Comparing a Blue-Diode Laser with a Mercury-Arc Lamp

in the Curing of a Water-Soluble Resin by Photo-DSC and Photo-DEA

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Photocuring of liquid monomers and oligomers is employed in a variety of industries as an environmentally friendly, safe, fast and easily controlled approach to forming inks, coatings, adhesives and structural materials. The expansion of applications for photocuring since its introduction in the 1960s has been accompanied by an evolution in the light sources used for its processes. For example, stereolithography (an additive process for manufacturing 3-dimensional objects from photocurable photopolymer resin) requires a laser to trace complex patterns on each layer of liquid resin.

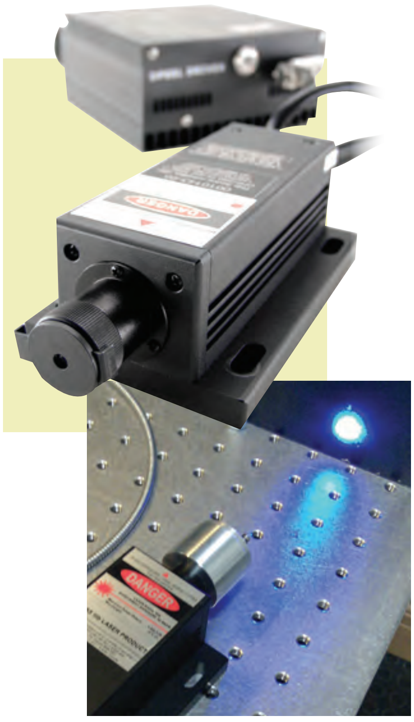
The ability to measure curing kinetics and degree-of-cure is essential for the selection of suitable UV and visible-light sources; identification of optimal curing times and conditions; and development of new, photocurable resins. Photo-differential scanning calorimetry (Photo-DSC) and photo-dielectric analysis (Photo-DEA) are powerful analytical tools for accomplishing these measurements.

In the example presented here, the efficiencies of two different UV light sources were compared in the curing of a water-soluble, blue-curing adhesive. Laser curing was employed for the first time in combination with DSC and DEA measurements and compared with the standard mercury (Hg) arc lamp. The pre-polymer formulation consisted of polyethylene glycol diacrylate (PEGDA) with camphorquinone (CQ) photoinitiator (1% by weight relative to PEGDA) and N, N dimethyl p-toluidine (DMPT) as a coinitiator (1:1 by weight relative CQ). This formulation has been used to fabricate complex hydrogel scaffolds with a fully interconnected pore network for use as bioreactors.[1]

Photo-DSC Measurements

DSC measurements were performed using a NETZSCH DSC 204 F1 Phoenix® interfaced with either an OmniCure® S2000 200 watt Hg short-arc lamp

Differential scanning calorimeter



Collimated diode laser system

with a band-pass filter delivering a spectral range of 320-500 nm with an irradiance of 10 W/cm^2 or a LASERGLOW Technologies LRD-0447 Series collimated diode laser system delivering 447 nm wavelength light with an irradiance of 0.74 W/cm^2.

Figures 1 and 2 show the results of three sets of DSC measurements for the resin curing under multiple two-second pulses from the Hg-arc lamp and from the laser, respectively. Degree-of-cure calculations based on peak areas from the three lamp runs and the three laser runs are listed in Table 1 and Table 2, respectively. The measurements exhibited good reproducibility.

The total resin-curing enthalpy was greater for the laser (129±5 J/g) than for the lamp (91±6 J/g).[2] The corrected enthalpy of each peak from the laser runs were, on average, greater than the corresponding peak from the measurements with the lamp. Furthermore, unlike the lamp, the laser continued to generate additional curing enthalpy up to the final pulse in the measurement.

The residual peak area at the end of the cure (e.g., pulse No. 15) is attributable to the heating effect of the light source on the sample, which was nine times greater for the lamp than for the laser.

Photo-DEA Measurements

DEA monitoring of the resin photocuring process at ambient temperature using the two different light sources were performed using a NETZSCH DEA 288 *Epsilon*®. The results are compared in Figure 3. Two measurements was performed with each radiation source in order to demonstrate reproducibility. Both the laser and lamp were run continuously with the exception of a two-minute interruption in irradiation from the lamp during one of the runs. Curing progress is indicated by an increase in ion viscosity, which levels off as curing completes. The initial slopes of the ion viscosity curves are slightly greater for laser-cured samples than for the lamp-cured ones, indicating more efficient curing from the

Figure 1

Results of three separate DSC measurements (shown in different colors) of resin-sample curing under multiple two-second pulses by the Hg-arc lamp

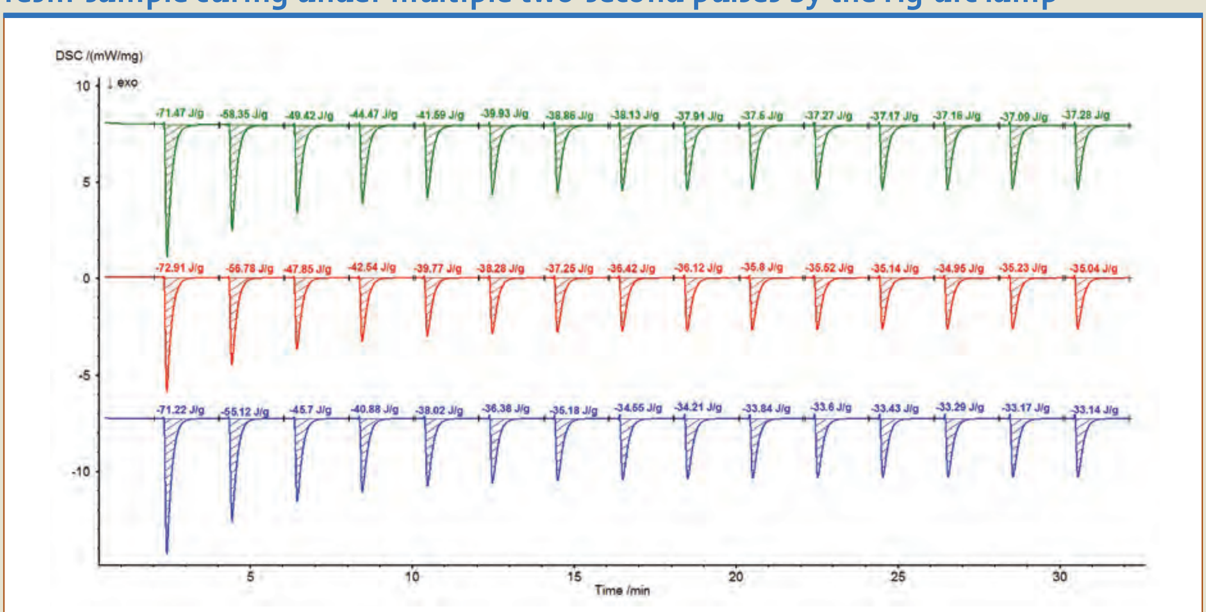


Figure 2

Results of three separate DSC measurements (shown in different colors) of resin-sample curing under multiple two-second pulses by the blue-diode laser

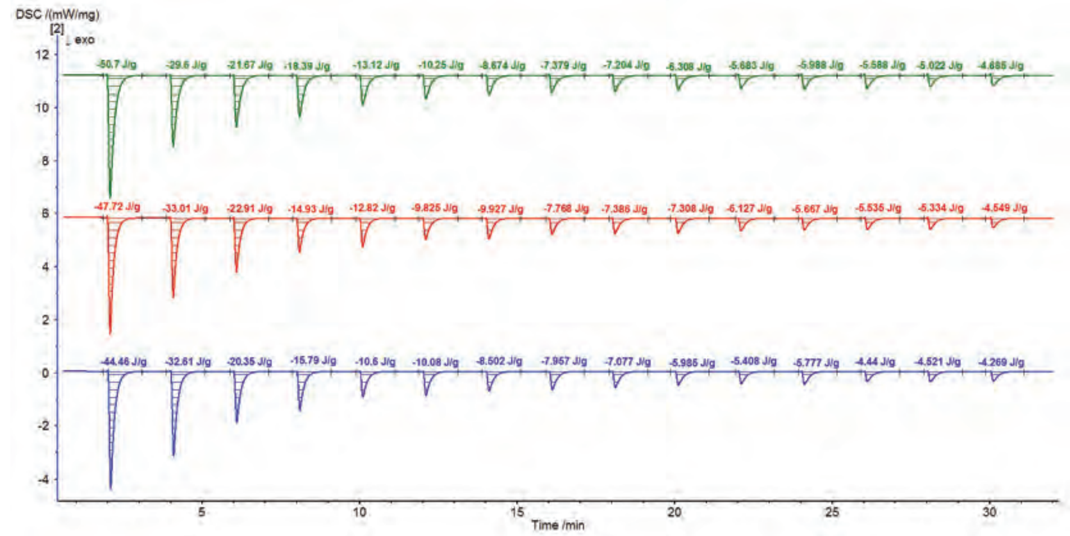


Table 1

Degree-of-cure calculations (Hg-arc lamp)

	First run			Second run			Third run		
Pulse No.	Peak Area (J/g)	Corrected Enthalpy (J/g)	Conversion (%)	Peak Area (J/g)	Corrected Enthalpy (J/g)	Conversion (%)	Peak Area (J/g)	Corrected Enthalpy (J/g)	Conversion (%)
1	71.47	34.19	40.51	72.91	37.87	40.29	71.22	38.08	40.24
2	58.35	21.07	24.96	56.78	21.74	23.13	55.12	21.98	23.23
3	49.42	12.14	14.38	47.85	12.81	13.63	45.7	12.56	13.27
4	44.47	7.19	8.52	42.54	7.50	7.98	40.88	7.74	8.18
5	41.59	4.31	5.11	39.77	4.73	5.03	38.02	4.88	5.16
6	39.93	2.65	3.14	38.28	3.24	3.45	36.38	3.24	3.42
7	38.86	1.58	1.87	37.25	2.21	2.35	35.18	2.04	2.16
8	38.13	0.85	1.01	36.42	1.38	1.47	34.55	1.41	1.49
9	37.91	0.63	0.75	36.12	1.08	1.15	34.21	1.07	1.13
10	37.50	0.22	0.26	35.80	0.76	0.81	33.84	0.70	0.74
11	37.27	-0.01*	-0.01*	35.52	0.48	0.51	33.60	0.46	0.49
12	37.17	-0.11*	-0.13*	35.14	0.10	0.11	33.43	0.29	0.31
13	37.16	-0.12*	-0.14*	34.95	-0.09*	-0.10	33.29	0.15	0.16
14	37.09	-0.19*	-0.23*	35.23	0.19	0.20	33.17	0.03	0.03
15	37.28	0.00	0.00	35.04	0.00	0.00	33.14	0.00	0.00
	Total Enthalpy = 84.40 J/g			Total Enthalpy = 94.00 J/g			Total Enthalpy = 94.63 J/g		

* Negative values for corrected enthalpy and % conversion are an artifact of using the final peak as the baseline reference value and show the variability of this value.

TABLE 2

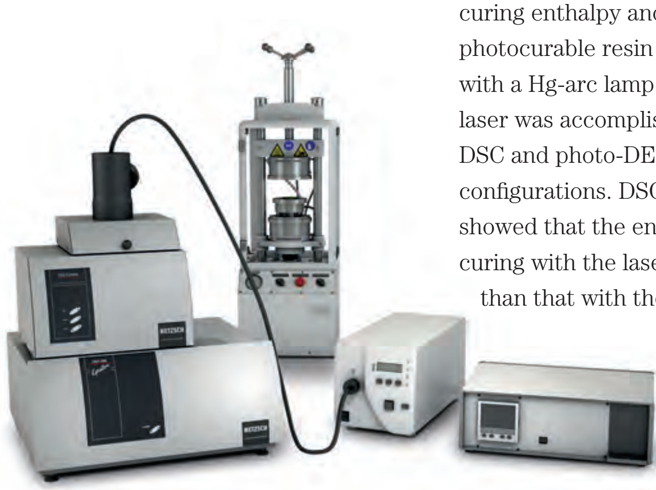
Degree-of-cure calculations (laser)

Pulse No.	First run			Second run			Third run		
	Peak Area (J/g)	Corrected Enthalpy (J/g)	Conversion (%)	Peak Area (J/g)	Corrected Enthalpy (J/g)	Conversion (%)	Peak Area (J/g)	Corrected Enthalpy (J/g)	Conversion (%)
1	50.70	46.02	35.40	47.72	43.17	32.56	44.46	40.19	32.47
2	29.60	24.92	19.17	33.01	28.46	21.47	32.61	28.34	22.89
3	21.67	16.99	13.07	22.91	18.36	13.85	20.35	16.08	12.99
4	18.39	13.71	10.54	14.93	10.38	7.83	15.79	11.52	9.31
5	13.12	8.44	6.49	12.82	8.27	6.24	10.6	6.33	5.11
6	10.25	5.57	4.28	9.83	5.28	3.98	10.08	5.81	4.69
7	8.67	3.99	3.07	9.93	5.38	4.06	8.502	4.23	3.42
8	7.38	2.69	2.07	7.77	3.22	2.43	7.957	3.69	2.98
9	7.20	2.52	1.94	7.39	2.84	2.14	7.077	2.81	2.27
10	6.31	1.62	1.25	7.31	2.76	2.08	5.985	1.72	1.39
11	5.68	1.00	0.77	6.13	1.58	1.19	5.408	1.14	0.92
12	5.99	1.30	1.00	5.67	1.12	0.84	5.777	1.51	1.22
13	5.59	0.90	0.69	5.54	0.99	0.74	4.44	0.17	0.14
14	5.02	0.34	0.26	5.33	0.78	0.59	4.521	0.25	0.20
15	4.69	0.00	0.00	4.55	0.00	0.00	4.269	0.00	0.00
	Total Enthalpy = 129.99 J/g			Total Enthalpy = 132.58 J/g			Total Enthalpy = 123.79 J/g		

laser. In addition, the final ion viscosity was approximately three times greater for the laser-cured samples.

DEA measurements are more sensitive to small changes in the degree-of-cure than DSC measurements. Hence, increases in the ion viscosities of the samples due to curing were still measurable after 50 minutes of continuous lamp or laser irradiation.

Due to sample heating by the lamp or laser (which causes an increase in ion mobility), sharp steps in the curves are observed as soon as the light source is removed.



Dialectric analyzer with light guide, lab furnace and computer

Summary

In summary, a comparison of the curing enthalpy and curing kinetics of photocurable resin under irradiation with a Hg-arc lamp and a blue-diode laser was accomplished using photo-DSC and photo-DEA instrument configurations. DSC measurements showed that the enthalpy of resin curing with the laser was greater than that with the lamp, indicating possibly greater crosslinking of the sample with the laser. This is consistent with the greater increase in ion viscosity of the laser-cured sample measured by DEA. The DEA measurements also showed that the resin curing rate was slightly greater with the laser than with the lamp. Finally, the DSC measurements indicated greater sample heating by the lamp radiation than by the laser radiation. Sample heating can be an issue in cases where temperature changes during the polymerization lead to polymer shrinkage stress.

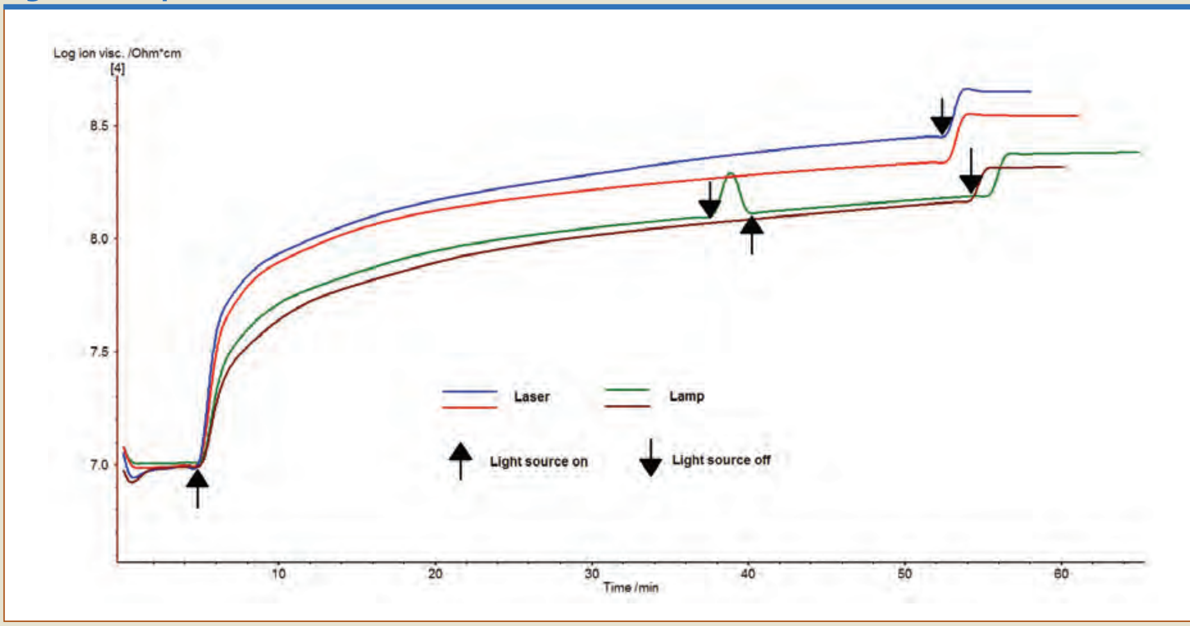
Overall, the lower intensity, monochromatic blue laser proved to be a more suitable light source for curing this particular resin formulation than the Hg-arc lamp with a broadband filter.

References

1. Paul Calvert, Swati Mishra, Amrut Sadachar, Dapeng Li, University of Massachusetts, Dartmouth, NTC Project: F06-MD14, National Textile Center Research Briefs: June 2010

Figure 3

Ion viscosity curves measured at 10 Hz frequency of curable resin irradiated with Hg-arc lamp and laser



2. Total curing enthalpy was calculated by totaling the peak areas and subtracting out the baseline contribution from differential heating of the sample and reference crucibles, which was calculated from the enthalpy of the final pulse in the series. The timing of the Omnicure lamp pulses was controlled by the NETZSCH Proteus software. The timing of the laser pulses was controlled manually.

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