Comparison of Different UV Light Sources in Radical Curing of PEGDA and PEGDA/HDDA Resins by Photo-DSC and Photo-DEA

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Introduction

The development of efficient UV-curing processes for the production of safe, fully-cured inks and resins requires tools for monitoring and optimizing curing conditions in both research and development and manufacturing settings. Photo-differential scanning calorimetry (photo-DSC) and photo-dielectric analysis (photo-DEA) are useful tools for this purpose. Both tools enable the user to measure curing kinetics. Additionally, photo-DSC affords curing enthalpy information, and photo-DEA is especially sensitive to residual curing and measures the conductivity and permittivity of the materials throughout the curing process.

Since different applications, such as 3-D laser printing, screen printing and inkjet printing, and the curing of electronics coatings and dental composites employ different light sources, the ability to couple these different light sources with DSC and DEA measurements of these processes is important. For the studies described herein, DSC and DEA instruments were coupled with a mercury-arc lamp, a diode laser, and a high power LED in order to compare the efficiencies of these different UV light sources in curing formulations containing poly(ethylene glycol) diacrylate (PEGDA) and a 1:1 mixture of PEGDA and 1,5-hexanediol diacrylate (HDDA) with different photoinitiators. Some of this work was published previously.[1]

Experimental Methods

DSC measurements were performed with a NETZSCH DSC 204 F1 *Phoenix*® coupled with either a LUMEN DYNAMICS Omnicure S2000® 200 watt Hg short-arc lamp with a band-pass filter delivering a spectral range of 320-500 nm, a LASERGLlOW Technologies LRD-0447 Series collimated diode laser delivering 447 nm wavelength light, or a DORIC LENSES LEDRV_1CH LED driver with a 385 nm high power LED source. DSC measurements were performed with open aluminum crucibles loaded with 5-10 mg of sample. DEA measurements were performed with a NETZSCH DEA 288 *Epsilon*®. Samples were loaded onto mini-IDEX interdigitated electrode sensors. All measurements were performed at ambient temperature (25-27°C).

Photoinitiators Irgacure® TPO-L and Irgacure® 2100 were kindly donated by BASF. Photoinitiator camphorquinone (CQ) and co-initiators triethylamine (TEA), and N,N-dimethyl-p-toluidine (DMPT) as well as resin components PEGDA and HDDA were purchased from Sigma-Aldrich and used as received.

Results and Discussion

Comparison of a Hg-arc lamp with a diode laser in the curing of PEGDA by CQ/DMPT/DEA

The purpose of the measurements described in this section was to compare the performance of the Hg-arc lamp with the 447 nm diode laser in the curing of a water soluble resin formulation consisting of PEGDA with 1% by weight CQ, 1% DMPT, and 1% TEA. This formulation has been used for the 3D printing of complex hydrogel scaffolds with a fully interconnected pore network for use as bioreactors.[2]

In the DSC experiments, samples were irradiated with multiple two-second-long pulses at two minute intervals. The Hg-arc lamp irradiance was 10W/cm^2, and the timing and duration of the lamp pulses were controlled by the DSC acquisition software. The diode laser irradiance was 0.74 w/cm^2, and the timing and duration of the pulses were controlled by manually switching the laser on and off. DSC curves from measurements with the Hg-arc lamp and the laser are overlaid for comparison in Figure **1**. The first peak due to the reaction exotherm in each measurement was the largest, with the peaks decreasing in magnitude with each subsequent pulse until it reached a plateau corresponding to background heating of the sample by the radiation rather than the reaction exotherm itself. The larger area of these background peaks for sample curing with the Hg-arc lamp as compared with curing with the laser indicates greater sample heating by the lamp vs. the laser. Three measurements with each light source were performed and showed good reproducibility. The total resin-curing enthalpy with the laser (129±5 J/g) was greater than that with the Hg-arc lamp (91±6 J/g), indicating that a higher level of cure was achieved with the laser.

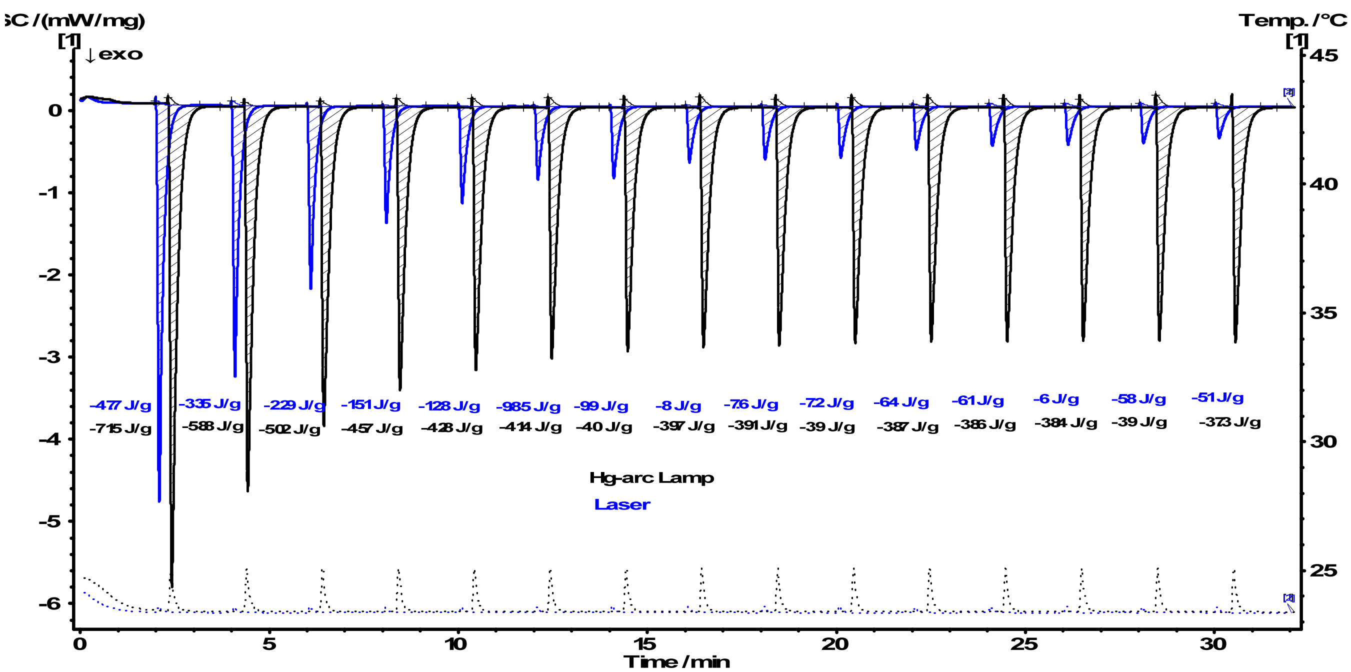

Figure 1. Comparison of DSC curves from PEGDA resin curing by the Hg-arc lamp (black) and the diode laser (blue)

In the DEA experiments, the samples were irradiated continuously over one hour by either the Hg-arc lamp or the laser at the same light intensities used for the DSC experiments. Consistent with the DSC measurements, the samples cured under laser irradiation achieved a higher ion viscosity value than the samples cured under Hg-ac lamp irradiation, indicating a higher level of cure for the former.

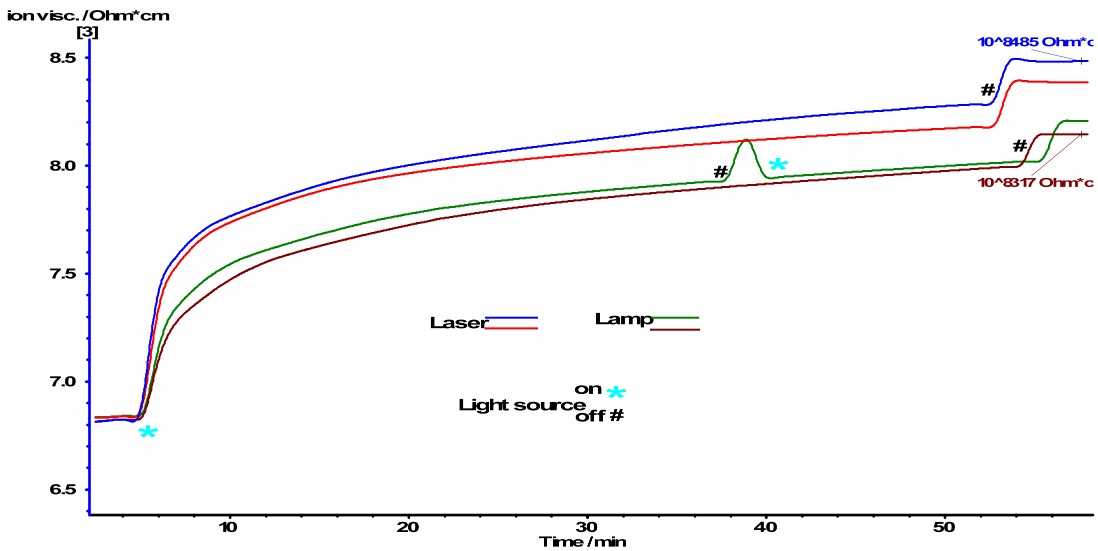

Figure 2. DEA curves from PEGDA resin curing by the Hg-arc lamp (green abd brown) and the diode laser (red and blue)

Comparison a high power LED with a Hg-arc lamp in the curing of a PEGDA/HDDA mixture of two different Irgacure® photoinitiators

The purpose of the measurements described in this section was to compare the performance of the Hg-arc lamp with a 385 nm LED in the curing of a 1:1 mixture of PEGDA:HDDA by two different Irgacure® photoinitiators, Irgacure® TPO-L (2, 4, 6-trimethylbenzoylphenyl phosphinate) and Irgacure® 2100, which contains Irgacure® 819 (phenylbis(2,4,6-trimethylbenzoyl)–phosphineoxide) as its major performance-determining component. According to their technical data sheets,[2] Irgacure® 2100 exhibits improved chemical and physical properties relative to TPO and is preferable for non-pigmented substrates due to longer wavelength absorption by TPO. The two photoinitiators were selected for these measurements because of their strong absorption at 385 nm, the wavelength of the LED source. Poor solubility of Irgacure® 2100 in PEGDA alone necessitated the inclusion of HDDA in the formulation. A 1.6% concentration by weight of each photoinitiator was used.

The maximum power of the LED source was 372 mW/cm^2. Preliminary DSC measurements indicated that the curing efficiency of 500 mW/cm^2 radiation from the Hg arc-lamp was close to that of the LED at maximum power, and these were the conditions used for the measurements described below.

Figures 3 and 4 show the results of DSC measurements on the resin formulations containing Irgacure TPO-L and Irgacure 2100, respectively, irradiated with five pulses of one second duration at one minute intervals with 385 nm light from the LED, operated manually, and broad band radiation from the Hg-arc lamp, controlled by the acquisition software. Two measurements using each light source are shown. The measurements exhibited good reproducibility, and, as can be seen from the data, the rate of cure and the total curing enthalpy were similar for the two radiation sources under the selected conditions. The total curing enthalpy of the formulation containing Irgacure® TPO-L was approximately 30 J/g higher than that of the formulation containing Irgacure® 2100, indicating that a higher level of cure was achieved using Irgacure® TPO-L as the photoinitiator.

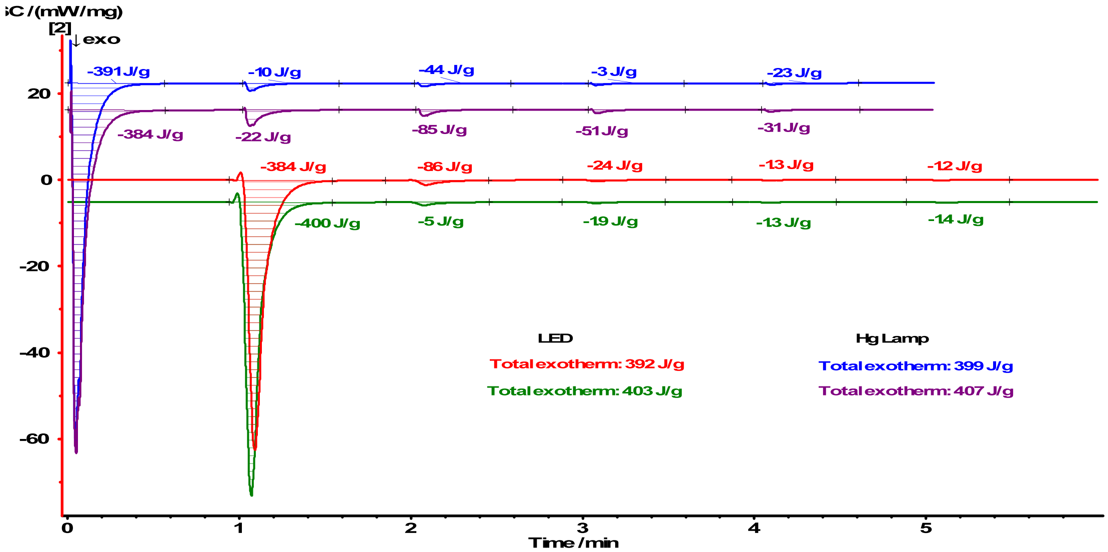

Figure 3. Comparison DSC curves from resin curing by LED and Hg-arc lamp DSC curves with Irgacure® TPO-L photoinitiator

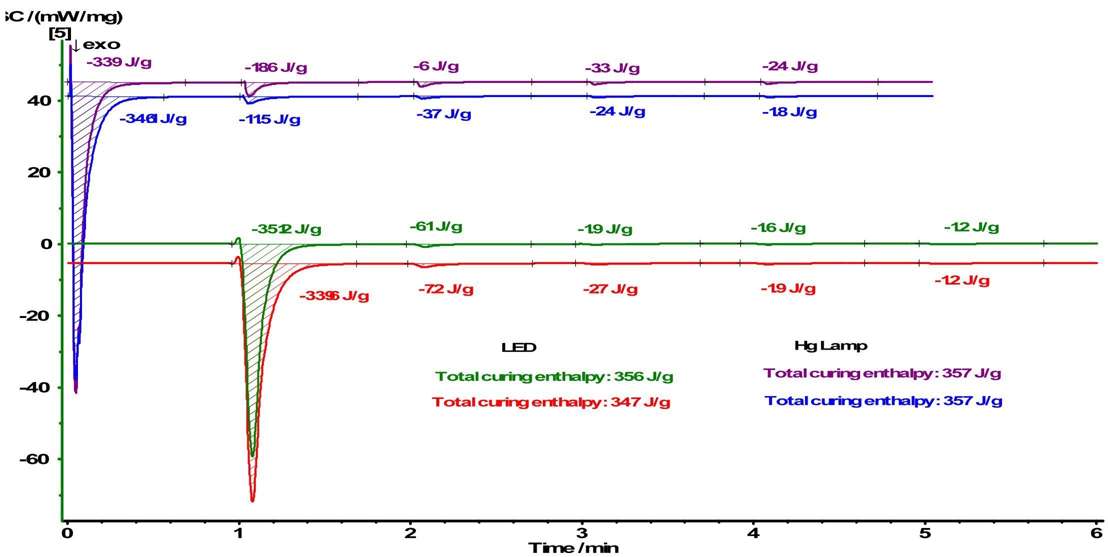

Figure 4. Comparison DSC curves from resin curing by LED and Hg-arc lamp DSC curves with Irgacure® 2100 photoinitiator

The results of DEA measurements of resin curing under five minutes of continuous irradiation from the Hg-arc lamp and the LED are shown in Figures 4 and 5 for Irgacure® TPO-L and Irgacure® 2100, respecively. Two measurements with each radiation source were performed. Differences in curing rate as indicated by the slope of the ion viscosity curves can be attributed to differences between the thicknesses of the samples. Nonetheless, similar ion viscosity values were achieved at the end of cure. Due to some sample heating by the light source, there is a slight increase in the ion viscosity values upon removal of the light sources. Notably, the ion viscosity values of the resin cured with Irgacure® TPO-L were an order of magnitude higher than that of the resin cured with Irgacure® 2100 ($10^{11.5}$ Ohm*cm vs. $10^{10.5}$ Ohm*cm), consistent with the higher curing enthalpy measured with Irgacure® TPO-L by DSC.

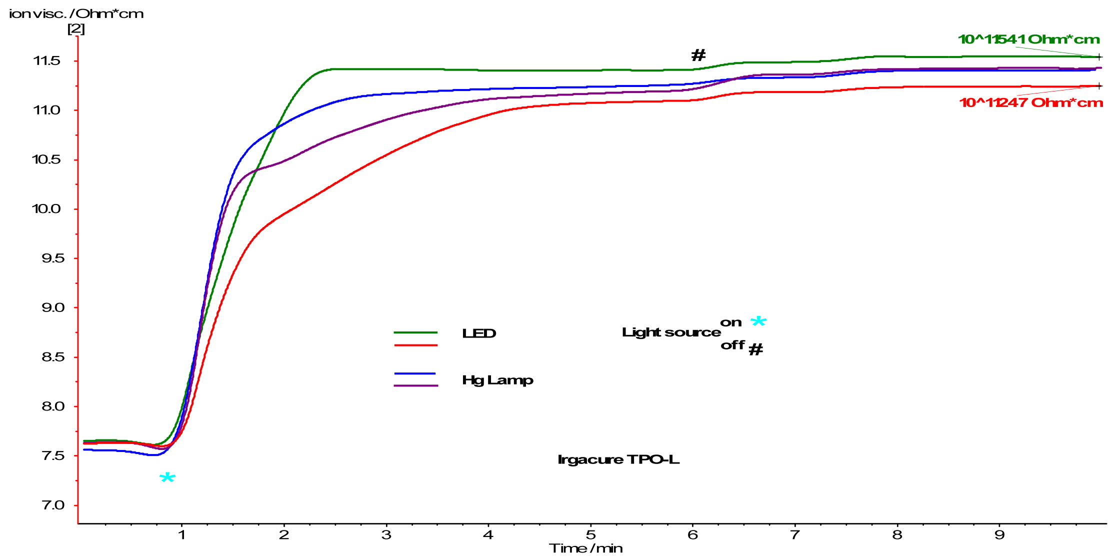

Figure 5. Comparison DEA Ion Viscosity curves from resin curing by LED and Hg-arc lamp with Irgacure TPO-L photoinitiator

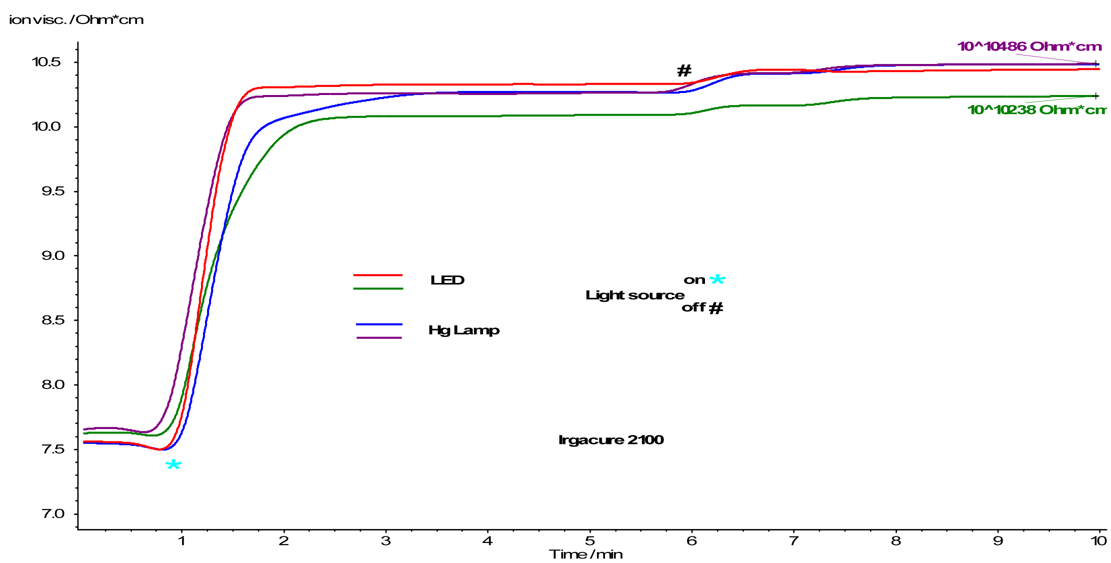

Figure 6. Comparison DEA Ion Viscosity curves from resin curing by LED and Hg-arc lamp with Irgacure 2100 photoinitiator

Summary

As demonstrated with these examples, DSC and DEA measurements can be coupled with a variety of radiation sources and offer an efficient and effective means of optimizing reaction conditions, including choice of photoinitiator and light source, for resin curing. Even with a substantially lower radiation intensity, the 447 nm diode laser performed better than the Hg-arc lamp in the curing of PEGDA with CQ (λ_{max} = 468 nm) as the photoinitiator. The 385 nm LED and the Hg-arc lamp, at similar light intensities, exhibited comparable performance in curing PEGDA/HDDA resins containing photoinitiators Irgacure® TPO-L and Irgacure® 2100. Differences between the performances of the photoinitiators were detected, however, with Irgacure® TPO-L affording a higher level of cure than Irgacure® 2100.

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[1]Pamela Shapiro, Gilles Widawki, Comparing a Blue-Diode Laser with a Mercury-Arc Lamp in the Curing of a Water-Soluble Resin by Photo-DSC and Photo-DEA, RadTech Report, Issue 4, December 2013.

[2] Paul Calvert, Swati Mishra, Amrut Sadachar , Dapeng Li, Blue-cured adhesives for bonding and 3D medical textiles, University of Massachusetts, Dartmouth, NTC Project: F06-MD14, National Textile Center Research Briefs: June 2010.

[3]a) Printing and Packaging Coatings Technical Data sheet Irgacure® TPO-L (old: Lucerin., Rev 4, March 2013, BASF. b) Printing and Packaging Coatings Technical Data sheet Irgacure® 2100., Rev 2, March 2010, BASF.