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# Photobleaching of transparent photopolymer resins for use in LED lighting optical elements

Jean Paul Freyssinier[a], Indika U. Perera[a], Nadarajah Narendran[a1], and Akila S. Udage[b]
[a]Lighting Research Center, Rensselaer Polytechnic Institute, 21 Union St., Troy, NY, 12180 USA
[b]formerly Lighting Research Center, Rensselaer Polytechnic Institute, 21 Union St., Troy, NY, 12180 USA (Align Technology, Inc., 2820 Orchard Parkway, San Jose, CA, USA)

## ABSTRACT

Photopolymer 3D printing of optically clear resins is a promising technology for producing custom optical elements for general illumination. However, the transparency of the final 3D-printed part may depend on secondary processes. Residual photoinitiator can result in a yellowish tint that can be photobleached after exposure of the 3D-printed part to a light source. The study was designed to understand the tradeoff between the spectral characteristics of the light source used for the photobleaching and the irradiance to which test samples were exposed on the rate of photobleaching. A total of 14 samples were tested at room temperature for 120 minutes under a combination of three light sources (xenon, phosphor converted white LED, and direct emission blue LED), and up to five irradiance levels for each source in the range 0.0025 to 0.2238 W/cm$^2$. The results showed that for the white LED, irradiance can increase the magnitude of the photobleaching. In this study, the maximum chromaticity shift was equivalent to a 4-step MacAdam ellipse. These results seem to indicate that it is possible to expedite photobleaching by increasing the irradiance, although more testing is necessary to find an optimum value. The results for the blue LED tests (peak wavelength 450 nm) showed that this spectrum can be as effective or slightly better at photobleaching than the white LED tested for the same total irradiance. The samples exposed to the xenon light source resulted in increased yellowish tint, presumably because of additional oxidation on the surface of the sample. For these samples irradiated with the xenon lamp, the tint increased with increasing irradiance.

**Keywords:** 3D printing, lens, secondary optics, LED, illumination, transparent, photopolymer, photobleaching

## 1. INTRODUCTION

Because of their relatively small size and the possibility to create arrays of distributed light sources, LEDs offer more flexibility for optical control with higher optical efficiency.[1] In turn, this means that lighting products can be designed with innovative optical designs for creating visually effective and energy-efficient lighting applications.[2] However, similar to other industries, two of the main challenges to achieve the benefits of custom optical designs have been the high cost of tooling and the long lead times to market.[3] 3D-printed custom optical elements hold great potential to alleviate these roadblocks. Additionally, 3D-printed lighting components can benefit local and domestic economies. Specifically, the US Department of Energy identified custom optics as one of the opportunities for 3D printing to increase domestic production of solid-state lighting.[4]

While there are challenges for mass producing optical elements comparable to traditionally manufactured optics, 3D printing of complex optic elements, including reflective and freeform transmissive optics, has been demonstrated.[5]-[8] Some of the challenges include careful consideration with respect to material properties that determine the optical quality, including transparency, homogeneity, and surface finish.[9]

[1] Corresponding author: N. Narendran
E-mail: narenn2@rpi.edu; Telephone: +1 (518) 276-7100; Website: https://www.lrc.rpi.edu/programs/solidstate/

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Photopolymer 3D printing of optically clear resins is a promising technology for producing custom optical elements for general illumination.[7],[8] However, the transparency of the printed parts may depend on post-processing to achieve optimum results. For example, parts produced by a multi-jet modeling (MJM) process using a photopolymer resin commonly used to simulate polymethyl methacrylate consistently have a yellowish tint immediately after being 3D-printed, due in part to residual photoinitiator from the photopolymerization process.[9] An example is shown in Figure 1. The yellowish tint is undesirable for general illumination applications where white light produced by the LED light source is expected to remain unchanged by secondary optical elements. Although unaided photobleaching occurs under ambient conditions, preliminary testing at light levels common from office lighting (~300 lx, triphosphor fluorescent lamps) showed that it can take several hundreds of hours to reach maximum photobleaching (unpublished results). Because a long waiting time is counterproductive to producing parts on demand, this study was designed to understand the effect of the spectrum and the irradiance to which 3D-printed parts are exposed on the rate of photobleaching. The overarching goal is to determine if photobleaching can be expedited and if the final clarity of printed parts can be maximized by controlling these two photometric characteristics.

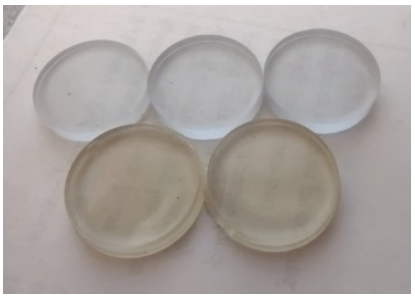

Figure 1. Examples of 3D-printed test samples before and after photobleaching. In the picture, the three samples in the top row have gone through complete photobleaching, whereas the two samples in the bottom row appear tinted immediately after being printed.

## 2. METHODOLOGY

The study was designed to better understand the effect of the spectrum and the irradiance to which 3D-printed parts are exposed on the rate and magnitude of photobleaching. Test samples were 3D-printed using a transparent resin in a multi-jet modeling (MJM) 3D printer and exposed to three spectra and up to five irradiance levels, at room temperature (73°F ±2°F). The change in the inline total hemispherical spectral transmittance of the test samples was used as a measure of the magnitude of photobleaching achieved for each combination of light source spectrum and irradiance value. For each sample, the spectral transmittance was used to estimate the 1931 CIE xy chromaticity before and after exposure to each test condition. The magnitude of the shift in CIE xy chromaticity was evaluated in terms of MacAdam ellipse steps for ease of comparison.

### 2.1 Light sources and irradiance levels

The light sources used in the study included a xenon lamp, which produces a broadband spectrum including UV and IR radiation; a 5000 K phosphor-converted white LED, which also produces a broadband spectrum with minimal gaps in the short-wavelength region; and a direct emission blue LED with a 450 nm peak wavelength. Each of the three light sources were controlled to produce irradiance levels from 0.0025 W/cm$^2$ to 0.2238 W/cm$^2$. The range of test irradiance values was chosen to be close to what the secondary optics of an LED system would be exposed to as reported in the literature.[11] A single sample was tested for each combination of spectrum and irradiance. The exposure time was 120 minutes. Table 1 lists the irradiance test conditions used in this study, and Figure 2 shows the relative spectral power distribution of each source.

Table 1. Irradiance values (W/cm²) used for each of the three light source spectra.

| Xenon | White LED | Blue LED |
|---|---|---|
| 0.0025 | 0.0189 | 0.0095 |
| 0.0241 | 0.0379 | 0.0126 |
| 0.0562 | 0.0785 | 0.0191 |
| 0.0713 | 0.1122 | 0.0252 |
| 0.2238 | 0.1655 | N/A |

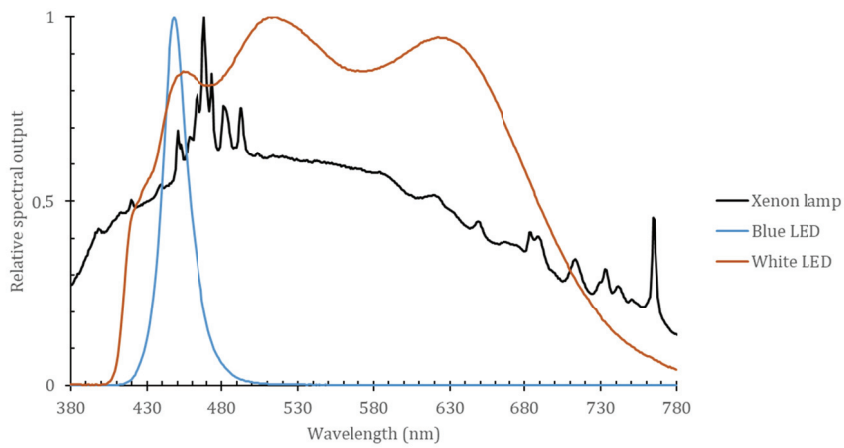


Figure 2. Relative spectral output of each of the three experimental light sources used for the study. Although it is not shown in the graph, it should be noted that the spectrum of the xenon lamp extends into the ultraviolet and infrared regions.

## 2.2 Test samples

Circular test samples measuring 25 mm in diameter and 6 mm in thickness were 3D-printed in-house at a nominal layer height of 15 µm. The samples were printed in one photopolymer resin using a MJM printer. The resin was selected based on its suitability for printing optical components, as previously reported.[1]-**Error! Reference source not found.** Immediately after printing, the support material was removed and the samples were cleaned and prepared for initial characterization.

## 2.3 Characterization setup

A similar setup as that reported by Privitera et al. [10] was used to measure the inline total hemispherical spectral transmittance of each test sample before and after exposure to photobleaching conditions. The setup uses a mechanicalapperture and converging lens to focus the beam of light from a 500 W xenon lamp onto the test sample being characterized. The test sample is located at the opening of an 8-inch integrating sphere. A fiber spectroradiometer then measures the light transmitted through the test sample. Dark readings and light source reference readings are also captured and used to determine the inline total hemispherical spectral transmittance of the test sample. Figure 3 shows the components of the characterization setup.

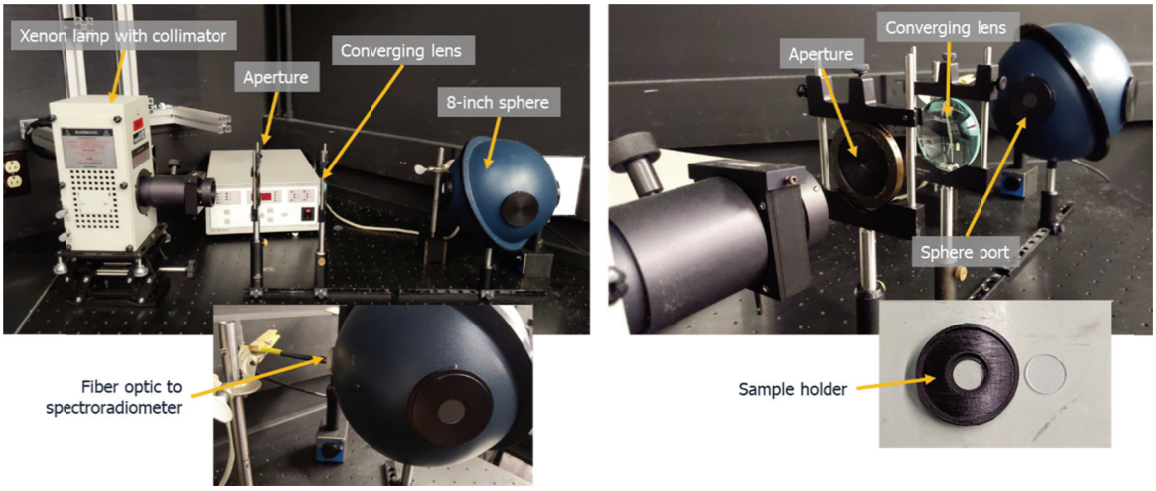


Figure 3. Experimental setup used to characterize the inline total hemispherical spectral transmittance of the samples under test. The setup builds on the original design reported by Privitera et al. (2019).[10]

In addition to being used to characterize each test sample, this setup, incluing the xenon lamp, was used as one of the light sources for photobleaching. The highest of the five irradiance values was simply the irradiance achieved by the setup in its normal configuration. The reminaing four irradiance values were realized by adding neutral density filters in front of the xenon lamp. A computer collected the measurements at regular intervals at the beginning of the test (t = 0 minutes) and throughout a photobleaching period of 120 minutes.

### 2.4 Irradiance test setup for LED light source conditions

A second setup was designed to hold the test samples, one at a time, and expose them to either the white or the blue LEDs. A programmable dc power supply was used to modulate the LED current to achieve the target irradiance values listed in Table 1. The light exiting the test sample was coupled to a 10-inch integrating sphere. A spectroradiometer was used to measure the relative change in inline total hemispherical spectral transmittance of each sample at regular intervals over a 120-minute exposure time. Samples were then characterized again using the setup described in the previous session. Figure 5 depicts the LED test setup.

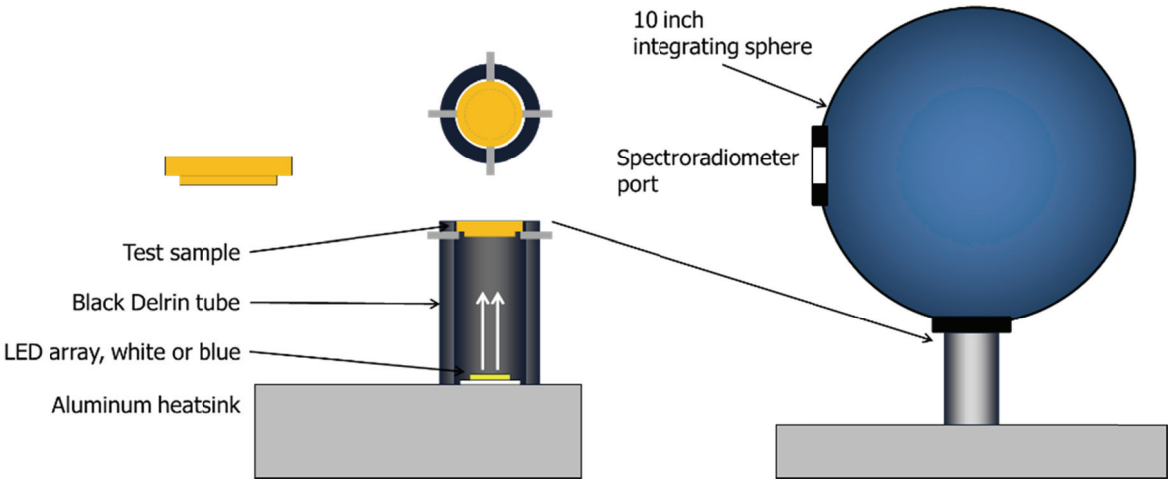


Figure 4. Schematic of the setup used to expose the 3D-printed test samples to either a blue (450 nm peak wavelength) or a phosphor-converted white LED (5000 K). The output of the LEDs was controlled by adjusting the forward current with a programmable dc power supply. An integrating sphere captured the light transmitted through the test sample throughout a 120-minute test period.

## 3. RESULTS

Figure 8 through 7 show the change in relative in-line spectral transmittance before and after photobleaching for the xenon, white LED, and blue LED conditions, respectively. In each one of the panels, the solid line represents the initial spectral transmittance, and the dashed line represents the final spectral transmittance after 120 minutes of exposure to the corresponding irradiance and light source spectrum combination.

The initial and final spectral transmittance of each sample (before and after photobleaching) was used to derive the 1931 CIE xy chromaticity using an ideal, equal energy spectrum in the calculation. Figure 8 shows a summary of the final CIE xy chromaticities for each of the 14 samples tested. The samples that exhibited the most photobleaching were those exposed to the white LED light source. The maximum shift in these samples is within a 4-step MacAdam ellipse. The center of the 4-step MacAdam ellipse is the average chromaticity of the 14 samples. As expected, the initial chromaticity of all of the samples was very similar because the variation from sample to sample was very small given that they were 3D-printed at the same time.

The MacAdam ellipse shown also encompases four of the five samples exposed to the xenon lamp. The sample exposed to the highest irradiance with the xenon lamp shifted by nearly 7 steps. However, the samples exposed to the xenon lamp became more tinted. As seen in Figure 8, the chromaticity of these samples shifted to the right and the up direction of the chromaticity diagram. It is not obvious from these data why these samples behaved in this way. Although it is possible that the yellowing is simply surface oxidation, it is also possible that the UV or IR in the xenon light source had a role in the oxidation. In contrast, samples exposed to the white LED with similar irradiance did experience photobleaching.

Figure 9 shows the change in chromaticiy of each of the 14 samples as a function of irradiance. The magnitude of the change in chromaticity is measured in MacAdam ellipse steps. To denote the shift in the opposite direction for the samples exposed to the xenon light source (i.e., yellowing), the data was arbitrarily assigned a negative magnitude.

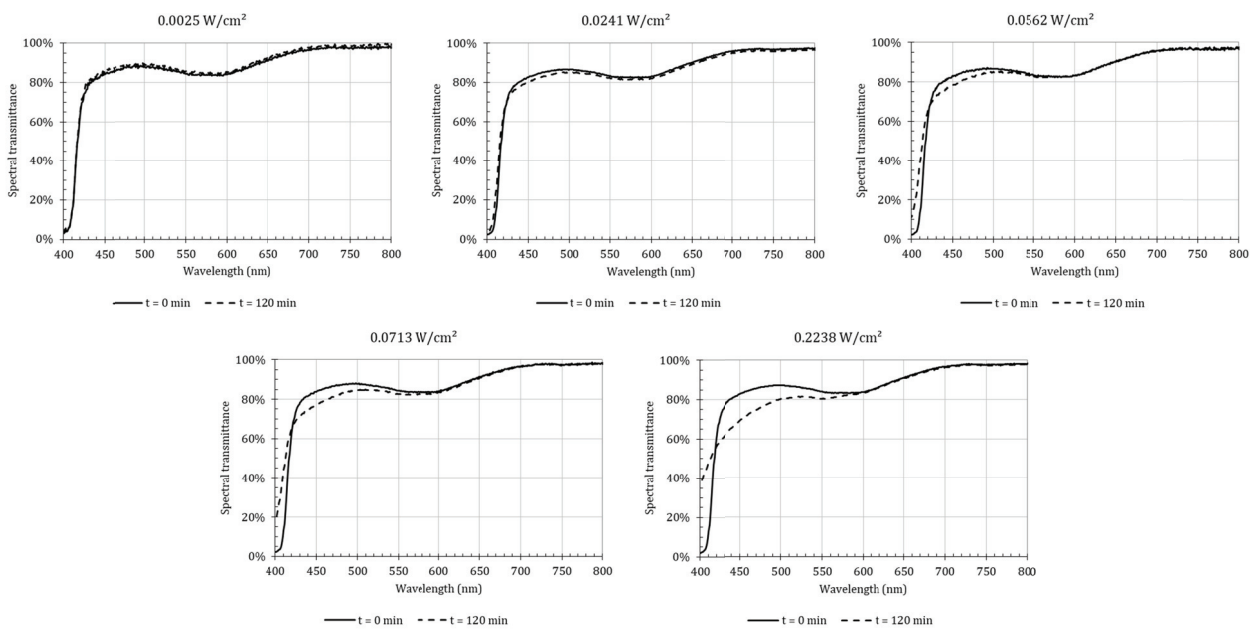


Figure 5. Initial and final in-line spectral transmittance of the five 3D-printed samples exposed to the xenon light source. The irradiance value for each sample is indicated at the top of each panel. Note the systematic decrease in spectral transmittance in the ~425 nm to 550 nm region. Although there seems to be an increase in the 400 nm to 425 nm region, which would indicate photobleaching, the decrease in the 425 nm to 500 nm region results in net yellow tint.

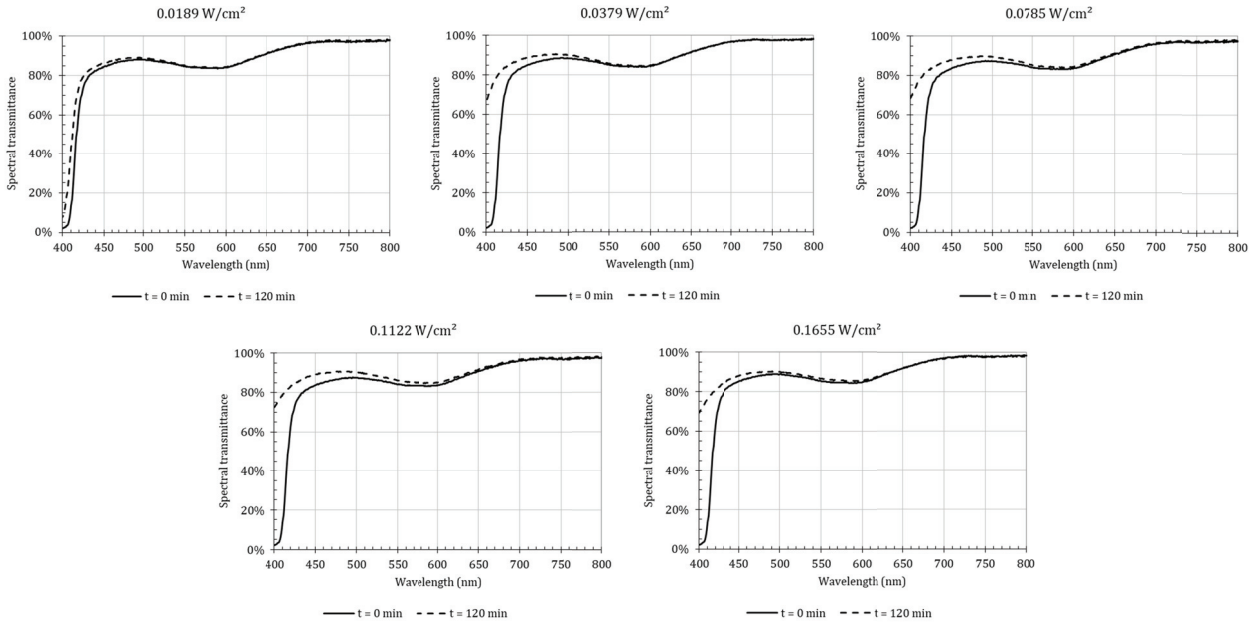


Figure 6. Initial and final in-line spectral transmittance of the five 3D-printed samples exposed to the white LED light source. The irradiance value for each sample is indicated at the top of each panel. Note the increase in spectral transmittance in the 400 nm to 500 nm region. This is an indication of the reduction of residual photoinitiator in the printed part.

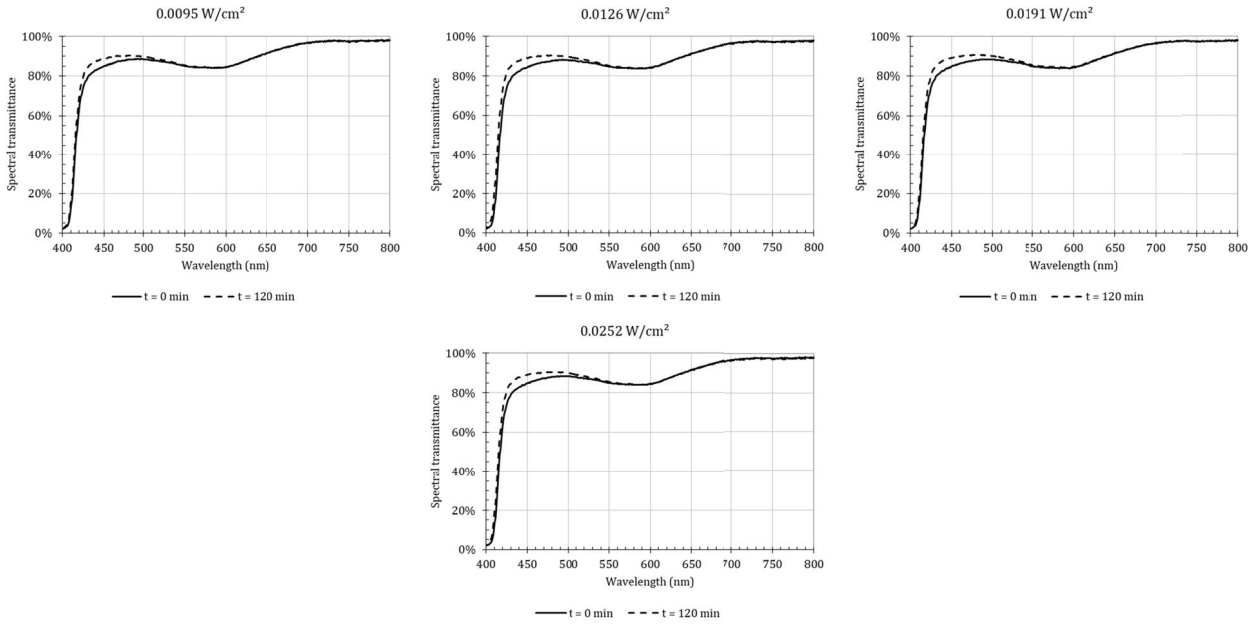


Figure 7. Initial and final in-line spectral transmittance of the four 3D-printed samples exposed to the blue LED light source. The irradiance value for each sample is indicated at the top of each panel. Note the systematic increase in spectral transmittance in the 400 nm to 500 nm region. This is an indication of the reduction of residual photoinitiator in the printed part.

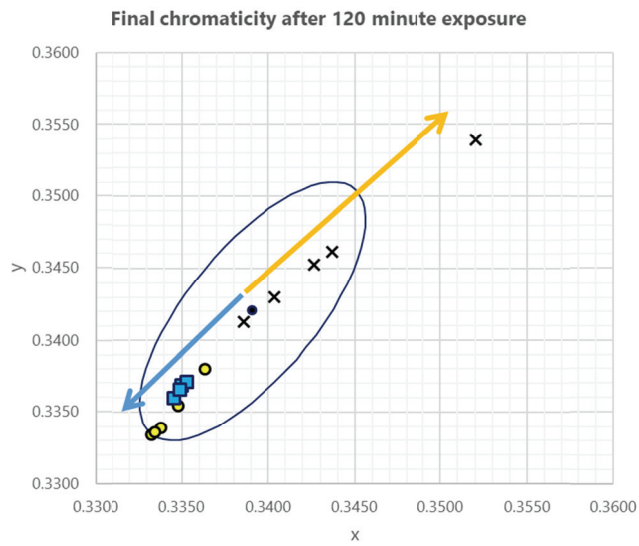


Figure 8. Final chromaticity of each of the 14 samples tested after 120 minutes of exposure. The center of the ellipse shows the initial chromaticity, on average, of all samples. Note the opposite direction in the chromaticity for the samples exposed to the xenon light source, which became more tinted. The samples exposed to the white and blue LEDs did experience photobleaching and became less tinted.

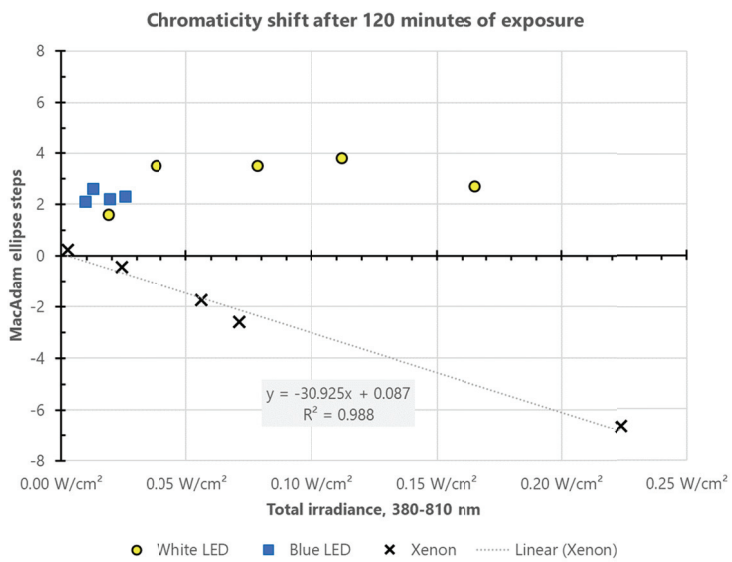


Figure 9. Chromaticity shift of each of the 14 samples tested after 120 minutes of exposure. The chromaticity shift is here indicated in MacAdam ellipse steps. A negative sign was given to the samples exposed to the xenon light source to indicate their shifting in the opposite direction to that expected; that is, these samples became more tinted as opposed to more clear.

## 4. SUMMARY

This paper summarizes the results of an initial study to understand the effect of light source spectrum and irradiance on the photobleaching of 3D-printed samples intended to be optically clear. A total of 14 samples were tested under a combination of three light sources and up to five irradiance levels for each source.

For the white LED light source, the experimental results showed that irradiance can increase the magnitude of the photobleaching when the exposure time is kept constant, in this experiment for 120 minutes. In this study, the maximum chromaticity shift was equivalent to a 4-step MacAdam ellipse, which is consistent with previous experience in our lab (unpublished results). In those previous experiments, the irradiance was lower and the exposure time was several hundreds of hours, but the magnitude of the shift became asymptotic, approximating a 4-step MacAdam ellipse. This seems to indicate that it is possible to expedite the photobleaching of 3D-printed parts by increasing the irradiance. More experimentation is needed to find an optimum irradiance value.

Although the range of irradiance values with the blue LED light source was limited to the lower end of the range tested, the results showed that a narrowband spectrum (e.g., peak wavelength of 450 nm) can achieve similar or slightly better photobleaching than a white LED for the same total irradiance (see Figure 9). This may not be surprising since the main photobleaching effect is determined by the absorption of the remaining photoinitiator in the 3D-printed part. Since photoinitiators are designed to operate in the short-wavelength range used to cure printed parts, a similar spectrum to complete the photobleaching of the part would be the most effective.

In this study, it was not possible to measure the magnitude of photobleaching with the xenon lamp because of the increase in tint. Although this tint is suspected to be oxidation on the surface, the tint increased with increasing irradiance. Further experimentation is required to determine if the oxidation is caused by the UV or IR in the spectrum of the xenon light source. For similar irradiance values, the blue and white LED sources produced photobleaching.

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## REFERENCES

[1] Narendran, N., J.P. Freyssinier, and Y. Zhu. 2016. Energy and user acceptability benefits from improved illuminance uniformity of parking lot illumination. Lighting Research and Technology, 48(7): 789–809; published online ahead of print 4 June 2015, doi:10.1177/1477153515587959.

[2] Narendran, N., I.U. Perera, X. Mou, and D.R. Thotagamuwa. 2017. Opportunities and challenges for 3-D printing of solid-state lighting systems. Proceedings of SPIE 10378, 16th International Conference on Solid State Lighting and LED-based Illumination Systems, SPIE Optics + Photonics, San Diego, Calif., August 2017, Paper 10378-35.

[3] Kianian, B., "Wohlers Report 2017: 3D printing and additive manufacturing state of the industry, annual worldwide progress report: Chapters titles: The Middle East, and other countries," (2017).

[4] U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, 2020 LED Manufacturing Supply Chain, March 2021. https://www.energy.gov/sites/default/files/2021-05/ssl-2020-led-mfg-supply-chain-mar21.pdf

[5] Heinrich, A., et al. "Additive manufacturing: a new approach to realize complex and unconventional optical components." Organic Photonic Materials and Devices XIX. Vol. 10101. SPIE, 2017.

[6] Heinrich, A., et al. "Additive manufacturing of reflective and transmissive optics: potential and new solutions for optical systems." Laser 3D Manufacturing V. Vol. 10523. SPIE, 2018.

[7] Rank, M. and A. Heinrich, [Three-Dimensional Printing of Optics], Spotlight vol. SL39. Bellevue: Society of Photo-Optical Instrumentation Engineers (SPIE) (2018).

[8] Udage, A.S., and N. Narendran. 2022. Optimizing 3D printable refractive spherical arrays for application-specific custom lenses. Proc. SPIE 12216, Novel Optical Systems, Methods, and Applications XXV: 122160H (3 October 2022); doi: 10.1117/12.2632746.

[9] Geisler, E., M. Lecompère, and O. Soppera. "3D printing of optical materials by processes based on photopolymerization: materials, technologies, and recent advances." Photonics Research 10.6 (2022): 1344-1360.

[10] Privitera, O., Y. Liu, I.U. Perera, J.P. Freyssinier, and N. Narendran, "Optical properties of 3D printed reflective and transmissive components for use in LED lighting fixture applications," Proc. SPIE 10940, Light-Emitting Devices, Materials, and Applications, 109401X (2 April 2019); doi: 10.1117/12.2510063 Event: SPIE OPTO, 2019, San Francisco, California, United States.

[11] Appaiah, P., Narendran, N., Perera, I.U., Zhu, Y., and Liu, Y., "Effect of thermal stress and short-wavelength visible radiation on phosphor-embedded LED encapsulant degradation," Optical Materials 46, 6-11 (2015).