

Internal Reference Validation for EB-Cured Polymer Conversions Measured via Raman Spectroscopy

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Advancement of electron beam (EB) technologies requires an increased understanding of polymerization kinetics to design targeted polymer performance properties. However, real-time characterization of EB polymerization is challenging in the harsh EB-curing environment. Initial conversion profiles obtained via confocal Raman microscopy were inconsistent with known cure behavior. Although the internal reference was selected using analogous real-time monitored UV polymerizations, the chemical bond associated with the reference was shown unstable under EB radiation. A new reference was chosen and confirmed stable, demonstrating Raman microscopy is a valid, quantitative technique to measure conversion profiles in EB-cured samples provided the stability of the reference peak is verified.

Introduction

EB curing offers a fast, low-energy and solvent-free means of polymerizing inks, films, coatings and adhesives.¹⁻³ This initiator-free technique is especially appealing for packaging

applications where molecular migration would be problematic. In addition, unlike photopolymerization, additives such as pigments, fillers, fibers and nanomaterials do not prevent penetration of the ionizing radiation, resulting in excellent product consistency.

Continued advancement of EB technologies requires an increased understanding of EB-induced polymerization to provide guidance for designing performance properties needed for targeted applications. However, there are very few published works on the kinetics of EB polymerizations.^{1,2,4,5} Several issues make characterization of EB kinetics particularly challenging. EB system design does not lend itself to online, real-time monitoring and EB bombardment is a harsh environment for sensitive monitoring equipment. In addition, web speeds are faster than the time resolution of monitoring equipment suitable for an industrial environment.

Raman spectroscopy is a well-established technique for the characterization of photopolymerizations, facilitating conversion and rate of

polymerization measurements and polymer identification.⁶⁻¹⁰ Raman confocal microscopy can also be used to probe polymer composition as a function of depth without destroying the sample. In order to obtain these quantitative measurements, significant peaks in the Raman spectrum must be identified and associated with specific bonds in the molecules comprising the sample. One of these peaks must serve as an internal reference and is typically determined by monitoring the photopolymerization in real time and noting peaks that do not change during the reaction.

Raman confocal microscopy could provide valuable data needed to gain a fundamental understanding of the EB polymerization process and how it affects the properties of the polymers that are formed. However, without the ability to monitor the EB reaction in real time, the reference peak stability cannot be directly confirmed for an EB-curing process and quantitative measurements would be suspect. In this study, we demonstrate Raman confocal microscopy can be used to characterize EB polymerizations by validating the stability of a reference peak through comparison with an UV-cured standard.

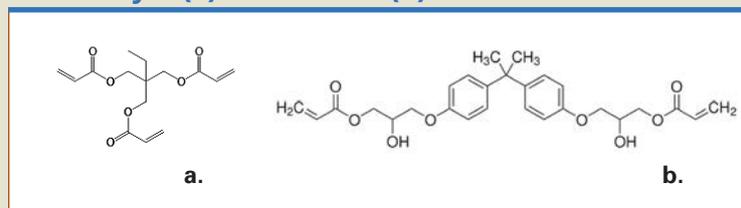
Experimental

Materials

Two formulations were used to validate spectroscopic-based conversion measurements for EB-polymerized coatings. The first formulation was neat trimethylolpropane triacrylate monomer (TMPTA, Cytec), and the second formulation was a 50/50 mixture (by weight) of TMPTA and bisphenol-A-diglycidylether diacrylate oligomer (BADGEDA, Ebecryl 3700, Cytec) (Figure 1). For corresponding UV studies, 0.5 wt% of the photoinitiator 2,2-dimethoxy-2-

FIGURE 1

Chemical structures of acrylate monomers used in this study—(a) TMPTA and (b) BADGEDA



phenylacetophenone (DMPA, Aldrich) was added to each formulation. All chemicals were used as received.

Methods

EB Coatings

Coatings of each EB formulation were made on aluminum Q-panels using a 52-rod drawbar, resulting in ~100 micron films. The coated panels were fed through an EB accelerator equipped with a variable-speed, fiberglass carrier web (BroadBeam EP Series, PCT Engineered Systems Inc.). The coatings were EB-cured with a 30 kGy dose; and web speed, voltage and N₂ flow rate were held constant at 50 feet/minute, 200 kV and 17 SCFM, respectively.

UV Coatings

Coatings of each UV formulation were made on aluminum Q-panels using a drawbar, resulting in ~100 micron films. The coated panels were fed three times through a belt-driven curing system (Model No. P300MT, Fusion) equipped with an H-bulb (Model No. LC-6B). The coatings were UV-cured with an effective irradiance of 1.8 W/cm² (measured with a UVICURE[®] Plus radiometer), and the belt speed was held constant at 8 feet/minute.

RT-Raman Spectroscopy

Real-time (RT) Raman spectroscopy was used to identify reference and reaction peaks for conversion

calculations (Figure 2). Samples of the UV formulations were illuminated at ambient temperature in 1-mm ID quartz capillary tubes using a high-pressure, 100-W mercury vapor short arc lamp with a 250-400 nm wavelength filter (Acticure[®] Ultraviolet/Visible Spot Cure system, EXFO Photonic Solutions Inc.). The effective irradiance was 50 mW/cm² measured with an OmniCure radiometer, Model No. R2000. Raman spectra were gathered using a holographic probehead (Mark II, Kaiser Optical Systems Inc.) with a single-mode excitation fiber delivering ~220 mW of 785-nm near-infrared laser intensity to the sample through a 10x non-contact sampling objective. The probehead was connected to a modular research Raman spectrograph by a 100- μ m collection fiber (HoloLab 5000R, Kaiser Optical Systems Inc.). Spectra were collected continuously over five minutes with a 250-ms exposure time and one accumulation. Conversion α was calculated in real time as the photopolymerization proceeded:

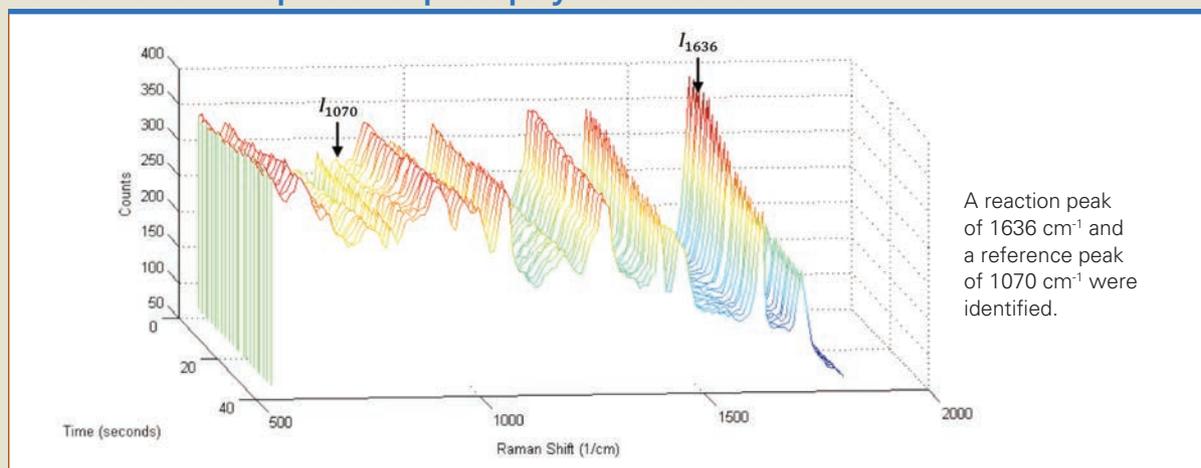
Equation 1

$$\alpha = 1 - \frac{I_{rxn}(t)/I_{ref}(t)}{I_{rxn}(0)/I_{ref}(0)}$$

where $I_{rxn}(t)$ is the peak intensity of the reaction peak at time t and $I_{ref}(t)$ is the peak intensity of the reference peak at time t .¹⁰ This formula is useful

FIGURE 2

Real-time Raman spectra for photopolymerization of TMPTA



for conversion measurements during real-time monitoring of reactions, as well as conversion measurements taken post-cure. The inclusion of a reference peak eliminates instrumental variation that occurs over time and signal-to-noise (S/N) changes that can occur at increasing sample depths during depth profiling.

RT-Raman spectroscopy assists in the selection of peaks used in Equation 1 (see Figure 2)—the reaction peak decreases as the reaction progresses, while the reference peak remains constant. For the TMPTA formulation, the reference peak was chosen at 1070 cm^{-1} (indicative of the -C-C-C-C- bond in the backbone of the molecule), and the reaction peak was chosen at 1636 cm^{-1} (indicative of the -C=C- bond in the acrylate moiety). For the TMPTA/BADGEDA formulation, the reference peak was chosen at 1613 cm^{-1} (indicative of the -C=C- bond in the aromatic rings); however, the reaction peak remained at 1636 cm^{-1} .

Confocal Raman Microscopy

Confocal Raman microscopy was used to determine conversion as a function of depth in 100- μm thick coatings of

the formulations. Raman spectra of the samples were collected using an optical microscope (DMLP, Leica) connected to a modular research Raman spectrograph (HoloLab 5000R, Kaiser Optical Systems Inc.) via a 10- μm confocal collection fiber. The beam from a 785-nm near-infrared laser was directed through a single-mode excitation fiber to the microscope with ~8 mW delivered to the sample through a 100x objective with a numerical aperture of 0.9 and a working distance of 0.27 mm. Monomer spectra were collected with an exposure time of 120 seconds and three accumulations. The peak height of both the reaction and reference peak were averaged over five monomer spectra to provide accurate values for $I_{\text{rxn}}(0)$ and $I_{\text{ref}}(0)$ to use in Equation 1. Spectra for depth-profiling studies were also collected with a 120 seconds exposure time and three accumulations, using a one to three μm step size.

Reference Peak Stability

Multiple Raman spectra were collected for both EB-cured and UV-cured coatings. The Raman microscope detailed previously was used with

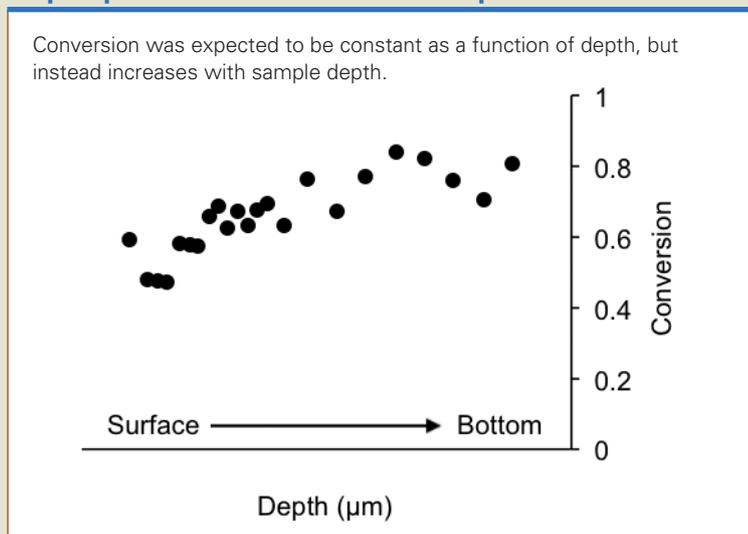
an 100- μm collection fiber and 10x objective (numerical aperture of 0.25 and a working distance of 5.8 mm). Spectra were collected with a 15 seconds exposure time and three accumulations. For each sample, 20 spectra were collected at various points in the sample area (x and y axes) at constant sample depths (z axis). A ratio of $I_{\text{rxn}} : I_{\text{ref}}$ was calculated for each spectrum (HoloReact™ Revision 2.4.4, Kaiser Optical Systems Inc.); and for each data set, the standard deviation of these ratios was computed. The stability of the reference peak in the EB-cured coatings was evaluated by comparing the standard deviations of this ratio for EB-cured coatings to those for UV-cured coatings, for which a stable reference peak was demonstrated through RT-Raman measurements (see Figure 2).

Results and Discussion

Although Raman microscopy has been shown to be useful in determining conversion as a function of depth in UV-cured samples, its efficacy in providing similar information for EB-cured samples must be established.

FIGURE 3

Depth profile of an EB-cured sample of TMPTA



In initial studies, conversion profiles were acquired as a function of depth for EB-cured TMPTA coatings. Based on the consistent energy deposition predicted by Monte Carlo simulations for the selected voltage level, the conversion was expected to be constant through the full depth of the coatings. The coatings were fully nitrogen-inerted to eliminate oxygen inhibition effects and the irradiated coating surfaces were completely tack-free. However, as seen in Figure 3, Raman results indicated the opposite—the conversion increases with increasing depth and the surface conversions are less than 50%. In addition, the standard deviation in the conversion profile is greater than can be attributed to the instrument, which is typically $\pm 3\text{--}4\%$.

Based on these contradictory results, it seemed improbable that the Raman measurements were providing a true picture of coating conversion for these EB-cured samples. Therefore, it was hypothesized that the chemical bond corresponding to the chosen reference peak was not stable during EB irradiation. To test this hypothesis,

the standard deviation of the Raman peak intensity ratios, $I_{1636} : I_{1070}$, was compared for UV-cured and EB-cured TMPTA coatings in which the conversion as a function of depth was expected to be constant (see Figure 4a). If the reference peak, I_{1070} , is stable

under both types of initiating radiation, the standard deviations for the two curing modes should be approximately equal. Instead, the standard deviation for the EB-cured coating is more than three times larger than that for the UV-cured coating.

Since the chemical structure and Raman spectrum of TMPTA (Figures 1(a) and 2, respectively) did not offer any suitable alternatives for a new reference peak, BADGEDA was added to the coating formulation. BADGEDA contains a phenyl ring, which should be stable even under EB irradiation. With this addition to the formulation, the standard deviation of the Raman peak intensity ratios, $I_{1636} : I_{1613}$, was compared for UV-cured and EB-cured coatings in which the conversion as a function of depth was expected to be constant (see Figure 4b). The standard deviation for both curing modes was equal and within the range expected for the instrument.

For final validation of the new reference peak choice, conversion profiles were acquired as a function of

FIGURE 4

A comparison of the standard deviation of the Raman peak intensity ratios

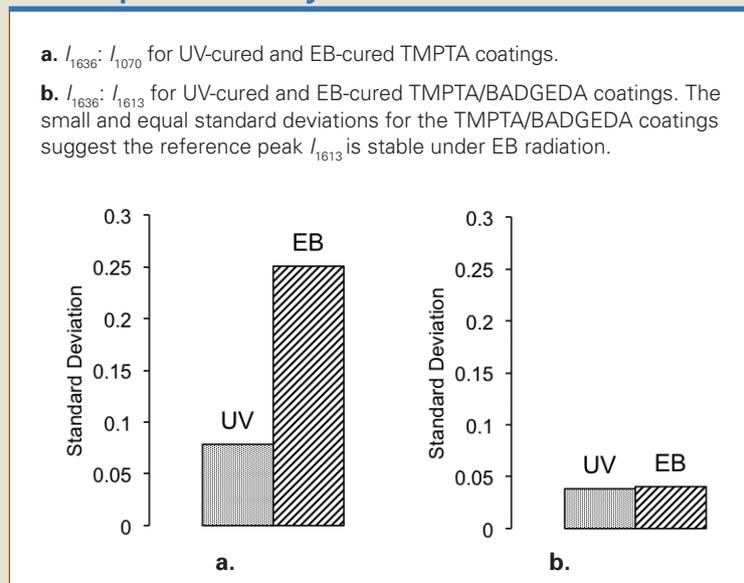
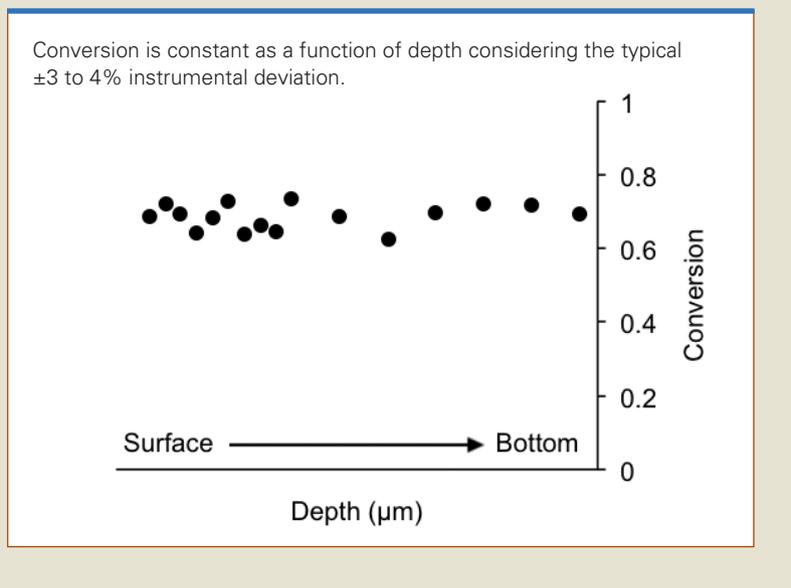


FIGURE 5

Depth profile of an EB-cured sample of TMPTA/BADGEDA



depth for EB-cured TMPTA/BADGEDA coatings. As seen in Figure 5, Raman results confirmed consistent conversion throughout the coating, as predicted by Monte Carlo simulations for the selected voltage level. Thus, the new reference peak, I_{1613} , is stable under EB irradiation and can be used to obtain accurate conversion measurements of EB-cured samples using Raman microscopy.

Conclusions

Characterization of EB polymerization is difficult because real-time monitoring techniques are not well-suited for use in the EB-curing environment. However, kinetic information is needed to develop a fundamental understanding of EB-induced polymerization in order to make future processing and material advancements. We have demonstrated Raman confocal microscopy is a valid, quantitative technique to measure conversion as a function of depth in EB-cured samples, provided the stability of the reference

peak is verified. This preliminary investigation sets the stage for future work using Raman confocal microscopy to determine effects of critical processing factors (such as nitrogen inertion and energy deposition) on conversion of EB-cured monomers and oligomers. In addition, since we can compare the stability of Raman peaks from UV- and EB-cured samples, we will be able to identify which chemical bonds are most susceptible to EB radiation, thereby providing further information about the kinetics during EB irradiation.

Acknowledgements

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