

RadTech 2020 UV+EB Technology Conference

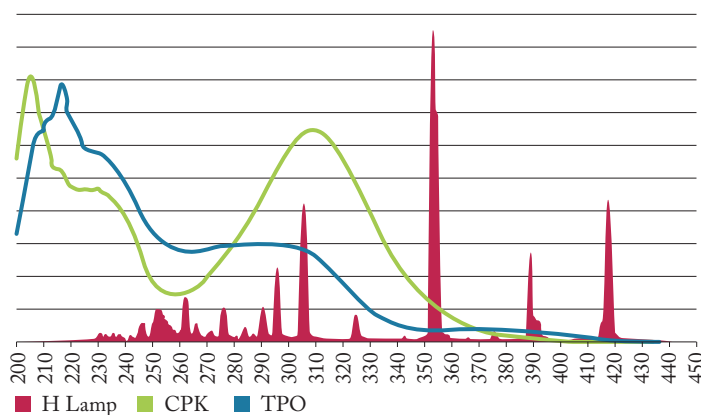
The Use of Anthracene Derivatives in UV-LED Curing

There is a strong interest in UV-LED curing of coatings, inks, adhesives, etc., due to the benefits of using UV-LED as the energy source. To meet the end user's needs, resin formulators need to draw on the list of available materials. While the range of monomers and oligomers that can be used is quite large, formulators are somewhat limited by the photoinitiators available. The UV-LED lamps that are most used today further limit the available useful photoinitiator options. Currently, TPO is one of the more popular photoinitiators. However, recent shortages in the availability and impending regulatory reclassification of TPO has focused attention on the limited options a formulator has when using a UV-LED lamp for curing.

One of the key conditions that formulators must consider is how well the photoinitiator absorption bands will overlap with the wavelengths emitted by the light source. For Arc and microwave lamps, this is easy as both types of lamps produce UV energy in a wide assortment of wavelengths resulting in a high probability that there will be overlap. Figure 1 shows a typical H Arc lamp emission with several common photoinitiator absorptions. Both CPK (CyclohexylPhenyl Ketone) and TPO (Trimethylbenzoyl Phosphine Oxide) can be used with an Arc lamp and H bulb combination.

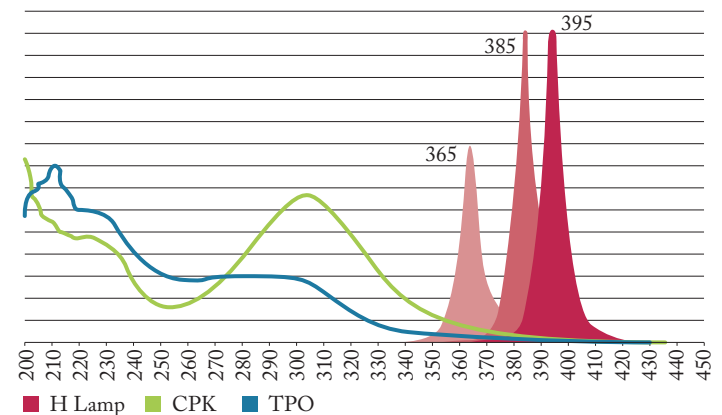
UV-LED lamps are not so forgiving. A characteristic of an UV-LED lamp is the production of very narrow UV wavelength emissions. This results in a high probability that the photoinitiator absorptions and the lamp emissions will not overlap; this can be seen in Figure 2. While CPK is not sensitive to the UV-LED lamp in this case, there is enough absorption by TPO to allow it to react. This is a key reason why TPO is one of the preferred photoinitiators when using a UV-LED lamp. Another factor is the cost advantage that TPO has over other photoinitiators such as BAPO that are effective when using UV-LEDs as the light source.

Figure 1: PI-Spectral Response H Arc Lamp¹



¹ Miltec UV

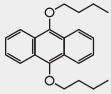

Figure 2: PI – Spectral Response UV-LED¹



¹ Miltec UV

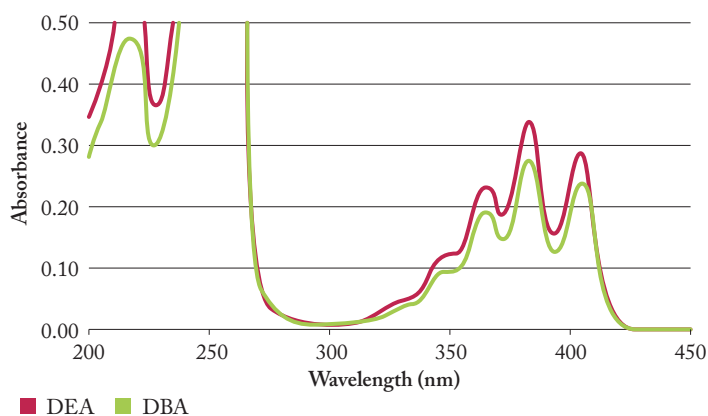
Anthracene derivatives are a potential solution to broadening the range of photoinitiators that can be used with UV-LED lamps. Table 1 lists a few common anthracene derivatives that are commercially available (trade names are UVS-1101 and UVS-1331).

Table 1

| Chemical Name | 9,10-DiButoxyAnthracene | 9,10-DiEthoxyAnthracene |
|-------------------------|---|---|
| Abbreviation | DBA | DEA |
| Structure |  |  |
| Typical Characteristics | Appearance: Yellow powder Purity: 98% or more | Appearance: Yellow powder Purity: 97% or more |

9,10-DiButoxyAnthracene (DBA) and 9,10-DiEthoxyAnthracene (DEA) both absorb at wavelengths that overlap well with the currently available UV-LED lamps on the market. (Figure 3)

Figure 3



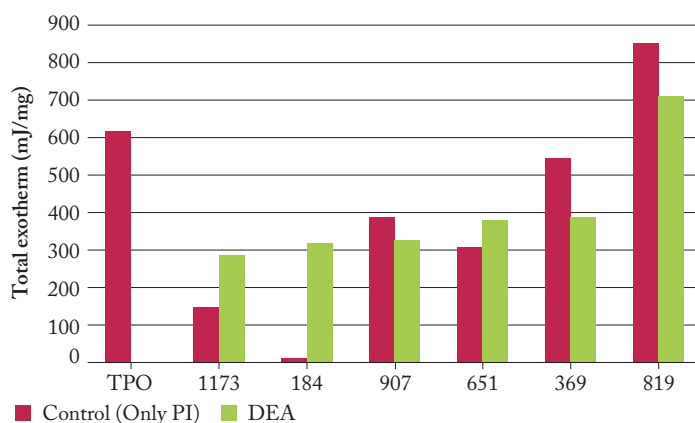
Although both DBA and DEA absorb energy at wavelengths such as 385 nm and 405 nm produced by commercially available UV-LED lamps, they cannot form free radical species by themselves. However, they can transfer energy to photoinitiators that absorb at lower wavelengths which can then produce free radical species. These free radical species are then able to initiate polymerization. The mechanism by which the anthracene derivatives transfer energy is not clear and is now under investigation in the lab. Based on data to date, the energy is transferred by either a Triplet Energy Transfer process or an Excited State Energy Transfer (Table 2).

Table 2

| | | | |
|---------|---|---------|--|
| DBA+UV | → | DBA* | |
| DBA*+PI | → | DBA+PI* | Triplet Energy Transfer or Excited State Electron Transfer |
| PI* | → | PI• | Initiator Produces Radicals |

TPO is an excellent photoinitiator due to its ability to absorb at wavelengths that are emitted by 385- and 405-nm UV-LED lamps. However, both the cost and periodic supply issues result in the search for potential substitutes to TPO. We compared TPO with a range of commonly found free radical photoinitiators. The experiment was run using the photoinitiator alone and with 0.2 phr of DEA. The reaction was monitored by observing the total exotherm by Photo-DSC (Figure 4).

Figure 4

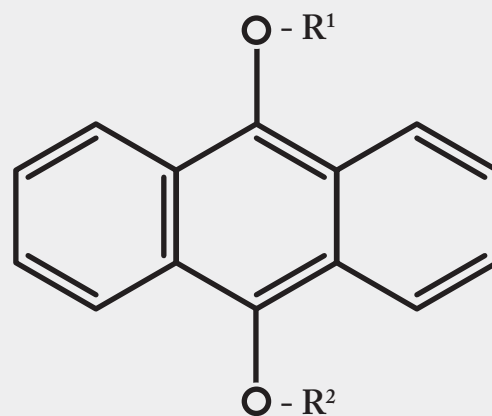


Formulation: Monomer: TMPTA, PI: 5.0 phr and TPO @ 3.0 phr, Sensitizer: DEA 0.2 phr, Light source: 405nm UV LED (100 mW/cm²)

In this test, photoinitiators 1173, 184 and 651 showed an increase in the reaction when compared to the photoinitiators by themselves. However, in each case, the total reaction was less than that of TPO.

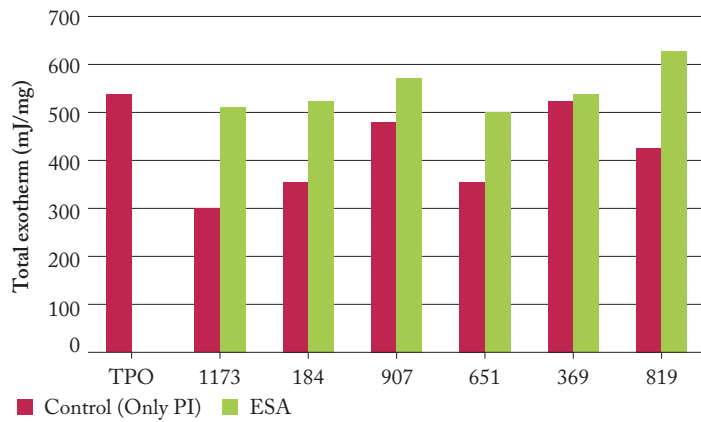
Based on these initial promising results, it was believed that a modified anthracene derivative may increase the photopolymerization to meet or exceed that of TPO. A new anthracene derivative -designated ESA - was developed in the lab with the general structure shown in Figure 5.

Figure 5



A second series of experiments was run using the photoinitiator alone and with 0.2 PHR of ESA. The reaction was monitored by observing the total exotherm by Photo-DSC (Figure 6).

Figure 6



Formulation: Monomer: TMPTA, PI: 5.0 phr and TPO @ 3.0 phr, Sensitizer: ESA 0.2 phr, Light source: 395nm UV LED (100 mW/cm²)

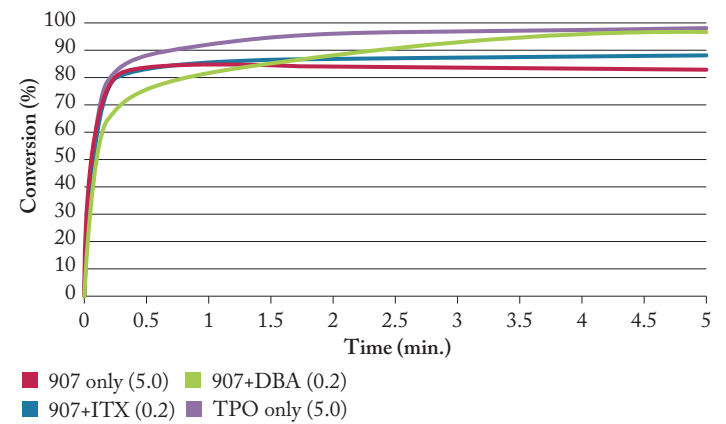
In this case, most combinations of photoinitiator and the anthracene derivative ESA demonstrated reactivity equal to or better than that of TPO.

Thioxanthone type sensitizers such as ITX have traditionally been used as sensitizers for free radical photopolymerizations. To compare the effectiveness of anthracene derivatives to ITX when using UV-LED lamps for cure, the experiment shown in Table 3 was run and the results given in Figure 7. TPO was used as the control photoinitiator.

Table 3

| | |
|----------------|--|
| | TMPTA 100 part + 907 5 PHR+DBA 0.2 PHR |
| Test Condition | TMPTA 100 part + 907 5 PHR+ITX 0.2 PHR |
| | TMPTA 100 part + TPO 5 PHR |
| Light Source | LED 365 + 405nm |

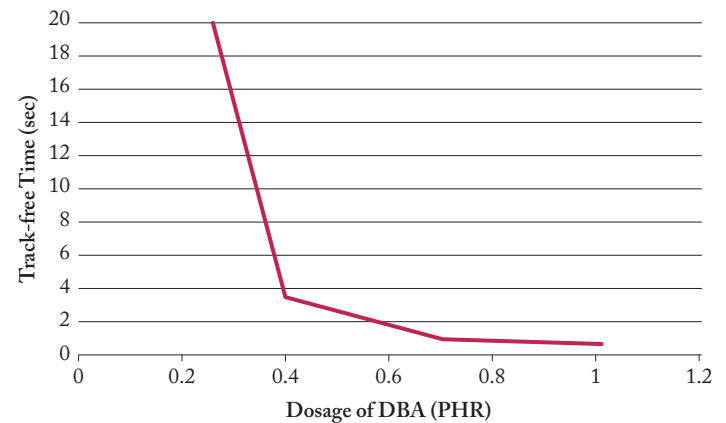
Figure 7



After 5 minutes of exposure, the combination of the photoinitiator 907 and DBA outperformed both the use of 907 by itself and the combination of 907 and ITX. In fact, the anthracene derivative DBA matched with the 907 photoinitiator gave essentially the same conversion as TPO.

To complete the work on free radical curing, we examined the use of anthracene derivatives in pigmented coatings. In this case, a simple black pigmented coating was cured using an iodonium salt as the photoinitiator. The Optical Density of the cured coating was greater than 1.5 and a UV-LED lamp at 365 nm was used as the UV source (Figure 8).

Figure 8

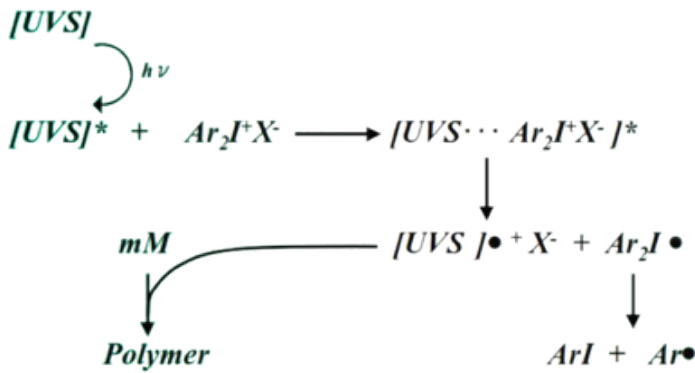


Formulation: Tetraacrylate monomer, PI: Iodonium Salt (4.1 phr, Film Thickness 18 μ m, OD value > 1.5, Light source: UV LED 365 nm (30mW/cm²) covered with PET

In this case, curing was negligible if the photoinitiator was used without any sensitizer present. As the anthracene derivative DBA is added at increasing levels, the amount of time needed to achieve surface cure drops dramatically.

Like the use of anthracene derivatives in free radical curing, these sensitizers can also play a role in UV-LED cationic cure. The overall mechanism is believed to be like the mechanism of anthracene derivative sensitization in free radical cure mentioned earlier in this paper. J. Myoung-Souk and J. Crivello have suggested the following process for the role of anthracene derivatives in cationic cure (Figure 9)

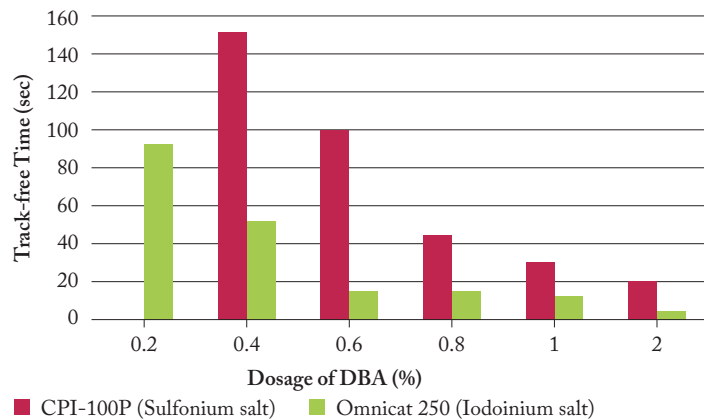
Figure 9



UVS = UV Sensitizer

The performance of the anthracene derivatives varies with the type of photoinitiator used in cationic cure. Figure 10 illustrates the impact that the addition of DBA has on iodonium photoinitiators when compared to sulfonium initiators while cured using a 405 nm UV-LED lamp. DBA is particularly effective at a dose range of 0.4 – 0.6%.

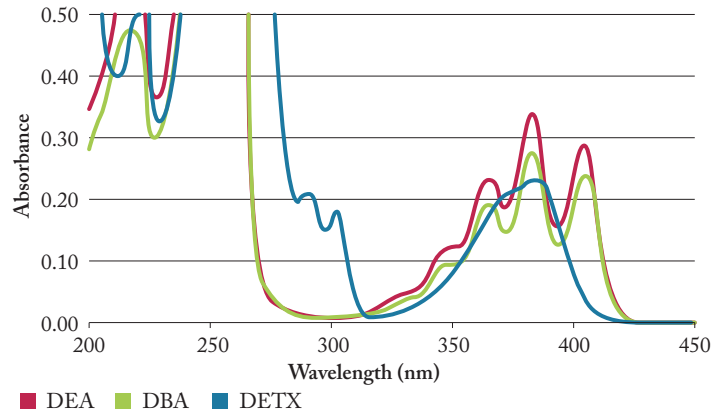
Figure 10



Formulation: Cycloaliphatic Epoxy, PI: Sulfonium or Iodonium, Anthracene: DBA, Thickness: 5µm, Light source: UV LED 405nm (50mW/cm²)

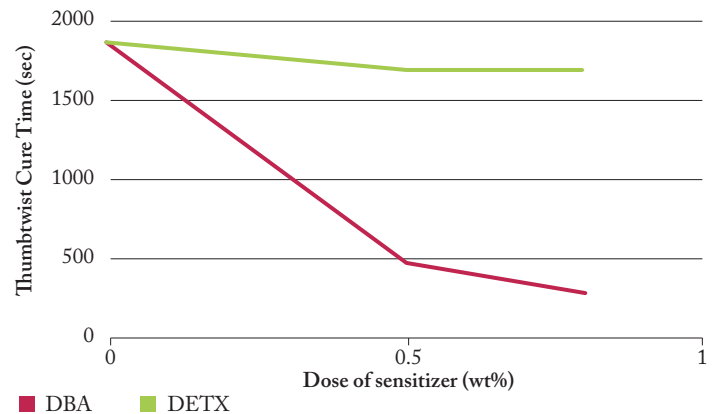
A traditional class of sensitizers used in cationic cure is thioxanthenes. When comparing the absorption spectra of DEA and DBA with a typical thioxanthone DETX, one would predict that DEA, DBA and DETX would be interchangeable when it comes to their use in UV-LED cationic cure applications (Figure 11).

Figure 11: PI-Spectral Response H Arc Lamp¹



However, a comparison between DBA and DETX has shown there to be a surprising difference between the two sensitizers (Figure 12). In this case, the use of DBA was shown to achieve a threefold reduction in the time to pass the thumb twist cure test required by the customer.

Figure 12



Formulation: Cycloaliphatic Epoxy, PI: Sulfonium salts 5 wt%, Sensitizer: DBA or DETX diethyl thioxanthone, Blue pigments (P.B.15): 30 wt%, thickness: 30 µm, Light source: 365nm UV LED (< 1 mW/cm²)

In this case, the formulation tested contained 30 wt % blue pigment. The use of pigments in cationic cure coatings and inks is common. The use of anthracene derivatives in pigmented coatings could allow the utilization of the higher wavelength absorption bands of the anthracene derivative followed by the transference of energy to a photoinitiator that may be blocked by the pigment. In this experiment, a black matrix coating used in LCD displays was cured using a 365 nm UV-LED lamp. The base formulation did not exhibit any cure. When DBA was added to the formulation, the time to cure was reduced in line with the amount of DBA used with a tack free state achieved using a 1.0 phr level of the anthracene derivative (Table 4).

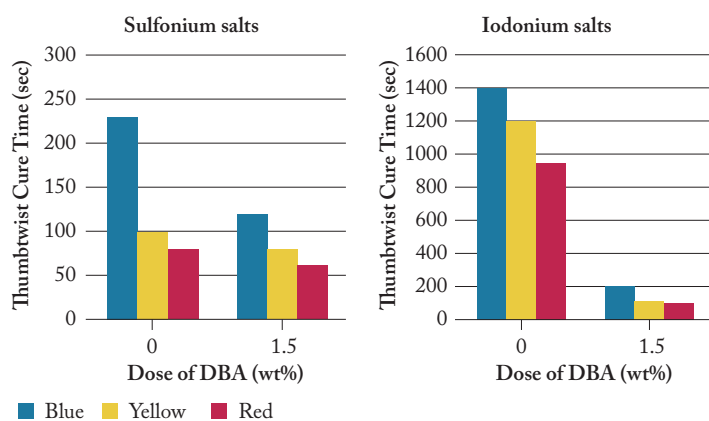
Table 4

| DBA (phr) | Tack-free time (sec) |
|-----------|----------------------|
| 0.0 | NA |
| 0.4 | >600 |
| 0.7 | >60 |
| 1.0 | 30 |

Formulation: Cycloaliphatic Epoxy, PI: Iodonium salt in propylene carbonate, Sensitizer: DBA, Black Paste – 7 phr (1.3 O.D.), thickness: 12 μm , Light source: 365nm UV LED (30 mW/cm²)

The use of anthracene derivatives is applicable across a range of pigmented cationic-cured inks. Figure 13 illustrates the use of DBA in blue, yellow and red cationic cured inks. The lamp used in all cases was a 365 nm UV-LED. In all cases, a reduction in cure time was seen with the largest reduction obtained when iodonium salts were used as the photoinitiator. It should be noted that, using 1.5 wt% of DBA, the cure speed of the iodonium salt-initiated formulation approached that of the sulfonium salt-initiated formulation.

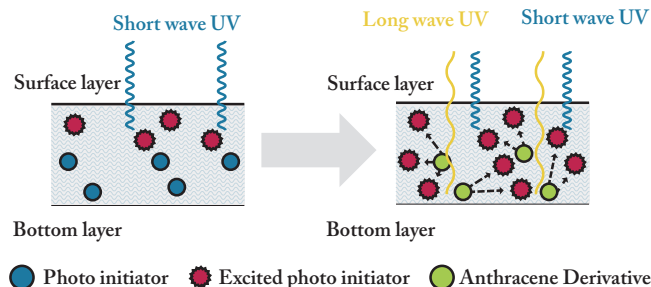
Figure 13



Formulation: Cycloaliphatic Epoxy, PI: Sulfonium or iodonium salts 10 wt%, Sensitizer: DBA or DETX diethyl thioxanthone, Pigments: 20 wt%, Light source: 365nm UV LED (< 1 mW/cm²)

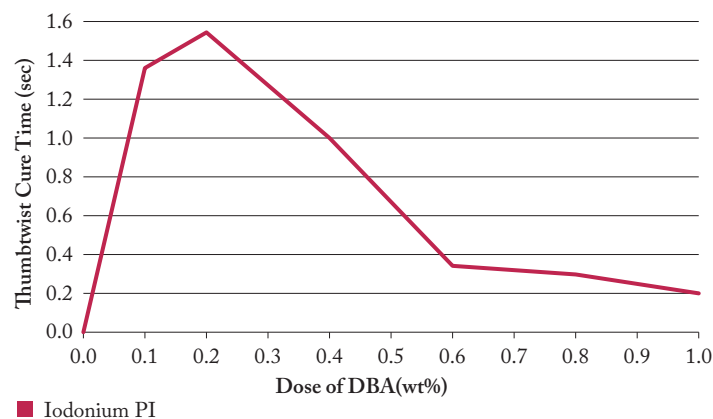
The ability an anthracene derivative molecule to transfer energy to a photoinitiator is not only useful in pigmented systems but can also be used to enhance cure in thick films. Anthracene derivatives are excited by long wavelength light which can reach the bottom of a thick layer. This leads to a more complete cure due to the transfer of energy to the photoinitiators in the bottom layer (Figure 14).

Figure 14



In the following experiment (Figure 15), the amount of cure was determined at various levels versus the amount of DBA used in the formulation. In this example, DBA, at a 0.2 wt% level, was able to cure a 1.6-mm thick film. Note that the cure thickness is dependent on the amount of the anthracene derivative.

Figure 15: Optimization of Dosage for Thick Film



Formulation: Cycloaliphatic Epoxy, PI: Iodonium salt 2.5 phr, Anthracene: DBA, Thickness: varied, Light source: UV LED 405nm (50mW/cm²), Time: 120 seconds

Application Example

The information discussed in this paper so far is based on laboratory data. A recent example of a commercial use of anthracene derivatives to promote cure can be seen in the innovative work at Polymer Gvulot (Polymer-G for short), an Israeli company creating formulations for new 3D printing technology. Based on their development work, anthracene derivatives were selected for their hybrid formulations in order to facilitate cure when using 395-nm and other UV-LED light sources. This has allowed the rapid cure of very thick objects made by Gel Dispensing Technology (GDT)-type 3D printing (see example below, source: Polymer-G).



Summary

Anthracene derivatives are effective sensitizers for UV-LED cured systems. They can be used in both free radical and cationic cure reactions. By combining anthracene derivatives with a wide range of free radical photoinitiators, a large increase in reaction rate and/or conversion can be obtained. This now provides formulators with an increased number of photoinitiator options that can be used to replace more expensive or hard-to-obtain photoinitiators for UV-LED cured formulations. Depending on the requirements, anthracene derivatives are typically used at the 0.2 to 1.0 % level.

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