Cure Speed Measurements of UV-LED Curable Optical Fiber Coatings

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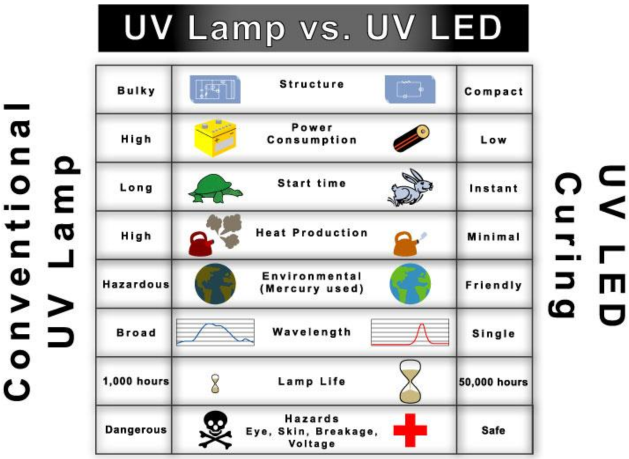
Abstract

Thanks to its tremendous potential of energy savings, UV-LED cure is rapidly gaining popularity in optical fiber manufacturing. In addition, to meet ever growing demands, many manufacturers are making efforts to increase draw speed. Therefore, there is a need to develop cure speed tests in the laboratory, to characterize optical fiber coatings, to ensure they have sufficient cure response to UV-LED light sources. In this paper, preliminary results of such tests are reported.

Keywords: Optical fiber coatings, UV-LED, cure speed, oxygen inhibition, photo-DSC, real-time FTIR, ATR.

1. Introduction

In the past decade, UV-LED cure has begun to revolutionize the radiation cure industry, with many distinct advantages over traditional and established UV arc or microwave curing technologies.



UV Lamp vs. UV LED

Conventional UV Lamp		UV LED Curing
Bulky	Structure	Compact
High	Power Consumption	Low
Long	Start time	Instant
High	Heat Production	Minimal
Hazardous	Environmental (Mercury used)	Friendly
Broad	Wavelength	Single
1,000 hours	Lamp Life	50,000 hours
Dangerous	Hazards Eye, Skin, Breakage, Voltage	Safe

Figure 1. Comparison – Conventional UV vs UV-LED [1]

In recent years, industry wide conversion to UV-LED is gaining momentum, primarily due to its tremendous energy savings over traditional broadband UV technologies, as well as its environmental-friendly nature.

Many governments are joining forces to promote energy efficiency for environmental protection purposes. One example is the recently announced "Green Manufacturing" initiative by China in its 13th 5-year plan for economic and social development [2], outlining ambitious goals toward environmental protection by manufacturing practices that are more energy efficient, with less hazardous emissions and/or reduced waste to the environment.

Figure 2. Green Manufacturing initiative [3]

While many radiation cure applications are in the process of converting to UV-LED technology, the optical fiber manufacturing industry has been catching up in recent years.

Table 1. UV-LED Conversion Status

Application	UV-LED Conversion Status
Digital Inkjet	Majority Completed
Spot Curing	Majority Completed
Industrial Printing (Offset, Flexo, Screen)	In Progress
Optical Fiber Manufacturing	In Progress
3D Printing	Exploring

Due to the combination of relatively lower intensity and longer wavelength (Figure 3), UV-LED cure is more susceptible to oxygen inhibition than conventional UV lamps, Figure 3. There have been numerous publications [4][5][6][7] to address such challenges in recent years. With the technical know-how, including mitigating oxygen inhibition, UV-LED curable coatings have been formulated to support the industry-wide adoption that is currently taking place.

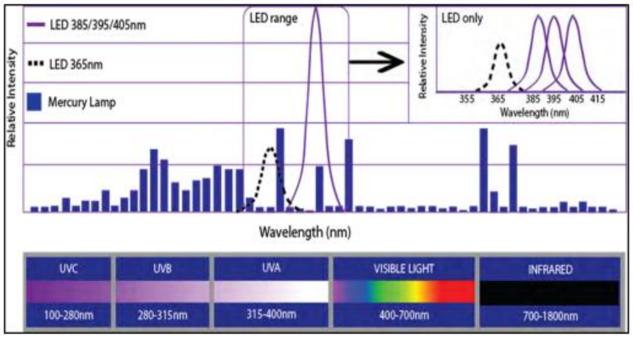


Figure 3. Emission Spectra, Mercury Lamp vs LED lamp [8]

It's been reported [9], that, more than 80 % energy savings, have been realized in actual fiber manufacturing, with good fiber properties.

Another study [10] revealed various cure efficiencies with several UV-LED lamps from industry-leading suppliers.

Another prevailing trend in optical fiber manufacturing is the pursuit of high draw speeds to meet the continuously growing global demand. With draw speeds of only 25 m/min [11] in the beginning of the industry in early 1970s, to the current reported processing speeds of up to 2500 m/min and structure speeds of 3000 m/min [12], the increase of draw speed has been phenomenal and will continue.

2. Experiments

2.1 Coating samples

Table 2 listed the three secondary coating samples that are evaluated in this paper.

Table 2. Coating Samples

Designation	Description
Coating A	Commercial coating for conventional UV cure
Coating B	Formulated for UV-LED cure, approach #1
Coating C	Formulated for UV-LED cure, approach #2

2.2 Photo – Differential Scanning Calorimeter (DSC)

DSC, differential scanning calorimeter, is a well-known laboratory technique to measure the heat generated in a reaction (in this case photopolymerization) and give us information such as percent conversion as well as polymerization rate.

Photo-DSC is a traditional DSC equipped with a UV light source to induce photopolymerization. To augment a conventional UV light source that has been in place for many years, a UV-LED light source was recently brought in-house.

2.2.1 Equipment

At the heart of photo-DSC is a TA Instrument Q2000 DSC unit. Providing the UV-LED light source is a ULM-2-395 LED head and SA7050 AccuCure Intelligent Controller from Digital Light Lab. The data were analyzed by Universal Analysis 2000 software, Version 4.5A.

Figure 4. Photo-DSC set-up

2.2.2 Experiment Description

A 1.5 mg sample was added to a Tzero pan using a capillary tube and the pan was put in the DSC unit. The sample was cured and monitored under the conditions listed in Table 2.

Table 3. Photo-DSC test conditions

UV wavelength	395 nm
Temperature	55 °C
Intensity	50 mW/cm^2
Nitrogen Flow	50 mL/min
Irradiation Time	9 s

2.3 Real-time Fourier Transfer Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR)

Fourier Transfer Infrared Spectroscopy (FTIR) is the most common laboratory test to measure degree of cure, the percentage of carbon-carbon double bond that have polymerized. Therefore, the degree of cure (DOC) is also referred to as reacted acrylate unsaturation (RAU).

Real-time IR is more advanced. It is used to collect RAU data points in a continuous fashion, while the radiation is ongoing, to allow following cure for the whole process (vs traditional IR when RAU is taken after conversion has reached a plateau).

In this paper, coatings were analyzed by the ATR sampling technique, attenuated total reflectance. As illustrated in Figure 5, the ATR technique allows for evaluating RAU in 0.5 to 2 micrometer thickness of sample, making it a powerful tool to measure surface RAU (vs. conventional transmittance IR for the whole thickness of the sample where IR beam goes through).

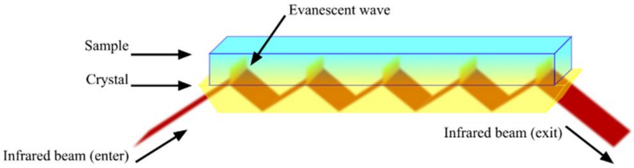


Figure 5. ATR illustration [13]

2.3.1 Equipment

Nicolet 8700 FTIR of Thermo Scientific is the spectrometer, ATR is from ASI Applied Systems, and UV-LED light source were from ULM-2-395 LED head, supplied by Digital Light Lab.

Figure 6. Real-time FTIR-ATR set-up

2.3.2 *Experimental Description*

A drop of coating was placed on top of a diamond ATR crystal, followed by a draw down with a 3 mil draw down bar across the diamond to create a 75 micrometer thick coating film. Then the adapter and UV-LED lamp were set-up above the coating layer. Dry air purge was conducted, and maintained throughout the test. Finally, a spectra collection was started before turning on the UV-LED lamp at 2 seconds. 45 data points were taken in 30 s.

Data were analyzed by OMNIC 8.3 software, of Thermo Scientific, as well.

3. Results and Discussion

3.1 Photo-DSC

3.1.1 *Peak Heat Flow*

Peak heat flow in Photo-DSC is a measurement of maximum reaction (photopolymerization) rate. As shown in Figure 7, in terms of reaction rate, coating C > coating B > coating A.

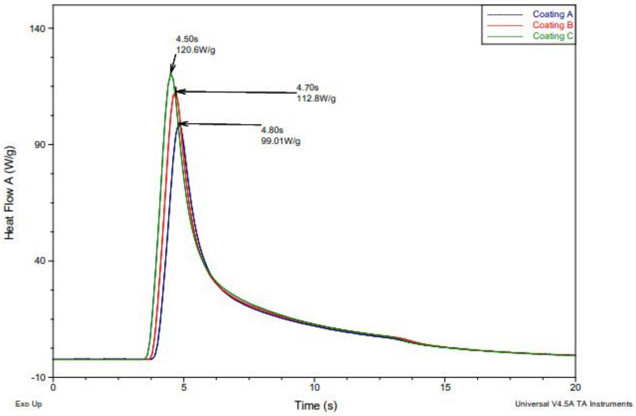


Figure 7. Photo-DSC Peak Heat Flow

3.1.2 *Total Heat Generated*

Total heat generated in Photo DSC is a good measurement of how much double bond of an acrylate group has reacted, which was obtained by integrating the area underneath the DSC curve for each coating sample. Results are summarized in Table 4.

Table 4. Heat Generation in Photopolymerization

	Heat Generation (J/g)
Coating A	257
Coating B	283
Coating C	303

It's interesting to note that the total heat generated follows the same relative reactivity as Peak Heat Flow, demonstrating excellent correlation and consistency between the two measurements.

3.2 Real time FTIR – ATR

Due to the dry air purge in the current experiment set-up, oxygen inhibition is too great for the surface cure. What is measured, instead, is thin film bottom % RAU, an estimation of the through cure. We are planning to implement dry nitrogen purge, in the future, to be able to measure surface cure as well.

3.2.1 *Maximum Slope of %RAU Curve*

Unlike the need for conversion in Photo DSC, % RAU in FTIR is a direct measurement of double bond conversion. Thus, maximum slope of RAU curve in real-time FTIR-ATR is also a direct measurement of peak polymerization rate.

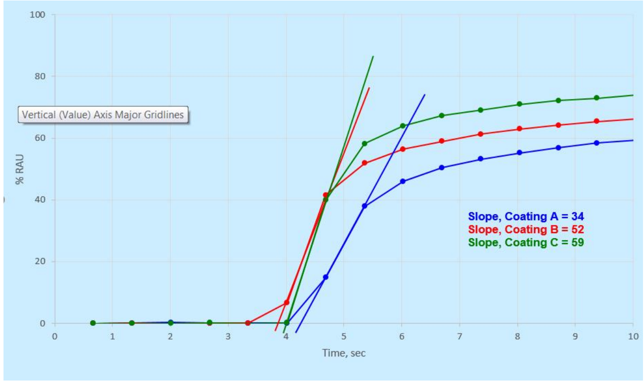


Figure 8. Maximum slope of % RAU Curve

Just as expected, the maximum photopolymerization rate, as measured as maximum slope of RAU curve, indicated the same relative cure speed among the three coatings, C>B>A (Figure 8).

3.2.2 *Plateau % RAU*

As seen in Figure 9, % RAU reached plateau after 20 seconds, demonstrating that the reaction has taken place within 18 seconds of the UV-LED irradiation (Note that the lamp did not turn on until after 2 seconds).

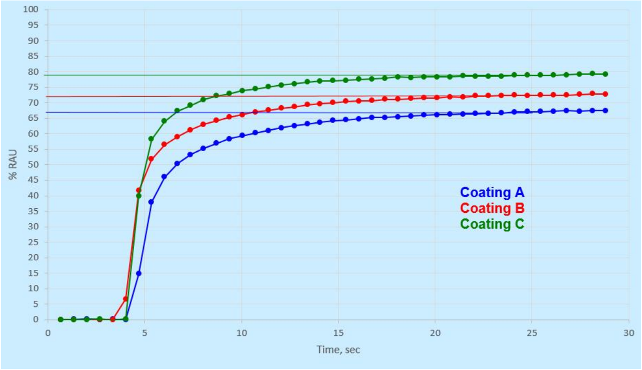


Figure 9. Plateau % RAU

And, once again, coating C reached highest % RAU, followed by coating B, and coating A.

3.2.3 Induction Time

Induction time is an additional piece of information from real-time FTIR that is not available in Photo-DSC.

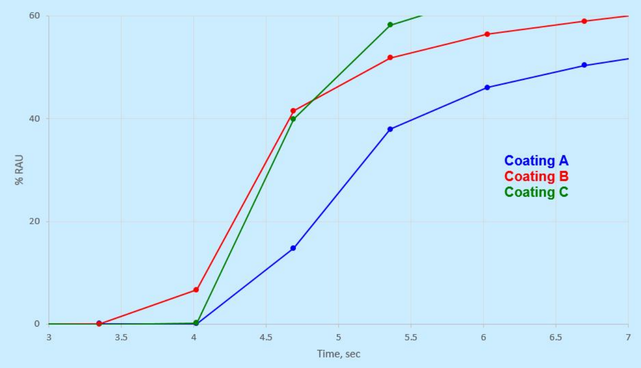


Figure 10. Induction Time

Induction time is the time in the beginning of (photo)polymerization when initiating radicals were consumed by radical scavengers, such as inhibitors and oxygen.

Since coatings A, B and C have similar level of inhibitors, the induction time is an excellent indicator of oxygen inhibition effect on the through cure (as what measured is the bottom % RAU).

As expected, coating A, the conventional secondary coating, is more susceptible to oxygen inhibition, resulting in longer induction time.

Between Coating B and Coating C, Coating B has quite shorter induction time (by about 0.7 second), suggesting that the formulation approach in Coating B is more effective in reducing inhibition time. Despite of longer induction time, Coating C reacts faster and eventually reaches higher conversion (Plateau % RAU).

Such insight into induction time, reaction rate, and double bond conversion is crucial in understanding structure-property relationship in coating development, to meet stringent requirements in high speed draw of optical fiber manufacturing.

4. Work in Progress

A complementing approach to characterizing the cure speed is to measure mechanical property buildup over time, for example, UV Rheology [14].

To respond to the much lower modulus of modern primary coatings, and the need for a more precise and reliable tensile mechanical property test method, RTDMA was developed at DSM Functional Materials [15], and has been implemented as QC test method. Both plateau modulus and gel time are reported (Figure 11) in such test.

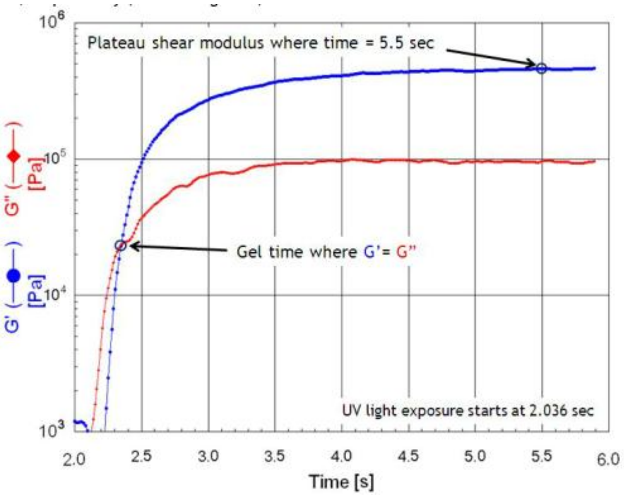


Figure 11. RTDMA test result illustration

Work is underway to develop a similar method to characterize secondary coatings, whose modulus is typically 1000 times as much as primary coatings. A state-of-the-art ARES-G2 rheometer (Figure 12) from TA Instrument has been acquired in house, coupled with UVLED light source, to accomplish the task.

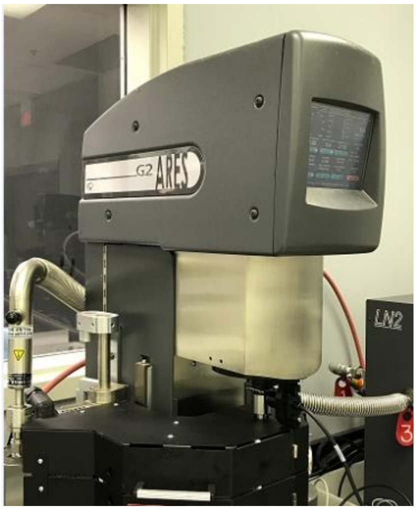


Figure 12. ARES-G2 Rheometer

5. Conclusions

Due to its unique monochromatic emission, UV-LED cure is different than conventional broadband UV. Therefore, there is a need to retrofit laboratory analytical equipment with UV-LED light source, to conduct cure speed measurement.

Recently, both Photo-DSC and Real-time FTIR-ATR have been equipped with UV-LED light source, in DSM Functional Materials R&D Lab.

When measuring the cure speed of three secondary coatings with both techniques, the same cure speed ratings were obtained, demonstrating excellent correlation and consistency between the two tests.

Inhibition time in Real-time FTIR-ATR is a good indicator of the severity of a given coating's susceptibility toward oxygen inhibition.

Positive results obtained in this study suggest that formulation approaches in Coating B and C are effective in enhancing cure responses to UV-LED.

Development of RTDMA test method is underway to characterize secondary coatings of much higher modulus, to have a full understanding of cure behavior of the material.

6. Acknowledgement

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