Investigation of UV/EB dual cure method to mitigate oxygen inhibition

*Nicole L. K. Thiher,[1] Sage M. Schissel,[*2] and Julie L. P. Jessop[3]*
[1]Department of Chemical & Biochemical Engineering, University of Iowa, Iowa City, IA
[2]PCT Ebeam and Integration, LLC, Davenport, IA
[3]Mississippi State University, School of Chemical Engineering, Mississippi State, MS

Abstract.

Nitrogen inertization is typically used to mitigate oxygen inhibition during EB polymerization. However, continuous nitrogen flow is expensive, and it is desirable to identify a cheaper method to overcome oxygen inhibition. A spray method in combination with UV/EB dual cure was investigated as a means to overcome oxygen inhibition, while reducing the required amount of photoinitiator in the formulation. Successful reduction of the oxygen inhibition layer was quantified using confocal Raman microscopy.

Introduction.

In previous work, a dual-cure UV/EB processing method was presented to mitigate the oxygen inhibition that is typically associated with EB polymerization, while addressing depth of penetration issues typically associated with UV polymerization.[1] The dual-cure process was successful at achieving through-cure in the absence of nitrogen inerting for both pure monomer and pigmented monomer samples. However, adding the UV processing step requires the addition of a photoinitiator. EB is chosen as the curing mechanism in many applications, such as food packaging, because the absence of initiators avoids any initiator migration. Thus, having initiator in the formulation is not suitable for all EB applications. Yet, there are still other applications that could benefit from the dual-cure process even with the addition of photoinitiator.

For these suitable applications, it is likely still advantageous to reduce the amount of photoinitiator required to achieve through-cure. Not only does initiator pose a migration risk, it can also be one of the most expensive components in a formulation. This paper investigates a means of reducing the photoinitiator concentration during the dual-cure process by using a spray application technique. Here, a base layer of monomer containing no photoinitiator is sprayed with a thin, top layer of monomer containing photoinitiator. The results from this study are still preliminary, and there is more work to be done to optimize this spray process. However, results indicate that the spray technique could be useful for reducing initiator concentration required for complete cure during the UV/EB hybrid process.

Experimental.

Materials.

One of the monomers used for experiments in previous work,[1] benzyl acrylate (BA, TCI America), was chosen to investigate the feasibility of the spray method. The low viscosity of BA

made it easier to find a nozzle suitable for spray delivery. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, TCI America) was used to achieve photopolymerization in this study. All chemicals (Figure 1) were used as received.
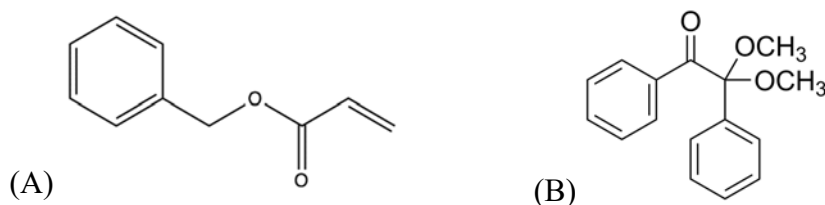

(A)   (B)

Figure 1. The chemical structures of (A) the monomer BA and (B) the photoinitiator DMPA used in this study.

Methods.

Formulations and experimental variables.

To prepare samples for UV/EB exposure, ~200 μm of pure BA was added to a PDMS mold. Then, a spray bottle was used to apply a thin layer of BA containing 1wt% photoinitiator DMPA to the surface of the pure monomer. UV polymerization was initiated with an Omnicure® S1000 Ultraviolet/Visible Spot Cure System (Excelitas, 250-450 nm band pass filter) with a 3 mm liquid lightguide and adjustable collimating lens attachment (Lumen Dynamics, Model No. 810-00041) at ambient temperature and atmosphere. A 20 cm distance was set between the collimating lens and the sample surface to ensure a consistent irradiance profile over the entire exposure area. The effective irradiance was measured by a radiometer (Versaprobe Pro, Con-Trol Cure). EB polymerization was performed on an EBLab unit (Comet, Inc.) at an accelerating voltage of 200 kV to ensure uniform EB energy deposition throughout the bulk of each sample. The dual-cure sample was first exposed to UV light followed by EB. The dose of the EB was varied to determine how much energy was required to achieve through-cure (Table 1). All samples were polymerized in air.

Table 1. The EB and hybrid processing conditions used to determine the effectiveness of the spray method.

	UV Conditions	**EB Conditions**
EB Only 1	-	100 kGy, 3 m/min
EB Only 2	-	200 kGy, 3 m/min
Hybrid 1	20 mW/cm2, 30 s	100 kGy, 3 m/min
Hybrid 2	20 mW/cm2, 30 s	200 kGy, 3 m/min

Confocal Raman Microscopy.

Confocal Raman microscopy was used to determine the conversion as a function of depth of the polymer films. In order to eliminate error from instrumental variation and reaction under the EB, a stable reference peak was used.[2] Previous work has established the reaction peak at 1636 cm^{-1} (indicative of the -C=C- bond in the acrylate moiety) and a reference peak at 1613 cm^{-1} (indicative of the -C=C- bonds in the phenyl ring). Fractional conversion (α) was calculated using the following equation:

$$\alpha = \left(1 - \frac{I_{rxn}(P)/I_{ref}(P)}{I_{rxn}(M)/I_{ref}(M)}\right) \quad (1)$$

where $I_{rxn}(P)$ and $I_{ref}(P)$ are the peak intensities of the reaction and reference peak of the polymer, respectively; $I_{rxn}(M)$ and $I_{ref}(M)$ are the peak intensities of the reaction and reference peak of the monomer.[3]

Raman spectra of the polymerized films were collected using an optical microscope (DMLP, Leica) connected to a modular research Raman spectrograph (HoloLab 5000R, Kaiser Optical Systems, Inc.) *via* a 20-µm collection fiber. A single-mode excitation fiber carried an incident beam of 785-nm near-infrared laser to the sample through a 100x objective with a numerical aperture of 0.9 and a working distance of 0.27 mm. Laser power at the sample was ~13 mW. Spectra were collected with an exposure time of 1 minute and 3 accumulations. Ten monomer spectra were collected and averaged to provide accurate values for $I_{rxn}(M)$ and $I_{ref}(M)$ in Equation 1. Polymer spectra were collected in 3-µm increments starting at the surface of the film and continuing into the depth. Slight differences between optical and physical depth are possible with this microscope configuration.[4-6] The optical depth (*i.e.,* the distance the microscope stage was moved, not the depth of the laser focus) is reported in this paper.

Results and Discussion

The spray method combined with the dual-cure UV/EB process was successfully used to mitigate oxygen inhibition (Figure 2).
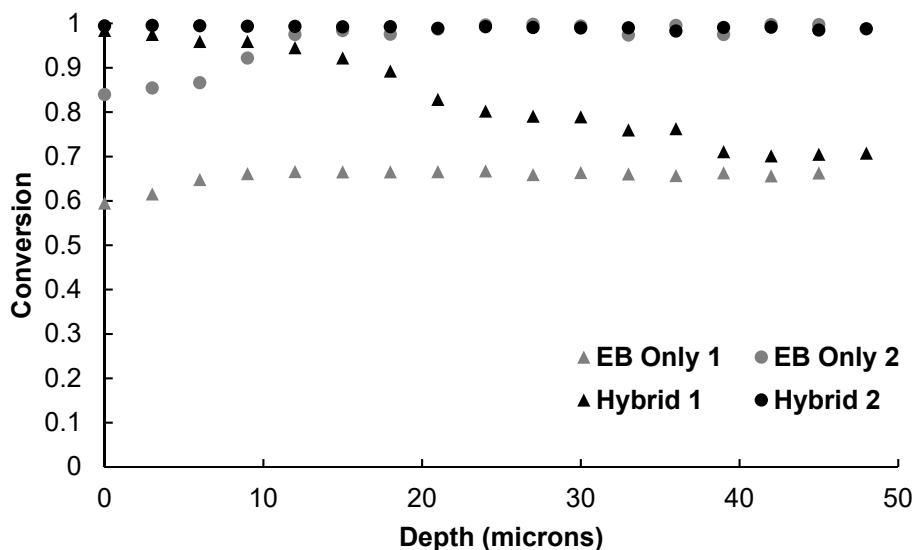

Figure 2. Conversion vs. depth profiles of EB- and UV/EB hybrid-cured samples, collected using confocal Raman microscopy. The spray hybrid process (*Hybrid 1* and *2*) can be used to overcome the oxygen inhibition seen in EB samples cured in air (*EB Only 1* and *2*); however, through-cure is only achieved in the hybrid sample cured with the higher EB dose (*Hybrid 2*).

In the previous work, through-cure of BA was achieved using a 30-s UV exposure at an effective irradiance of 20 mW/cm^2 combined with an EB exposure at 100 kGy with a speed of 3 m/min (see Figure 5 in Ref. 1).[1] Using these same processing conditions in combination with the spray application, complete conversion was not achieved (Figure 2, *Hybrid 1*). The energy provided by the UV light was enough to produce near-complete conversion at the surface, but conversion dropped rapidly in the depth of the sample. When spraying monomer containing photoinitiator onto the surface of the sample, the photoinitiator can migrate into the sample but will likely not reach all the way through to the depth. Photoinitiator is required to transform the energy from the UV light into radicals that initiate polymerization. Thus, below the surface of the sample, where no initiator is present, UV light is not useful in inducing polymerization, and the conversion of the *Hybrid 1* sample approaches the conversion levels of the *EB Only 1* sample.

For hybrid-spray samples, increasing the EB dose from 100 kGy to 200 kGy was enough to achieve through-cure. Using the *Hybrid 2* conditions, the sample reached a fractional conversion of nearly 1.0 throughout the entire sample depth (Figure 2, *Hybrid 2*). The conversion in the depth of the hybrid-spray sample closely matches the conversion in the depth of the EB-only sample. These results indicate that, to achieve though-cure in hybrid-spray samples, the EB dose must be sufficiently high to achieve complete conversion in the depth without the aid of UV light.

Conclusions

Oxygen inhibition was successfully mitigated using a spray application dual-cure process. In order to achieve complete conversion using the spray method, higher EB energy was required than what was necessary to achieve the same levels of conversion during the conventional dual-cure process in which the photoinitiator is present throughout the entire sample. Despite the need for higher EB energy, these results indicate that the spray method may be a viable solution for reducing initiator concentration during the dual-cure process.

These results are preliminary and provide a proof of concept, but more work is needed to optimize this spray process. The goal of the spray method is to reduce the photoinitiator concentration required to achieve through-cure. Studies should be conducted to determine the optimal initiator concentration and determine if this concentration is dependent on monomer chemistry. Additionally, it is important to confirm that the spray application results in a homogeneous deposition across the film surface. One type of spray nozzle was used in this study, but another nozzle style may provide better results.

References.

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