Multicure Techniques for Reducing Thermal Deformation, Surface Overexposure, and Charring in Very High Intensity UV Curing

By Dennis DeCoster

One of the primary drivers for transitioning from conventional thermal cure or two-part cure processes to photoinitiated or light curing is process speed. It is not unusual to experience an improvement from minutes or hours for full cure of adhesives, coatings or potting materials, to mere seconds. As dramatic as this may be, it is still not optimal for many high-speed process lines. To make the change from seconds to sub seconds, it is often necessary to use extreme intensity (effective irradiance) UV curing. However, conventional very high irradiance light curing routinely brings unwanted heat that can deform substrates, char surfaces, prevent through-cure, or cause other detrimental process issues which might preclude its use. This paper describes proven techniques for applying extreme photocuring irradiance, while still maintaining favorable heat control. Resultant cures are typically at least as strong as those achieved through constant wattage exposure, and for some applications substantially stronger. Supporting empirical data is presented.

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Introduction

Process speed is clearly becoming increasingly critical in a variety of industrial and commercial processes in an owner's quest for higher throughputs and lower overall costs. Printed circuit board manufacturing, ink jet cartridge manufacturing, disk drive manufacturing, credit card or lens coating, and many fiber optic device or medical device manufacturing lines are examples of process areas that become far more profitable with speed improvement. In the ink jet printer market, it is well established that printers can quite literally be given away for free (and many times are with rebates) to secure the much more profitable and recurring replacement cartridge business. Many ink jet cartridges are so popular that the manufacturer can sell as many as they can produce. Adhesive or potting cure time often becomes the gating factor in these manufacturing operations and split second cures are mandated. It goes without saying that these cures be completely polymerized and any potential thermal deformation be controlled.

With extreme intensity UV-spot curing, sufficient power can be brought to bear to allow special multi-furcated fiber light delivery of UV light to multiple, discrete cure sites on a high-speed line. The result is sub-second cures, benefiting from dark-cure strength improvement and polymerization continuation. Since much of the effective irradiance initially generated at the source is lost to light-guide delivery losses and furcation splits, it is key that the spot cure unit itself is of an extreme intensity to begin with. In fact, for certain process cures, particularly those involving metallic substrate bonds, adequate bond strength from UV cure is simply not possible without extreme intensity and the dark cure that follows.

High Intensity Issues

Today, extreme irradiance UV-curing systems of 20W/cm^2 or even 30W/cm^2 (in the standard UVA range—320 to 390 nm) are available in mercury spectra spot cure equipment types. Since extreme irradiance can be precisely delivered to multiple discrete cure locations, spot cures and precision, fiber optic light-guide delivery systems are the equipment of choice for the vast majority of high-speed automated and semi-automated processes. Conveyorized, rotary, flood and waveguide curing systems are also now available in very high intensities from some vendors for the remaining larger cure area applications. Through a combination of bulb dopant and filter choices, high-irradiance wavelength profiles can be set to match any photoinitiated chemistry.

High-curing irradiance levels have sometimes been avoided for a variety of concerns, some valid, some not. In some cases, perceived equipment cost is the issue. High-intensity equipment naturally carries a higher initial price tag than low-intensity counterparts do. However, properly implemented, high-intensity gear can often demonstrate a significantly lower life cycle cost (LCC) than low-intensity light sources. This overall cost differential varies, but is primarily due to process speed improvements once thermal issues have been resolved. For example, if an automated line replaces a 2-or 4-second gating curing stage with one or two 0.2 second extreme intensity cure operations, cumulative energy density may remain the same, but overall line speed improvement may result in doubling or tripling final line output.

The most pervasive and potentially valid concern in extreme irradiance curing is thermal rise and the resultant array of problems associated with it. The first step in heat control is optimal infrared (IR) filtering, usually accomplished at the UV-cure lamp. Dichroic filters, reflectors and good lamp design go a long way here. Even with the best IR filtration, substantial heat will always accompany extreme UV intensity due to the sheer energy involved and pass through IR components. Training 25W/cm^2 of extreme UV intensity on a subject cure area will certainly cause surface overcure, substrate deformation, charring, and even fire, if exposure times are prolonged. Surface overcure and charring in the extreme will prevent through-cure to the substrate in thick film potting, coating and adhesive applications and even present problems in some thin film applications. In particular, photocationic polymerization is easily inhibited by thermal degradation of the surface area from excess heat generated by the cure reaction exotherm from conventional curing.

A landmark study, by Dr. S. Jonsson et al., several years back dramatically underscored the fact that very high-intensity (but short exposure time) cures were most often far stronger and more completely polymerized than longer, low-intensity cures of the same dosage. In a model evaluation system,[1] he confirmed that increasing intensity 10 to 20 times increased the polymerization rate by almost 50%. The results of his testing implied that "by using high-intensity irradiators one can increase the production speed by a factor of 20 and still be able to obtain 25% higher degree of conversion."

Dr. Jonsson attributed the majority of demonstrated cure improvement to a phenomenon we now call dark cure, which is the exothermic cure mechanism that continues after the UV light is extinguished. To quote, "Especially for the shorter exposure times at higher intensities, it is now obvious that the dark portion of the polymerization is responsible for more than 90% of the total conversion..." An analogy often used is that of a straw piercing a potato. If you apply mild pressure (or thrust speed) on a straw, you may not be able to pierce more than a few millimeters, even if the pressure is sustained for quite a while. Nevertheless, if you apply extreme pressure (or thrust speed) for just an instant, you might find that the straw has pierced the entire mass of the potato. Obviously, this does not apply for all chemistries, wavelengths or surface effects, but generally speaking, extreme intensity penetrates deeply during initial exposure(s).

Surface Tack and Oxygen Inhibition

Another major benefit of extreme intensity UV application for free radical initiator chemistries lies in mitigating surface cure problems due to oxygen inhibition. In short, in addition to "punch through" deep-cure mechanisms, extreme intensity effectively seals the surface instantly, preventing unwanted oxygen diffusion into the film afterwards. The effects of this high-intensity mitigation were shown dramatically and documented by Jonsson. When very high intensities were used in a comparative study, initial rates of polymerization in air were the virtual equal of those cured in a Nitrogen purged environment.[2] This was not the case with low-intensity irradiance.

The Multicure Technique

Techniques have now been perfected to deploy extreme irradiance cure levels and take advantage of its myriad benefits, yet eliminate the great majority of downside issues. Simply put, "multicuring" involves exposing chemistries to very high intensities for controlled multiple short-duration cure cycles, typically yielding equivalent dosage (or energy density) to low-intensity, long-exposure curing. For instance, rather than applying a 10-joule dosage with a 10-second single exposure at 1 W/cm^2 intensity; perhaps four 250-millisecond duration at 10 W/cm^2 exposures would be applied with perhaps 1-second cool-down periods between. Joule count would remain the same. Muticuring is now practical with various vendor spot curing, conveyor curing, and waveguide curing equipment lines. In the following experimental discussions, two effective multicure case studies are examined. In these particular cases, process speed and/or thermal rise were improved using a multicure technique.

Conveyor-Based Multicuring for Reduction in Thermal Rise

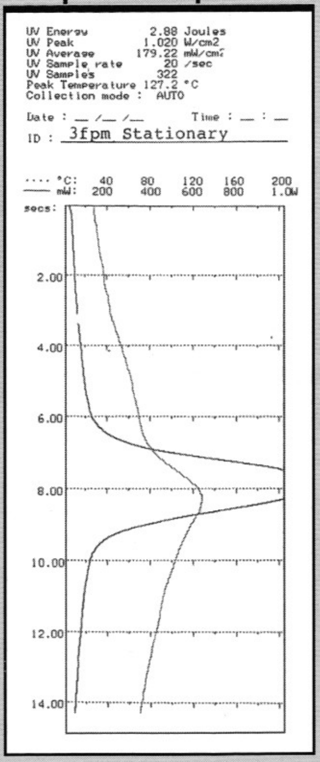
In this example, a conventional conveyor-based UV-single cure operation was compared with a multicure conveyor operation at similar cumulative dosage levels. A UV conveyor capable of both single cure and multicure operation was used. This device employs a precision reciprocating lamp assembly allowing usage of either microwave or arc lamp UV sources. For this experiment, Fusion lamps with type "D" bulbs were chosen due to their wide application. The system was arbitrarily set at 3-feet-per-minute belt speed for both tests. A radiometer was used to take both irradiance and temperature measurements at the intended cure site. In the first run, approximately 3-joules of UVA radiant flux density was applied in a conventional single exposure taking about four seconds at 1.0 W/cm^2 effective peak irradiance. In the second test, identical belt speeds focal distances and effective irradiance levels were used, but the 3-joule dosage was applied using the multicure technique. Here, eight cure cycles were applied in four pairs spaced approximately two seconds apart. As demonstrated in Figure 1A and 1B, thermal rise was reduced from 127.2°C to 56.8°C with essentially the same energy density (dosage) and process time. The test was repeated multiple times with essentially identical results.

Spot Cure Multicuring for Elimination of Surface Charring/Overcure

In this example, a major disk drive builder required extreme intensity spot curing for shadow cure and dark cure advantage in head slider bonding. High instantaneous heat for dark cure exotherm was very desirable, but surface charring prevented complete through-cure. A study was conducted using droplets of the client's proprietary cationic photoinitiated adhesive to determine if multicuring would solve

FIGURE 1A

EIT UVI MAP™
UV intensity &
temperature profile



```
UV Energy           2.88 Joules
UV Peak            1.020 W/cm2
UV Average        179.22 mW/cm2
UV Sample rate        20 /sec
UV Samples           322
Peak Temperature 127.2 °C
Collection mode :   AUTO

Date : __ /__ /__        Time : __ : __
ID : 3fpm Stationary
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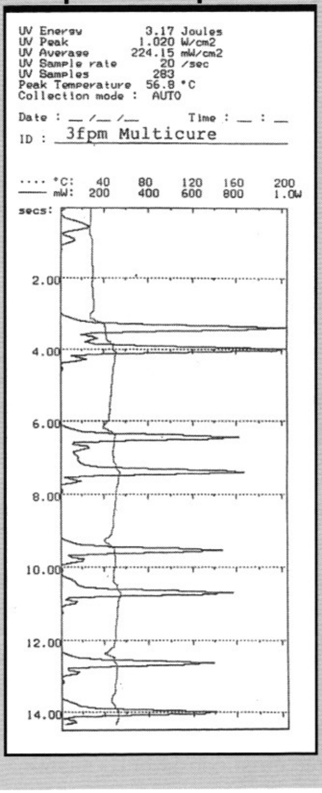
FIGURE 1B

EIT UVI MAP™
UV intensity &
temperature profile

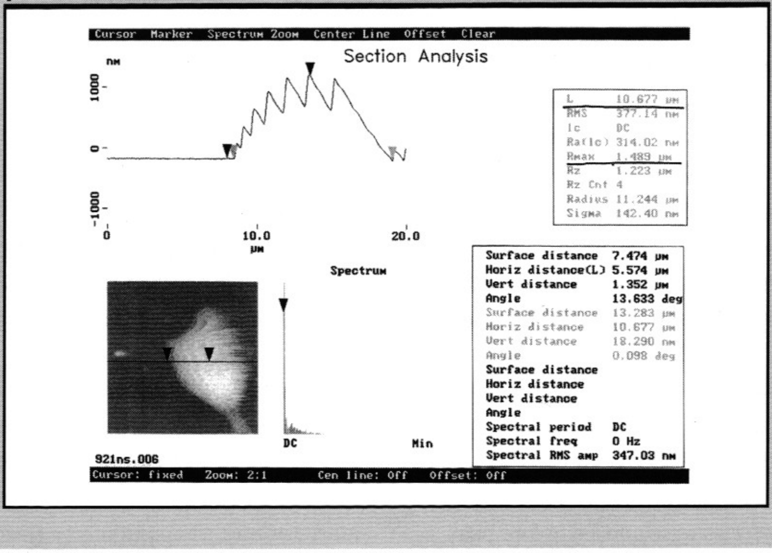


```
UV Energy           3.17 Joules
UV Peak            1.020 W/cm2
UV Average        224.15 mW/cm2
UV Sample rate        20 /sec
UV Samples           283
Peak Temperature  56.8 °C
Collection mode :   AUTO

Date : __ /__ /__        Time : __ : __
ID : 3fpm Multicure
```

FIGURE 2

Maximum surface deformation from droplet edge to point of maximum film thickness



```
L          10.677 µm
RMS        377.14 nm
Ic         DC
Ra(Ic)     314.02 nm
Rmax       1.489 µm
Rz         1.223 µm
Rz Cnt     4
Radius     11.244 µm
Sigma      142.40 nm

Surface distance     7.474 µm
Horiz distance(L)    5.574 µm
Vert distance        1.352 µm
Angle                13.633 deg
Surface distance     13.283 µm
Horiz distance       10.677 µm
Vert distance        18.290 nm
Angle                0.098 deg
Surface distance
Horiz distance
Vert distance
Angle
Spectral period      DC
Spectral freq        0 Hz
Spectral RMS amp     347.03 nm

921ns.006
Cursor: fixed   Zoom: 2:1      Cen line: Off   Offset: Off
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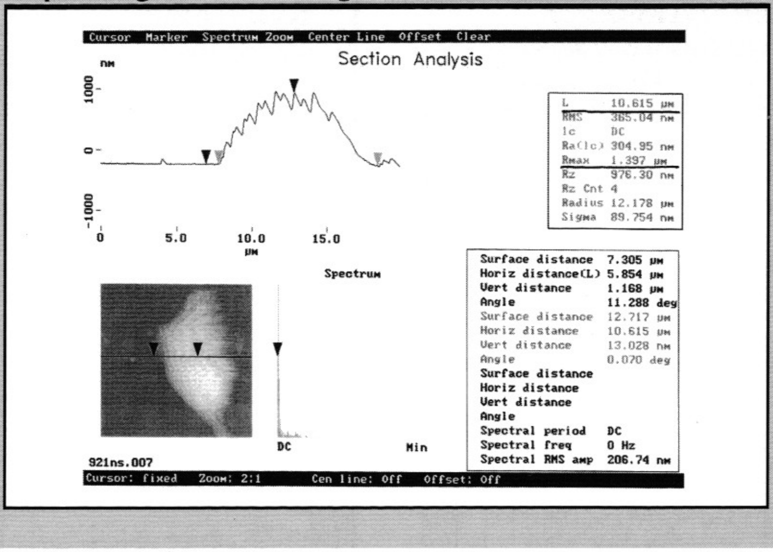
FIGURE 3

Improving center through-cure



```
L          10.615 µm
RMS        365.04 nm
Ic         DC
Ra(Ic)     304.95 nm
Rmax       1.397 µm
Rz         976.30 nm
Rz Cnt     4
Radius     12.178 µm
Sigma      89.754 nm

Surface distance     7.305 µm
Horiz distance(L)    5.854 µm
Vert distance        1.168 µm
Angle                11.288 deg
Surface distance     12.717 µm
Horiz distance       10.615 µm
Vert distance        13.028 nm
Angle                0.070 deg
Surface distance
Horiz distance
Vert distance
Angle
Spectral period      DC
Spectral freq        0 Hz
Spectral RMS amp     206.74 nm

921ns.007
Cursor: fixed   Zoom: 2:1      Cen line: Off   Offset: Off
```

the surface overcure issue. A spot cure unit was used in conjunction with a light delivery system. Effective UVA irradiance was measured at 13 W/cm^2 at the cure site using a barrel radiometer. Due to losses in the delivery system, UVA generated in the light source must consistently sustain 20 W/cm^2 irradiance levels. An atomic force microscope (AFM) was used to produce and precisely map small surface features on the test droplets. Droplets were syringe deposited on glass cover slips using a 3-mil thick stainless steel mask with 20-mil holes drilled. All test droplets were examined by stereomicroscope prior to cure to ensure absence of air bubbles or contaminants. A LESCO MAX spot cure was set to deliver a series of 0.1-second exposures at constant extreme intensity with 0.4 seconds dwell time between exposures. After each sample was irradiated, it was stage on the AFM then the probe lowered to the surface of the droplet until an RMS voltage reading of zero was achieved. The probe was then lowered 6-microns into the surface of the droplet and translated 100-microns horizontally. This produced a straight track in the surface of the adhesive film. The track was then imaged by the AFM in tapping mode, and track dimensions and surface morphology were determined.

The AFM scans show improving through-cure with higher multicured radiant flux density levels without surface charring or detrimental surface overcure. In Figure 2, an unexposed sample demonstrating maximum surface deformation from droplet edge to point of maximum film thickness (center) can be seen. In Figures 3 and 4, an improving center through-cure and complete edge cure can be seen. In Figure 5, one can see virtually zero center deformation indicating complete through-cure.

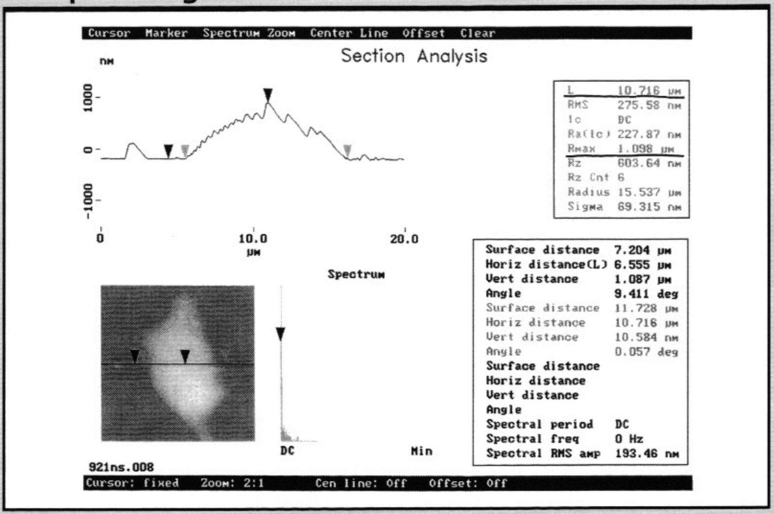
Conclusions

In the examples provided, cured film properties of multicured formulations were comparable to those of films cured in a single exposure of the same total UV dose. However, the multicured films could be applied to thermally sensitive substrates and cured without damage to the substrates, while those cured in a single dose could not. In addition, when comparing multicured films to those cured in a single dose, a reduction in total cure dose required in many cases was observed.

Very high-intensity UV curing is clearly headed for mainstream in a great variety of applications as more and

FIGURE 4

Complete edge cure



```
L              10.716 µm
RMS            275.58 nm
Ic             DC
Ra(Ic)         227.87 nm
Rmax           1.098 µm
Rz             603.64 nm
Rz Cnt         6
Radius         15.537 µm
Sigma          69.315 nm

Surface distance    7.204 µm
Horiz distance(L)   6.555 µm
Vert distance       1.087 µm
Angle               9.411 deg
Surface distance    11.728 µm
Horiz distance      10.716 µm
Vert distance       10.584 nm
Angle               0.057 deg
Surface distance
Horiz distance
Vert distance
Angle
Spectral period     DC
Spectral freq       0 Hz
Spectral RMS amp    193.46 nm

921ns.008
Cursor: fixed   Zoom: 2:1        Cen line: Off   Offset: Off
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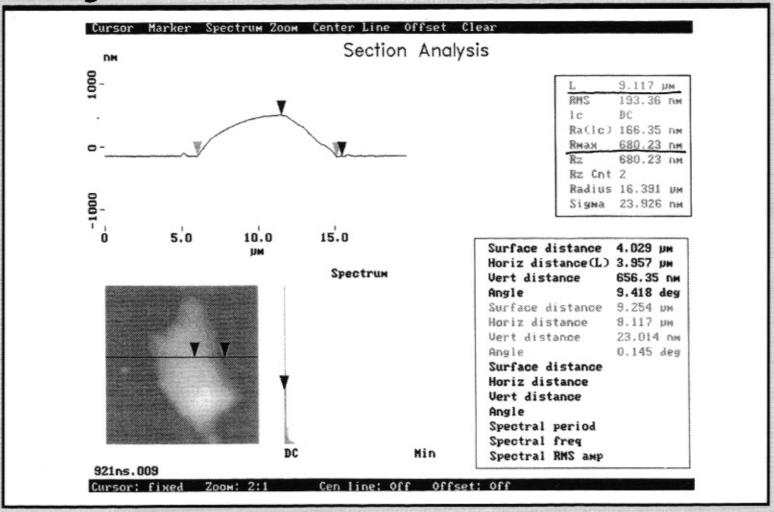
FIGURE 5

Zero center deformation indicating complete through-cure



```
L              9.117 µm
RMS            193.36 nm
Ic             DC
Ra(Ic)         166.35 nm
Rmax           680.23 nm
Rz             680.23 nm
Rz Cnt         2
Radius         16.391 µm
Sigma          23.926 nm

Surface distance    4.029 µm
Horiz distance(L)   3.957 µm
Vert distance       656.35 nm
Angle               9.418 deg
Surface distance    9.254 µm
Horiz distance      9.117 µm
Vert distance       23.014 nm
Angle               0.145 deg
Surface distance
Horiz distance
Vert distance
Angle
Spectral period
Spectral freq
Spectral RMS amp

921ns.009
Cursor: fixed   Zoom: 2:1        Cen line: Off   Offset: Off
```

more users become familiar with its benefits as compared to low-intensity techniques. Unwanted thermal rise, substrate deformation, surface charring, and incomplete through-cure issues attendant to constant exposure curing can be solved using multicure techniques. Exponential improvements in process speed performance can be demonstrated. Highly beneficial shadow and dark-cure mechanisms can be employed to allow more complete photoinitiated curing of non-transparent or metallic substrates than possible with constant exposure curing. Very high-intensity UV lamp systems and multicure capable systems will initially cost more; however, complete payback within the first year or two of operation from process speed improvements are not unusual. ◗

Acknowledgments

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References

1. HDDA monomer with 1% Irgacure 651 photoinitiator.
2. Secrets of the Dark, Dr. S. Jonsson et al.

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