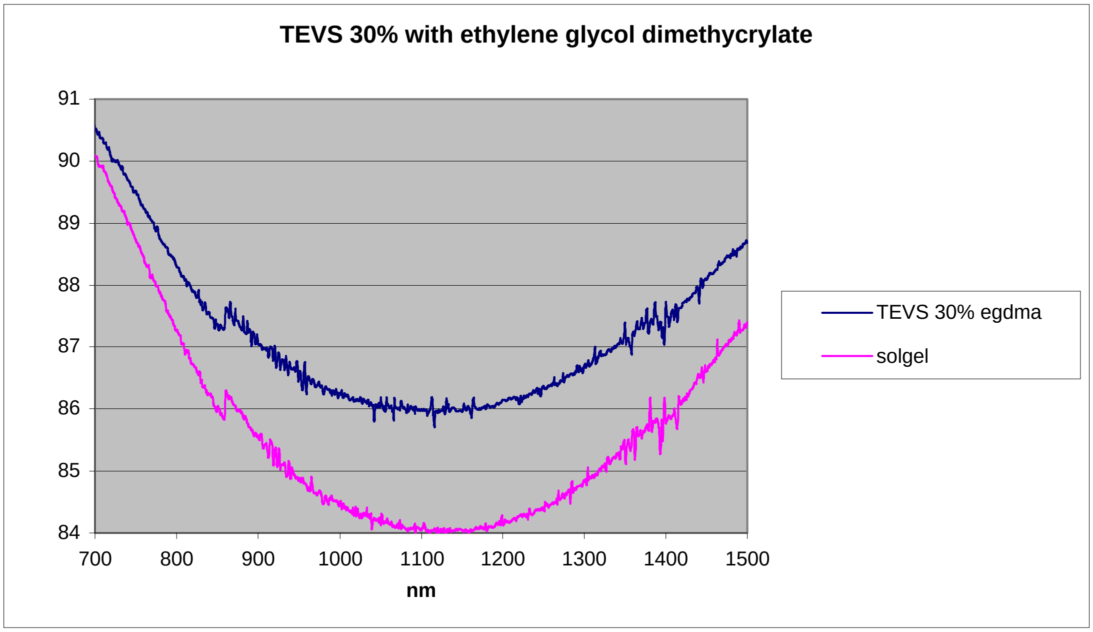


Fig. 9: Optical transmission of a TEVS –modified sol-gel AR sample. Data on a standard sol-gel AR is included for reference.

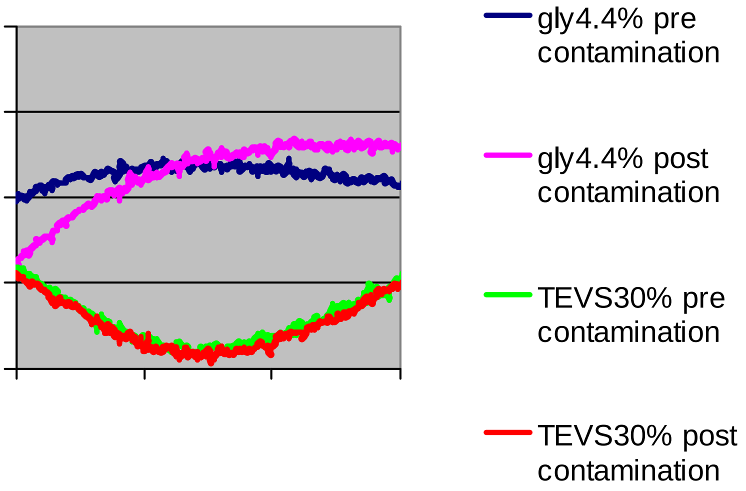


Fig. 10: Change in transmission of glyoxal and TEVS-modified sol-gel coatings after a 24 hr exposure to an environment saturated with iso-octane vapor.

4. Conclusion

Sol-gel AR coatings were modified by both vapor-phase and solution phase treatment with several organic cross-linking agents to improve their abrasion resistance. A drag-wipe protocol was developed to evaluate the abrasion resistance of these modified coatings. Glyoxal-treated sol-gels demonstrated a 6x – 20x improvement in abrasion resistance (depending on cross-linker concentration) that increased over time as the coating aged. Changes in the transmission of the coatings with time were also observed. Further research into the aging process, and how that affects the optical transmission of glyoxal-modified coatings may show how the transmission may be improved. Also, the surface morphology of the glyoxal-modified coatings and its effect on optical transmission is an area that will require further research. Triethoxyvinylsilane modified ARs showed very promising preliminary results, but need to be further tested.

For these new coatings to be viable for use in OMEGA and OMEGA EP, their laser resistance and contamination resistance needs to be further tested. If future work in this area continues to yield promising results, the mechanical durability and contamination resistance of these coatings will greatly extend their useful life in high peak power laser systems.

5. **Acknowledgements:**

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6. References:

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