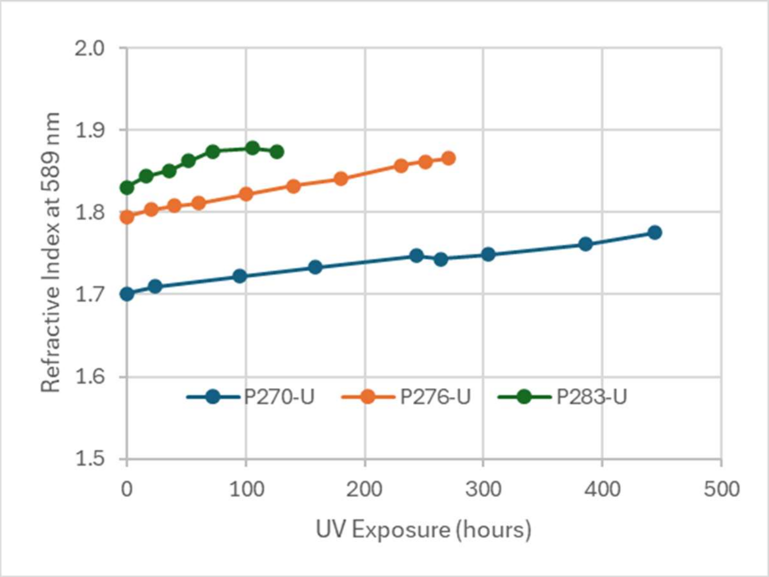
UV NIL Technology

Addison Clear Wave's UV-Stabilized High Refractive Index Nano-Imprint Lithography Resins: the LuxNIL® "U" Series



Addison Clear Wave's UV-Stabilized High Refractive Index Nano-Imprint Lithography Resins: the LuxNIL® "U" Series

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UV nano-imprint lithography (UV-NIL) is an economical method for embossing features on glass or silicon. In this method, an imprint resin is coated on the substrate, a working stamp is pressed into the surface of the resin, and the resin is cured by UV light. Using semi-conductor equipment, the substrate can be a 200 or 300 mm wafer, and multiple copies of imprinted wafers can be manufactured rapidly.

For AR/VR/MR applications of UV-NIL, very high refractive index (RI) resins can be used to permit wide field of view (FOV) images. A drawback for such an application is that high RI imprint resins contain titanium oxide (titania) nano-particle (NP) fillers, and titania is an efficient photo-catalyst. Titania absorbs the 300-400 nm UV component of sunlight, producing an electronically excited state that reduces and oxidizes molecules in competition with relaxation back to the ground state,[1] and the products of the redox reactions are radicals that lead to destruction of organic compounds including cured imprinted resins. Titania NPs are the only materials currently available with both high RI and transparency in the visible range, and imparting UV stability to high RI NIL resins containing titania NPs is an important objective for promoting general acceptance of UV-NIL for AR/VR/MR applications.

In ongoing development work, ACW has targeted the preparation of UV-stable high RI resins that are readily imprinted in UV NIL applications using mass production equipment. In this paper we describe our progress in moving towards this goal with UV-stress testing of our recently released LuxNIL® "U" resins. Overall, we have improved the stability to UV damage in sunlight by an order of magnitude in comparison to conventional titania NP-containing resins.

Methods

Resins. The LuxNIL® "U" series of UV NIL resins studied in this work is now commercially available. "Conventional" resins studied in this work are formulations containing functionalized titania NPs in acrylate pre-polymer resins which do not have the improvements in design incorporated in the LuxNIL® "U" resins.

Sample Preparation. 22 x 50 mm microscope cover glass slides (Fisher Scientific) were coated with titania-containing NIL formulations in 50% by volume PGMEA. The coated slides were heated in a convection oven at 100 °C for 60 seconds to remove solvent and then irradiated with 250 mW/cm^2 of 365 nm LED light for 100 seconds in a nitrogen atmosphere. The cured coupons were conditioned in a convection oven at 150 °C for 4 hours. The resin thickness in the samples studied ranged from 0.7 to 1.2 microns.

”Sunlight” Irradiation. A Q-Sun Model Xe-1 xenon arc lamp tester (Q-Lab Corporation) with a Daylight Q filter was employed. The irradiance was modeled after ASTM Method D5071[2] Cycle 1 employing continuous irradiation of 350 mW/(m^2·nm) at 340 nm but with the temperature set at 45 °C instead of 63 °C. The power setting with the Daylight Q filter gives UV (300-400 nm) irradiation of 41.5 W/m^2 and total artificial sunlight (300-800 nm) irradiation of 365 W/m^2. During irradiation, the samples were open to the atmosphere.

Damage Evaluation. The refractive indices (RI) at 25 °C of samples before and after irradiation were determined with a Metricon Model M2010 prism coupler equipped with four lasers (456.8, 516.0, 637.7, and 853.7 nm). The data was fit to a Cauchy function, and the RI at 589 nm was calculated from this function. All RI values reported herein are for 589 nm and 25 °C.

Results and Discussion

We adopted the seemingly simple concept that sunlight damage should be studied by placing objects in sunlight. Using a xenon arc lamp with a Daylight Q filter gives an irradiance spectrum that closely mimics sunlight reaching the surface of the Earth (Figure 1). At the power setting used in this work, the artificial sunlight in the tester had approximately twice the average energy of sunlight at the Earth’s surface. Conveniently, 1 hour irradiation in our test apparatus was equivalent to about 2 hours of average outdoor sunlight exposure.

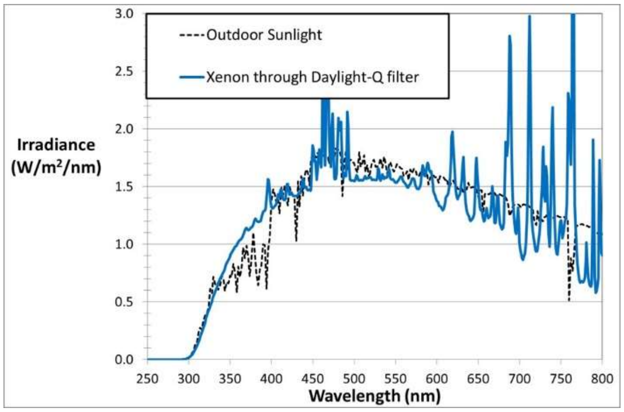

Figure 1. Outdoor sunlight spectrum compared to the spectrum from a xenon arc lamp filtered with a Daylight Q filter. Figure courtesy of Q-Lab Corp. (q-lab.com).

The RI behavior of conventional high RI UV-NIL resins is shown in Figure 2A. Within a few hours of irradiation, the RI increased by about 0.03 to 0.04 units. Subsequently, the RI rapidly decreased, ultimately dropping by about 0.2 units in 15 hours at which point the studies were terminated. At the point of termination, the originally rigid resins had become soft and tacky. In a parallel study, thicker samples (2-3 microns) of two of the resins were irradiated and weighed at intervals giving the results shown in Figure 2B; there was a smooth decrease in mass from the onset of irradiation.

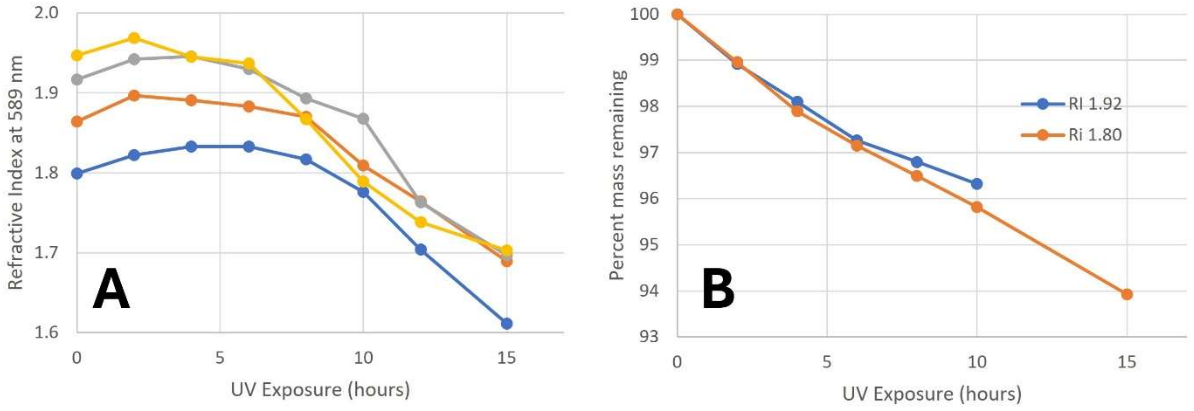

Figure 2. Results from irradiating conventional high RI NIL resins. **A.** Observed RI over 15 hours of irradiation. **B.** Average mass loss upon irradiation of 3 samples each of resins with initial RI values of 1.92 and 1.80.

Our interpretation of the results shown in Figure 2 is that photo-excited titania produced radicals by redox reactions, and this resulted in radical-based reactions of organic components of the mixture, the organic coatings of the NPs and the cured polymer. Small organic compounds formed in radical fragmentation reactions would evaporate from the resin, initially resulting in a higher percentage of titania and an increase in RI. As radical reactions proceeded further, we believe it is likely that the titania NPs lacking some or much of their organic coatings agglomerated resulting in a reduction in the RI. We note that increasing the average volumes of the NPs by agglomeration or pooling will give a reduced total cross-section for the NPs and, hence, a reduction in RI.

“Sunlight” irradiation of ACW’s recently introduced LuxNIL® “U” series of UV NIL resins gave results shown in Figure 3. The lower RI resins P270-U (RI 1.70) and P276-U (RI 1.80) shown in Figure 3A displayed very good UV-resistant behavior with the increase in RI occurring over several hundred hours of our artificial “sunlight” exposure. P276-U can be compared to an RI 1.80 conventional resin shown above in Figure 2A. In terms of RI growth, P276-U had about 10 times the stability of the conventional resin. P283-U, which has an RI of 1.83, displayed a considerably longer lifetime than the conventional resins with RI 1.80 and RI 1.85 shown in Figure 2A in terms of RI growth. The 100+ hours of artificial “sunlight” exposure for P283-U in our test translates to 200+ hours of average outdoor sunlight, and we consider this to be moderate UV stability.

Figure 3B shows results for LuxNIL® P-285-U (RI 1.90) compared to a conventional NIL resin that has RI 1.92. It is gratifying to see that this high RI resin appears to display about an order of magnitude increased UV stability in comparison to the conventional resin, but we consider the enhanced stability of P285-U to be only modest.

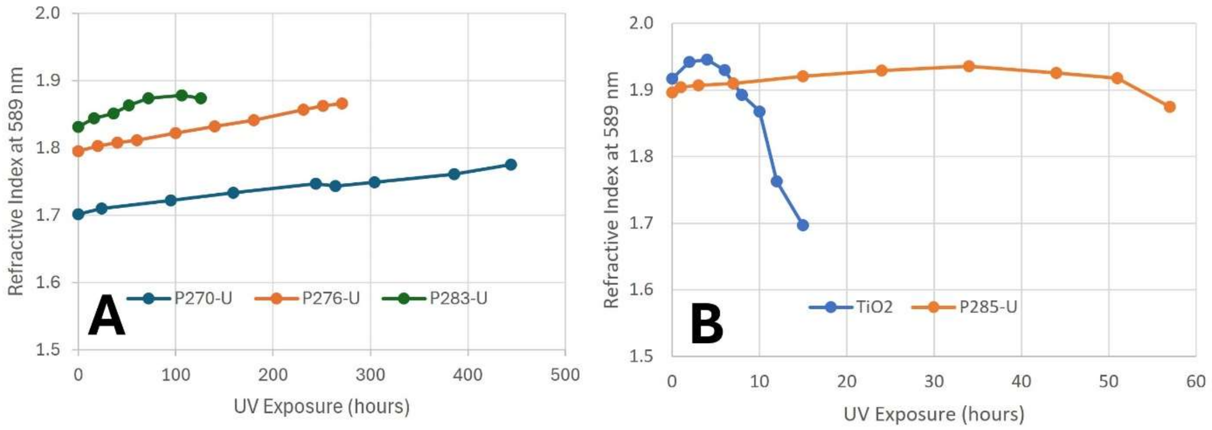

Figure 3. Results from irradiated LuxNIL® "U" series NIL resins. **A.** Low RI U resins. **B.** P285-U compared to a conventional NIL resin of similar RI (labeled TiO_2).

Conclusion

In this work we evaluated the UV-stability of NIL resins by following the RI of resins irradiated with artificial "sunlight" at twice the average power of sunlight that reaches the Earth's surface. We have made a logical assumption that changes in RI reflected the resin's UV stability. While it is seemingly apparent that reduction of the resin RI from, for example, 1.9 to 1.7 would effectively damage or destroy a diffractive optical element designed for operation at RI 1.9, it is possible that UV damage to a DOE might arise earlier if the imprint patterns collapsed before RI reduction was extensive. To our knowledge, studies of the behavior of nano-imprint patterns in UV stressed NIL DOEs have not yet been conducted, and such studies beg for attention.

The LuxNIL® "U" resins were designed for enhanced UV-stability, and we have made a significant step in that direction in that the "U" resins appear to be about an order of magnitude more stable than conventional NIL resins of similar RI. The promise from these results is that the future generations of stabilized high RI UV NIL resins will be even more UV resistant, and ACW is committed to fulfilling that promise.

References

(1) Ohtani, B. Titania Photocatalysis beyond Recombination: A Critical Review. *Catalysts* **2013**, *3*, 942-953. https://doi.org/10.3390/catal3040942

(2) ASTM D5071 Standard Practice for Exposure of Photodegradable Plastics in a Xenon Arc Apparatus. https://astm.org/d5071-06r21.html