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Photopolymer kinetics using light intensity gradients in high-throughput conversion analysis

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Abstract

Light intensity gradients and light exposure time gradients were combined to produce contours of constant dose on a sample substrate. These polymerized samples were subsequently analyzed using high-throughput Fourier transform infrared spectroscopy to measure conversion as a function of both gradients. Three (meth)acrylate monomers were analyzed over light doses ranging from 0 mJ/cm^2 to 920 mJ/cm^2, demonstrating that in thin films, higher light intensities at a constant light dose produce higher conversion due to a decreased oxygen inhibition time and larger thermal excursions. At a light dose of 75 mJ/cm^2, the conversion of 2-ethylhexyl acrylate increases from 40 ± 2% at a light intensity of 0.9 mW/cm^2 to 59 ± 3% at 7.2 mW/cm^2. The two acrylate monomers exhibited rapid photopolymerization up to a specific conversion, after which additional radiation dose produced only marginal increases in overall conversion. For hexanediol diacrylate, a light dose of 300 mJ/cm^2 was the minimum amount required to reach the maximum conversion over the entire range analyzed. For the dimethacrylate system, a similar effect was seen, with a reduced oxygen inhibition time and conversion above 70% showing a similar conversion at a constant light dose of 500 mJ/cm^2. In all three systems, dose contours were used to determine a range of light intensities at which a statistically similar conversion would occur for a specified light dose.

Keywords: Photopolymerization; Light intensity; High-throughput analysis

1. Introduction

The effect of light intensity and exposure time for photopolymerizations has been studied extensively, as these two factors control the light dose or radiant exposure received by the sample. Photopolymerization is a free radical polymerization where the absorption of light by a photoinitiator generates a reactive species that propagates to form a polymer network [1]. Since both of these parameters control the rate and number of radicals that are generated, this parameter is critical in the optimization of a formulation for an industrial application [2–4]. More importantly, the exposure time required for each sample will control the overall throughput of the photopolymerization process line.

A specific case where light dose is extensively studied is in the field of photopolymerizable dental restoratives, where a significant effort is undertaken to determine conversion and hardness measurements using various light sources, exposure times, and light intensities [4–11]. These results show low dose regions with little to no conversion, a high dose region with constant conversion, and a transitional region with potentially broadly varying properties. However, these regions are dependent on the light source used and the curing protocol employed, making the comparison of these results difficult [12]. In addition to dental restoratives, for non-planar surfaces, such as with automotive parts or adhesive bonding, light intensity profiles may vary across the surface and depth of the sample and lead to changes in conversion and polymer properties dependent on location [13–15].

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Light dose, the integration of light intensity over exposure time, has been used to compare results but still requires testing over multiple light intensities and exposure times to produce a wide range of light doses. Light intensity between processes can vary, and difficulties arise when there is a significant change that alters the overall quality or material properties of the end product. However, different photoinitiation systems and kinetic pathways show different scaling factors, and the initiation rate has been shown to have non-uniform scaling with light intensity. Attempts have been made to determine and predict this scaling factor, but the analysis requires extensive experimentation to evaluate a large number of photopolymerization conditions [16–19]. This effort is time consuming, so the ability to analyze multiple light intensities rapidly provides a significantly improved way to analyze multiple monomer systems systematically.

Since photopolymerizations are controllable both temporally and spatially, high-throughput techniques to analyze a wide range of parameters could be employed as an analysis route to increase the speed of experimentation. High-throughput techniques have been used in material science for over 15 years, beginning with work on luminescent materials and catalyst reactivity [20]. These techniques were expanded into polymer material science, employing a range of gradients already available from other high-throughput analysis methods. Gradients in composition, temperature, thickness, and exposure time have already been generated and validated for use in polymeric analysis techniques [21–26]. The combination of a light intensity gradient with a light exposure time gradient allows for the simultaneous generation of both gradients on a single sample substrate, producing contours of light dose with different light intensities and exposure times.

2. Experimental section

2.1. Materials

Hexanediol diacrylate (HDDA), 2-ethylhexyl acrylate (EHA), camphorquinone (CQ), ethyl 4-(dimethylamino)benzoate (EtDMAB), and hexanediol dimethacrylate (HDDMA) were obtained from Sigma–Aldrich (Milwaukee, WI). The photoinitiator dimethoxyphenylacetophenone (DMPA) and a UV absorber 2-(2*H*-benzotriazol-2-yl)-6-(1-methyl-1-phenylethyl)-4-(1,1,3,3-tetramethylbutyl)phenol (Tinuvin 928) were obtained from Ciba–Geigy (Hawthorn, NY). All reagents were used as received.

2.2. Light exposure time and intensity gradient production

The methodology for an exposure time gradient was explained in detail elsewhere, but a brief overview is given below [22]. The exposure time gradient is produced using a cover plate positioned above a sample substrate which is attached to a linear motion stage. This cover plate moves over the sample at a fixed velocity, preventing light from irradiating the monomer film. The position of the cover plate is known at all times, allowing for exposure time to be determined once the sample is analyzed.

Light intensity gradients were made using a formulation of HDDA with 0.6 wt% Tinuvin 928, 0.2 wt% camphorquinone and 0.1 wt% ethyl 4-(dimethylamino)benzoate (EtDMAB) added. Camphorquinone and the tertiary amine EtDMAB were added to polymerize the sample using visible light, as the Tinuvin 928 does not absorb in the range required for camphorquinone photoinitiation. Tinuvin 928 absorbs strongly in the ultraviolet region from 320 nm to 390 nm, while leaving the visible spectra available. To produce a thickness gradient, a 40 μm spacer was placed on one edge of a glass slide, and an additional glass slide was placed on top and clamped on both ends. This design produces a gradient in the length of the gap between the two glass slides. This gap was filled with the monomer mixture and then photopolymerized using a visible light source (3M Elipar FreeLight2, St. Paul, MN) at 10 mW/cm^2 for 2 min. The resulting polymer layer has a gradient of thickness, which produces a gradient of absorbance that varies as a function of position along the length of the gradient. The gradient used in this study ranged from 0.5 μm to 40 μm in thickness.

The light intensity gradient was analyzed to determine light absorbance as a function of position to characterize the sample fully and ensure its orthogonal nature. An ultraviolet light (Acticure, EXFO, Missaugua, Ontario) and a 365 nm bandpass filter were positioned over an X–Y stage to establish the light intensity gradient. Beneath the stage, a fiber optic cable connected to a UV–vis spectrometer (Ocean Optics USB 2000, Dunedin, FL) was positioned directly underneath the sample to record spectra at each position. The percentage of light absorbed was calculated from the integration of the intensity count from 345 nm to 380 nm. A baseline intensity area was calculated using a control thickness gradient which contained no light absorber. This gradient showed no significant difference in intensity as a function of thickness over the wavelengths measured above. Spectra from the light intensity gradient sample were collected at specific positions both parallel and orthogonal to the light intensity gradient. Light transmittance was then calculated at each point using the previously determined control intensity and the average intensity calculated at that point.

Repeats showed no significant difference in light intensity orthogonal to the gradient, with the standard error of a single data point at 1.5% and a maximum deviation of 1.3% from the average light intensity measured at any position in the orthogonal direction. The control gradient with no absorber present showed no significant difference in light intensity as a function of polymer thickness, so a single light intensity value was used for determining percent transmittance at all positions. Fig. 1 shows the transmittance of the gradient as a function of position. The light intensity decreases over the entire range of the gradient, with no significant change in light intensity at wavelengths above 400 nm.

The system used in this study produces a gradient from 27% to 99% absorption of the ultraviolet light. The gradient is nearly linear at the lower absorption levels, as the sample

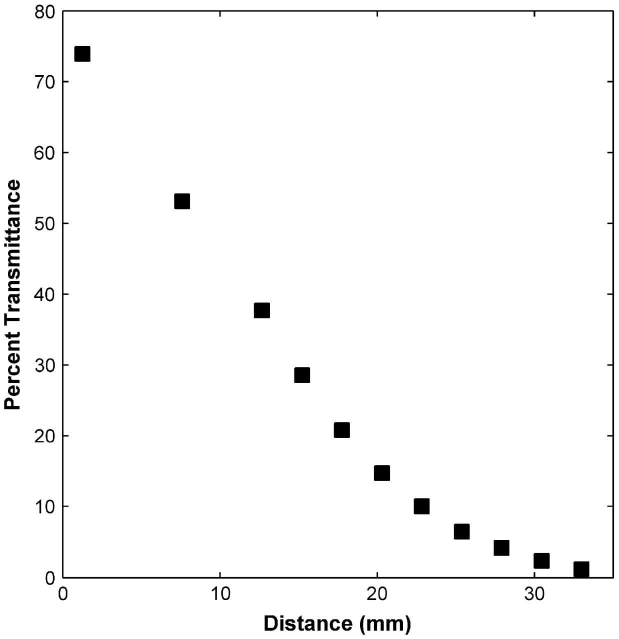

Fig. 1. Ultraviolet light transmittance through the light intensity gradient setup used in this analysis. A distance of 0 mm corresponds to the edge with no spacer, with error bars smaller than the marker size. A 100% transmittance reading would be equivalent to a similar gradient produced with no light absorber present.

deviates from a linear height gradient at small thicknesses. The light intensity gradient is integrated into the light exposure time gradient setup by attaching the gradient to the motion stage cover plate. When the cover plate is set in motion and the light source is turned on, both gradients are simultaneously generated. Since light dose is the integration of light intensity over exposure time, light dose contours are generated on the sample substrate.

2.3. High-throughput conversion analysis

The methodology to analyze the gradient sample has been explained previously using a sequential point mapping technique [22]. The sample is placed in a Fourier transform infrared (FTIR) microscope (Nicolet Continuμm, Thermo-Nicolet, Madison, WI) after both gradients have been generated on the sample. In this modified setup, the motion stage has been altered to generate set speeds, allowing for faster analysis using a continuous collection of spectra. The modification uses a motion controller card (Galil DMC1822) attached to the X–Y stage motors to produce a constant velocity profile. Positions are recorded as a function of time, allowing for calculations of both light intensity and exposure time once the sample is fully analyzed. Spectra are collected in series as the sample stage moves at a continuous speed of 100 μm/s across the sample. Accounting for the aperture window size and the spectra collection speed, each spectra collected traverses over an area 150 μm high and 107 μm in width, with a 57 μm gap between each spectral point. The motion control card tracks the position of the stage as a function of time, and the spectra collection, once finished, is then translated into a stage position. This collection method produces a data set of 1250 exposure time sample points over 10 light intensities in 24 min, which is faster than the previous technique while collecting additional data points [22]. Since conversion analysis using a light intensity gradient requires a wide range of exposure times for significant polymerization to occur, this collection technique enables longer exposure times previously unavailable with the sequential point mapping approach.

3. Results and discussion

Samples were generated over a range of light intensities and exposure times, which varied slightly depending on the overall light intensity. A dose colormap is shown in Fig. 2, which was calculated from integrating light intensity over the exposure time at each data point. The two gradients are converted into dose contours on the following color maps, showing the overall change in light dose over a sample.

Ethylhexyl acrylate was polymerized using this technique, and the conversion analysis is shown in Fig. 3. Dose contours of 25 mJ/cm^2, 50 mJ/cm^2, 75 mJ/cm^2, 100 mJ/cm^2, 200 mJ/cm^2, 300 mJ/cm^2, 400 mJ/cm^2, 500 mJ/cm^2, and 600 mJ/cm^2 were overlaid on the conversion colormap to allow for a comparison of conversion values at a constant dose, and the specific dose contours are labeled at the top of the figure.

Ethylhexyl acrylate achieves nearly complete conversion at very high dose contours, with regions above 300 mJ/cm^2 exhibiting at least 93% conversion. In this region, a large additional dose of light is required to increase the conversion, since the double bond concentration is low and the monomer mobility is more restricted due to the high polymer concentration. The required time for significant polymerization to occur decreases with increasing light intensity, but this trend does

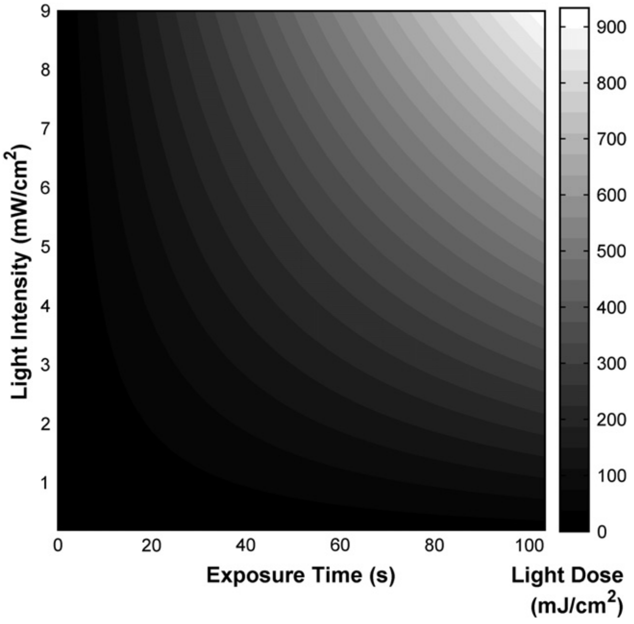

Fig. 2. Light dose map as a function of light intensity and exposure time using a 365 nm light source. Light dose ranges from 0 mJ/cm^2 to 920 mJ/cm^2.

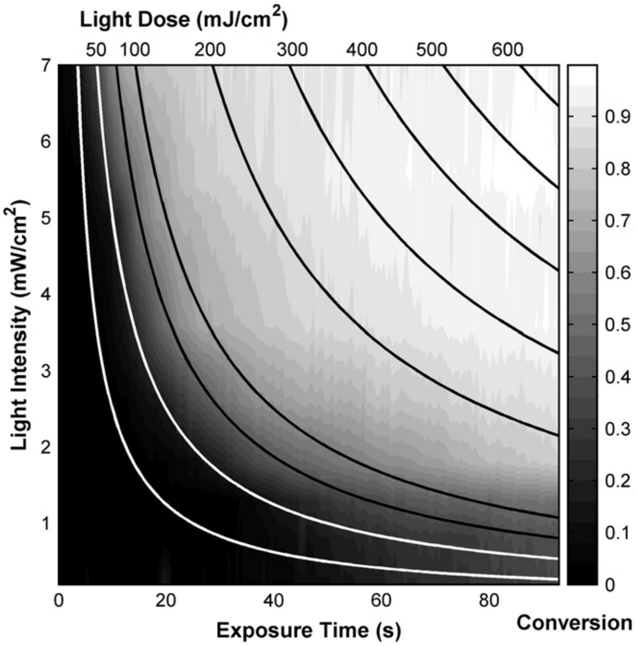

Fig. 3. EHA conversion colormap with light intensity gradient and exposure time. Contours of light dose are overlaid on the colormap, with labels showing the light dose in mJ/cm^2 contours on the top of colormap. The 25 mJ/cm^2 and 75 mJ/cm^2 contour lines are displayed but not labeled. Samples were polymerized with 0.5 wt% DMPA at 23 °C with a 365 nm light using an exposure time gradient of 0.2 mm/s.

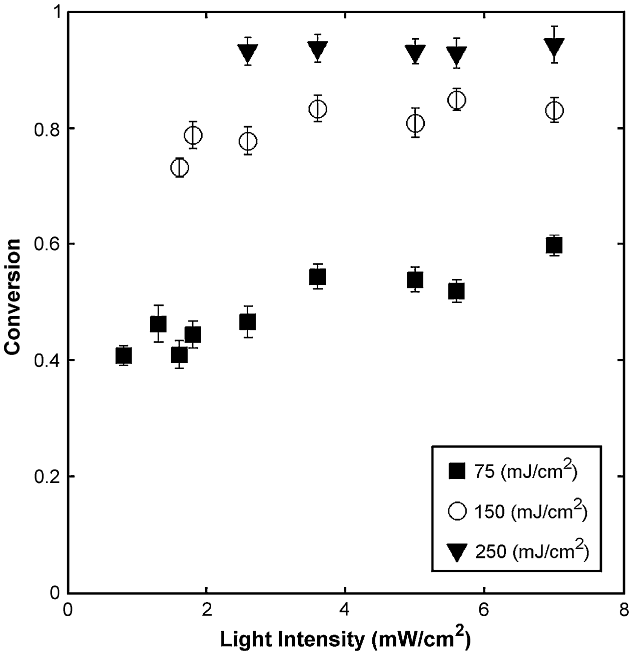

Fig. 4. EHA conversion as a function of light intensity for light doses of 75 mJ/cm^2, 150 mJ/cm^2, and 250 mJ/cm^2. Data points were extracted from the high-throughput data set, using points within 1% of the specified dose contour. Samples were polymerized with 0.5 wt% DMPA at 23 °C with a 365 nm light using an exposure time gradient of 0.2 mm/s.

not exactly follow the light dose contours on the plot. A light dose of 75 mJ/cm^2 exhibits a decrease in conversion from the highest measured light intensity, decreasing by 16% as compared to the conversion at 0.9 mW/cm^2 of light intensity. Fig. 4 shows observed data points along three different light dose contours.

An increase in conversion with light intensity is apparent at both the 75 mJ/cm^2 and 150 mJ/cm^2 dose contours, while the dose contour at 250 mJ/cm^2 is statistically constant. The decrease in conversion is caused by a decrease in photoinitiator efficiency at low light intensities, which decreases the polymerization rate and results in lower conversion. This photoinitiator efficiency is eventually negated at extremely high light intensities where a high radical generation causes increased termination. This effect is not as significant at the intensities in this study. For the 250 mJ/cm^2 data, all observed conversion data are at or near 93% conversion. At this point, conversion slowly increases with increasing light dose, but all conversion data points at a constant dose are statistically equivalent. In comparison to EHA, HDDA is a diacrylate monomer with a high degree of crosslinking, which results in a lower ultimate conversion than EHA. The light intensity gradient for HDDA is shown in Fig. 5.

For the HDDA polymerization, the analysis again shows similar trends to EHA. At the constant light dose contours 50 mJ/cm^2 and 100 mJ/cm^2, a reduction is seen in the conversion with lower light intensities at constant dose. In this system, the effect is more pronounced, since the polymerization proceeds rapidly in comparison to EHA. In addition, the region above 77% shows a similar trend where a slight increase in conversion requires a significant amount of additional light dose. This effect is similar to the results shown in EHA, where a relatively large additional light dose is required for a small amount of additional conversion. This difference in conversion

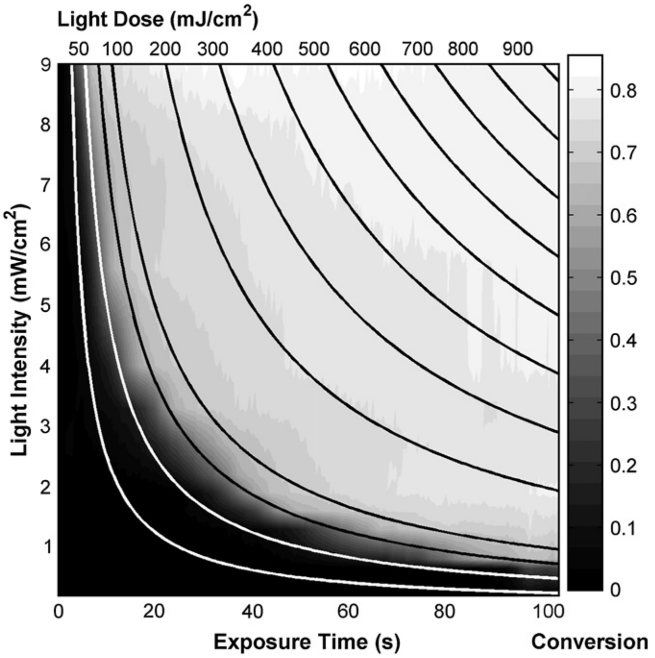

Fig. 5. HDDA conversion colormap with light intensity gradient and exposure time. Contours of light dose are overlaid on the colormap, with labels showing the light dose in mJ/cm^2 contours on the top of colormap. Samples were polymerized with 0.5 wt% DMPA at 23 °C using an exposure time gradient of 0.2 mm/s.

produces a higher modulus material and reduces the extractable monomer concentration, but the additional exposure time may not be warranted in certain applications. To show better the effects of light dose in slower polymerization regimes, HDDMA, the dimethacrylate analogue to HDDA, was analyzed using this technique. Methacrylates have slower polymerization rates than acrylates, and the slower rate and higher T_G polymer formed reduces the overall conversion at all data points. Fig. 6 shows the HDDMA conversion analysis as a function of light intensity and exposure time.

For the HDDMA polymerization, the slower polymerization clearly elucidates the trends seen in the previous two systems. Conversion is reduced as a function of decreasing light intensity for dose contours of 50 mJ/cm^2 and 100 mJ/cm^2. The slower polymerization after 50% conversion allows for a better analysis of the higher light dose contours. In the highest three light dose contours, the conversion remains statistically the same. Provided the light dose is kept constant, light intensity and exposure time are linked but controllable parameters within a specific region. This analysis route provides a method to determine a limit to the range of light intensities at which fixed light doses produce statistically insignificant changes in conversion. In Fig. 7, conversion for HDDA, HDDMA, and EHA are shown at a constant light dose of 150 mJ/cm^2.

In Fig. 7, the conversion of each system is compared at a constant light dose. While the highest observed conversion is from the EHA photopolymerization, the conversion of both diacrylates is limited due to crosslinking. However, HDDA rarely exhibits over 82% conversion under the polymerization conditions used in this study, and the conversion observed at this light dose is between 70% and 78%. HDDMA shows the slowest relative polymerization rate, with conversion near 42% independent of light intensity.

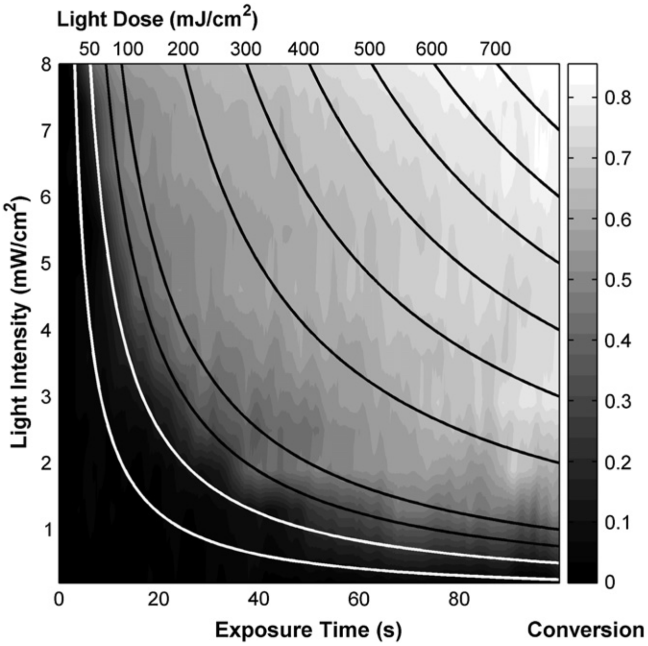

Fig. 6. HDDMA conversion colormap with light intensity gradient and exposure time. Contours of light dose are overlaid on the colormap, with labels showing the light dose in mJ/cm^2 contours on the top of colormap. Samples were polymerized with 0.5 wt% DMPA at 23 °C using an exposure time gradient of 0.2 mm/s.

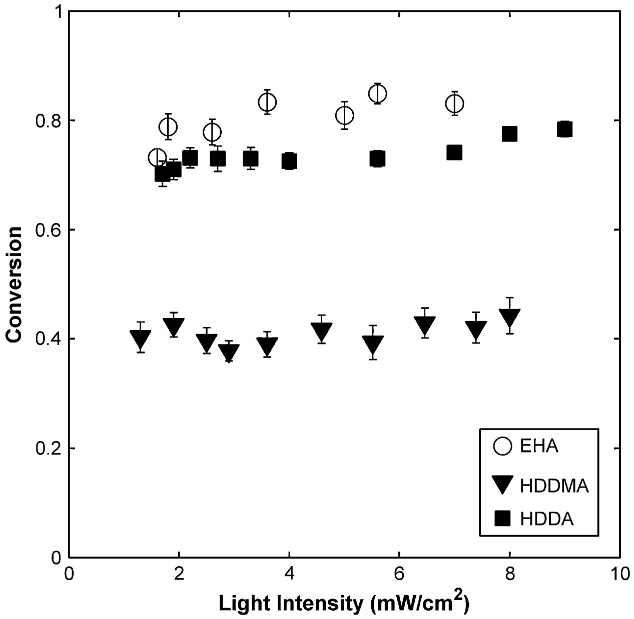

Fig. 7. EHA, HDDA, and HDDMA conversion as a function of light intensity for a light dose of 150 mJ/cm^2. Data points were extracted from the high-throughput data set, using points within 1% of the specified dose contour. Samples were polymerized with 0.5 wt% DMPA at 23 °C with a 365 nm light using an exposure time gradient of 0.2 mm/s.

If the previous two systems are analyzed in a similar manner, regions of light dose greater than 200 mJ/cm^2 are consistent in conversion over the range of light intensities and exposure time analyzed for EHA. Similarly, HDDA requires 500 mJ/cm^2, since the highest light intensity shows a slightly higher conversion at light doses lower than this limit.

An additional benefit of this technique is the combination with previous work studying composition and exposure time gradients [22]. Previous analysis of HDDA at the same initiation conditions was performed at a light intensity of 3.5 mW/cm^2 in a composition gradient with a monoacrylate. Conversion data from the HDDA system analyzed in this prior work is compared with conversion data from equivalent experimental conditions from the light intensity gradient analysis. This comparison is shown in Fig. 8. In this case, the polymerization of 100 wt% HDDA at 3.5 mW/cm^2 is common between both the composition–exposure time and light intensity–exposure time gradients.

Both conversion profiles show similar conversion at all time points measured, with good agreement between both analysis techniques. Even with a difference in exposure time gradient speed, both conversion profiles are similar and equivalent conversions are reached at 30 s of exposure time. Oxygen inhibition, which is dependent on radical generation, occurs at similar exposure times in both high-throughput analysis techniques. Longer or shorter exposure time gradients will generate similar results, independent of the requirements of the second induced gradient.

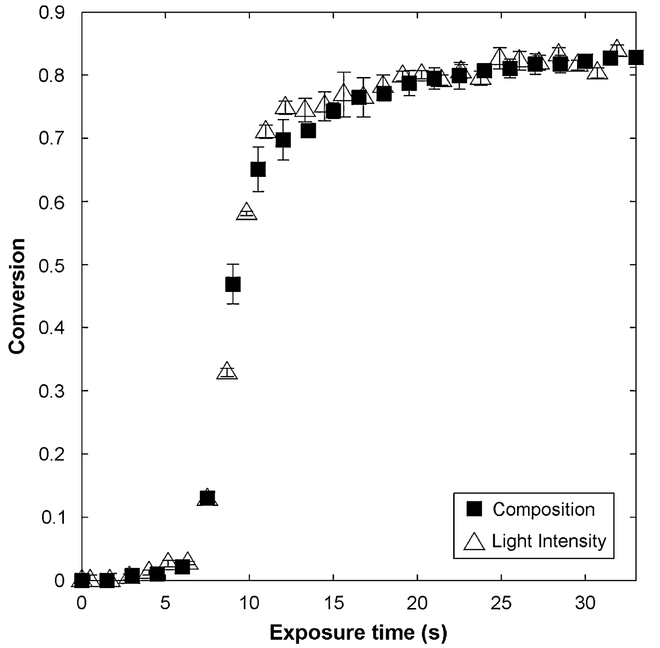

Fig. 8. HDDA (100 wt%) conversion profile as a function of exposure time, analyzed using a composition–exposure time analysis and light intensity–exposure time analysis. Both samples were polymerized with 0.5 wt% DMPA at 23 °C at 3.5 mW/cm^2 light intensity, with different exposure time gradient speeds of 1.33 mm/s and 0.2 mm/s.

4. Conclusion

The techniques shown here allow for a rapid analysis of conversion as a function of light intensity and exposure time. This work also correlates with previous work, showing that a light intensity gradient allows for a higher factor analysis. In addition, the similarity and applicability to industrial processes provide a better screening tool for the correct light dose at various light intensities in a faster manner than previous screening techniques. The EHA analysis shows a limiting dose where the polymerization has reached 99% conversion and any increase in light dose will have no significant effect on conversion.

The analysis of HDDA shows a similar trend as conversion becomes limited as the system is highly crosslinked and propagating radicals have a high mobility restriction. This effect becomes more prevalent at high conversion, and the effect of additional photoinitiation events does not cause additional polymerization, establishing a limiting dose. In comparison, the HDDMA copolymerization shows significantly slower kinetics, and a far stronger dependence on light dose than either acrylate system. A wide range of light doses are compared with this technique due to the fine resolution of the high-throughput analysis, which allows for conversion data to be extracted from the analysis and used to generate comparisons between monomer systems or conversions at different light doses.

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