Understanding Energy Density Response Effects
on UV Cure Applications Through Modeling

**By David Eaton,
Glen Thommes and
Jeff Thommes**

Radiation-sensitive systems can be defined as a subset of the broad class of "Energy Density Response Systems" where response can be measured in many ways. The response of interest from application developers and manufacturers is typically associated with physical property change or simply obtaining a result from a formulation and exposure system "that works." Obtaining a desired

This paper will discuss concepts of energy density response and then describe how these concepts can be practically applied to real systems through the use of modeling in conjunction with lab experimentation.

response varies with the interaction specifics of delivered energy density (D, typically expressed in mJ/cm^2), the formulation used and the production details for application curing. For formulator and manufacturer alike, defining and testing the variables associated with these interactions can be an overwhelming endeavor that limits complete practical analysis and understanding even with use of Design of Experiments (DOE). This paper will discuss concepts of energy density response and then describe how these concepts can be practically applied to real systems through the use of modeling in conjunction with lab experimentation.

In radiation-sensitive systems, generally categorized as "radcure systems," changes in response can be measured in relationship to delivered energy density, where energy density is the time integral of irradiance (I, typically expressed in mW/cm^2). For a system delivering constant irradiance (static exposure) for a period of time $d\mathbf{t}$: Energy density = $\mathbf{D} = \mathbf{I}*d\mathbf{t}$

The speed of the system would then be defined as the minimum required irradiance and time (energy density) to achieve a desired response or satisfactory rating for the critical property(s) of the intended application. Sometimes these properties are related to and measured as:

- Surface tack.
- Surface hardness.
- Cure to the base (Is adhesion to the substrate adequate? Is it over cured as shown by brittle failure at the interface?)
- Resistance to rubbing with wipes saturated with methyl ethyl ketone (MEK) or acetone.
- Brittleness as measured by bending around varying diameter mandrels and noting the diameter at which fracture occurs.
- Film modulus, elongation to break, degree of elastic recovery.

FIGURE 1

Characteristic curve

Typical Characteristic Curve (H&D Plot)

$\gamma = \Delta R / \Delta Log(D)$
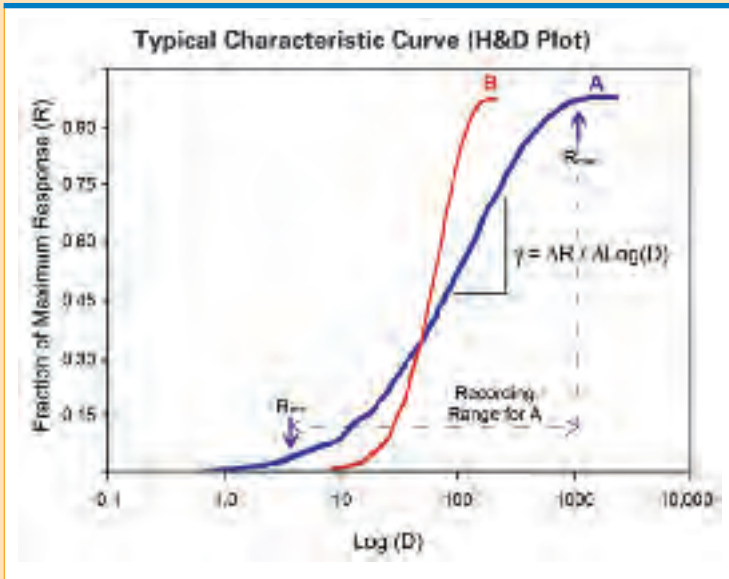
Further, one must recognize that static exposure systems (application and lamp are stationary), which are primarily the province of imaging systems, often require the ability to clearly resolve fine detail. This is generally not significant in dynamic exposures, such as protective coatings used for flooring or overcoats on printed material. Thus, in imaging, overexposure (energy density beyond that required to give the sought after response) can be fatal. Even though protective coatings can be quite tolerant of overexposure, they may be totally intolerant of under exposure, particularly when it is delivered at ineffective irradiance levels. So, what are the factors of significance in understanding the interaction specifics of delivered energy density, the formulation and the production details for an application? Some say formulation, peak irradiance or energy density is most important, but no one element tells the whole story.

Understanding and Defining System Response

The normal way of presenting the energy/response data is in the form of a plot of the measured response versus the log of the incident radiation-exposure energy. This curve is referred to as the characteristic curve and has the general shape shown in Figure 1. With regard to this curve, it is helpful to define a few terms associated with it that will be useful in understanding its application. These terms include:

R = The measured response at any given exposure.

R_{max} = The maximum response that the system can detect.

R_{min} = The minimum response that the system can detect.

D = The incident energy density exposing the system.

$\Delta Log(D)$ = Recording range. The log of the expo sure range over which information can be recorded and response can be discerned. It runs from the minimum detectable response to the point of maximum detectable response.

γ = Contrast. The slope of the response Log (D) curve at any point. Usually expressed as an average that covers the nominally

FIGURE 2

System response as a function of irradiance used in exposure
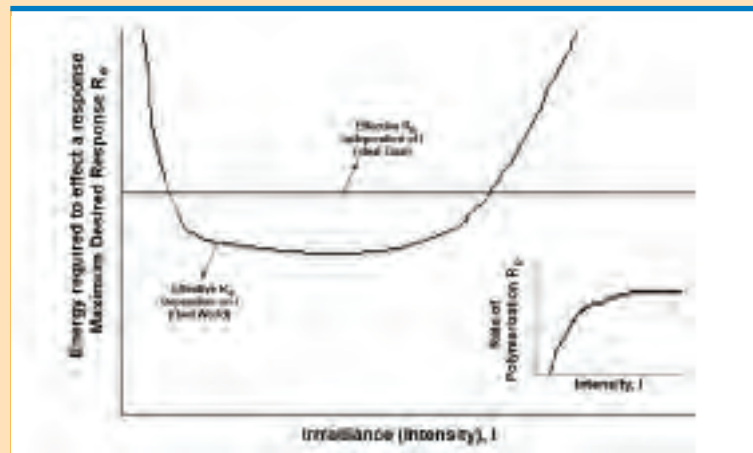
linear portion of the curve.
When the plot is response
versus exposure rather than
log of exposure, the slope of
the curve at 20% fraction
reacted ($R/R_m = 0.2$) is
converted to moles per
liter-second and is reported
as $R_{p\,max.}$

Figure 1 demonstrates two energy
density-response curves for the *same*
formulation and exposure system,
viewed for *two* different responses.
Curve A (in blue) has a minimum
detectable response at lower energy
than curve B (in red). That is, for the
two responses, A is more sensitive than
is B. Also, curve B is steeper than
curve A (higher γ or higher contrast).
Both maximize at $R_{max} = 1$ (relative
response). The two different responses
could be physical properties manifested
by the system in response to radiant
energy—for example, adhesion of the
cured film to the substrate (Curve B) and
tensile strength of the cured film (A).

Both of the physical properties
represented by the two curves in
Figure 1 derive from the overall
conversion of the system as a function
of input energy. However, most
responsive systems do not "read out"
in conversion units (exceptions are
those that directly follow properties
associated with molecular conversion,
such as real-time infrared methods,
like RT FTIR). "Read Out" is typically
in units associated with physical
properties such as optical density,
solubility or hardness.

In practical system response, there is
a minimum and a maximum detectable
response in which continued energy
density change above or below these
limits is essentially indiscernible. As an
example, where optical density is the
response measured, 0.01 is a reasonable
estimate of the minimum detectable
response and 3.0 approximates the
maximum beyond which the unaided

FIGURE 3

Dynamic exposure irradiance profile
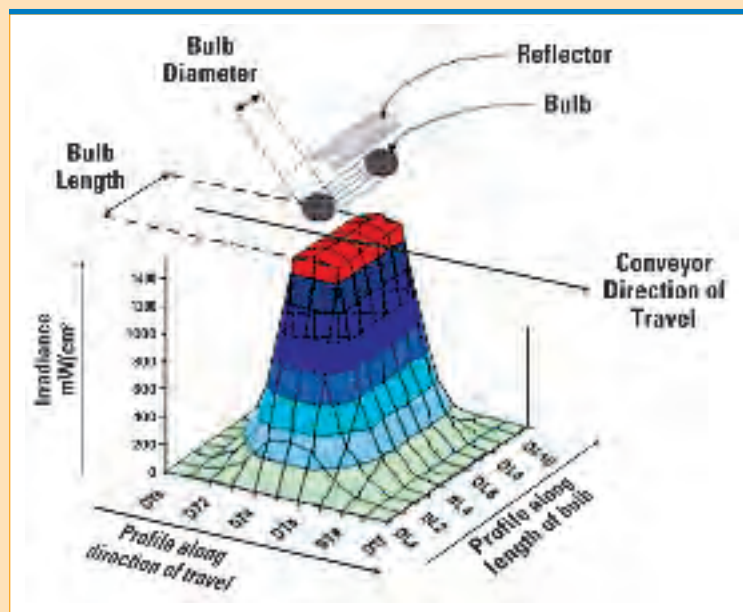
human eye does not easily discern
response change with exposure.
Accepting these circumstances, the
first discernible fraction of response is
0.01/3.0 = 0.00333.

Similar definitions can be developed
for *any* physical property associated
with a cured system and formulation.
The concept of defining and under-
standing a minimum detectable
fraction of response is important in
that it enhances understanding for
formulation and manufacturing
optimization, particularly through use
of modeling in combination with
targeted laboratory results. Essentially,
in any formulation and system where
the response measured is an observable
property, the minimum detectable
response and maximum detectable
response can be defined in terms
appropriate to that response or
property. Therefore, successful
application and process window
optimization requires recognition that
the rate and time of energy input is
critically important to response.

Matching a formulation, irradiance
and energy densities are all
critically important to achieving a
desired response.

Response Associated with Variable Irradiance

Examining response as it varies
with irradiance, the ideal system
response would be independent of the
level of irradiance. However, no known
energy-response systems behave in this
ideal way. This is illustrated in Figure 2.

The system response, R_e, that the user
desires is ideally independent of
irradiance. In practical systems, R_e varies
with irradiance as shown in the U-shaped
curve in Figure 2. At very low irradiance,
the energy required to affect the desired
response becomes very high (possibly
infinite—no response will occur no
matter how much energy is input—e.g.,
due to inability to overcome oxygen).
At intermediate irradiance levels, the
response may become relatively
independent of input energy and its
rate of input (flat region of the

U-curve). At very high irradiance, the energy required to affect response rises and it may become impossible again to obtain the desired response.

This seemingly bizarre behavior is due to a common property of all energy responsive systems. There is a competition between two processes: a first-order response developing process and a second-order, non-response developing process. Rather than describing this competition in general terms, we return to photopolymerization and radiation curing to illustrate this dilemma.

In Figure 2, the small insert to the lower right of the diagram shows the general progress of photopolymerizable systems (in the presence of air) as a function of irradiance applied. There is usually a power level at which the polymerization begins and, as irradiance is increased, the rate of the process (conversion versus time) increases. At higher irradiance levels, the rate of the conversion levels off (maximizes).

Why is that? At low irradiance, free radicals produced by exposure of the photoinitiator are trapped by ambient oxygen before they can effectively grow polymer chains and become large enough to develop a physical property sufficiently. A level of response required by the user for acceptable delivery to a customer cannot be achieved. In the "sweet spot" of the response-irradiance profile, good physical properties can be delivered. However, at excessively high irradiance so many free radicals are produced per unit time that they recombine (terminate) more often than they initiate new chain propagation. This dilemma is referred to as "low-intensity reciprocity failure" at low-irradiance levels and "high-intensity reciprocity failure" at high-irradiance levels. In photopolymerization, it occurs

because of a dependence of the key propagation metric, kinetic chain length (KCL), on irradiance when combined with a particular formulation.

Line Speed Exposure Challenges

Why is KCL, the number of monomer functional units converted to polymer per radical generated, important? KCL's dependence on irradiance, and thus of the conversion of monomers and oligomers to a final polymerized product, is critical to the dynamic or line exposure so commonly used in Web-based photocuring processes. Consider that a dynamic exposure system produces *irradiance profiles* that pose unique challenges as demonstrated in Figure 3, which depicts a three-dimensional irradiance profile as a function of the type of reflector, lamp dimensions, focus, direction and speed of travel as well as position on the conveyor.

Consider that a formulation exposed to a profile as depicted in Figure 3, may experience different peak irradiance values leading up to the point of "complete" conversion both as a result of traveling into the exposure area and or location on the conveyor. As a result, "true" peak irradiance values will vary and, in turn, so will the "true" energy density and system KCL.

How does KCL and conversion of a formulation vary with irradiance at constant energy density? Figure 4 shows the variation in KCL and conversion (as a percent of the theoretical limit) for a formulation in which the amount of initiator is varied (Table 1).

The formulations are coated at 20 micrometers thickness and exposed to a medium-pressure mercury arc lamp in air at variable intensities using modeling software. KCL and conversion values were tabulated and plotted *at a constant energy density delivered of* $100 \ mJ/cm^2$.

TABLE 1

Formulation conversion with varied amount of photoinitiator

	5 gram PI	2.5 gram PI
Initiator	weight (gms)	weight (gms)
Benzophenone	3.0	1.5
1-Hydroxycyclohexyl phenyl ketone	2.0	1.0
Monomer		
Tripropylene Glycol Diacrylate	20.0	20.0
Trimethylolpropane Triacrylate (TMPTA)	10.0	10.0
Ethocylated (3) TMPTA	25.0	25.0
Oligomer		
Aliphatic Urethane Diacrylate	40.0	40.0

FIGURE 4

KCL and conversion plots

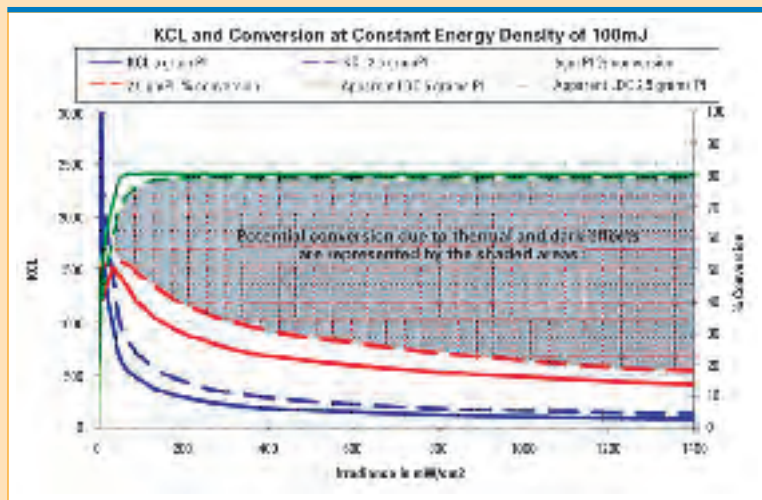KCL and Conversion at Constant Energy Density of 100mJ

Figure 4 shows that KCL decreases exponentially as irradiance increases (energy density held constant) and real-time conversion increases to a maximum value and then turns over and decreases as high-intensity reciprocity occurs. When the photoinitiator level is cut 50%, KCL and conversion (for constant energy density) increase slightly. Recall, that this constant energy density conversion is the *instantaneous* response of this system to the delivered energy density. However, at the end of the run, the observed conversion of the system (such as that measured by infrared spectroscopy) will show a continuation of polymerization toward a limiting degree of conversion (LDCa, represented by the green lines in Figure 4). This continuation of polymerization and the impact of thermal effects that occur above the instantaneous response (red lines on Figure 4) are often referred to as dark time polymerization. This behavior and relational interaction between irradiance, formulation and duration of exposure has important consequences for dynamic exposure.

Traveling Along the Web

Exposure of a photosensitive coating on a moving web presents challenges to modeling. If the system is monitored with a Power Puck or other integrating measurement device, the user is presented with a detailed view of the change of irradiance with exposure time (or distance traveled along the web). The profile in Figure 3 shows that because a reflector (elliptical or parabolic) is not a perfect focusing or collimating device and, because it is out of contact with the moving web, light at low intensity "leaks" out of the high-intensity exposure region. This low-intensity "foot" region occurs on both entry into the high-intensity region and exiting from it. But the behavior of the polymerizable film to the incident low-intensity light sections (feet) and high-intensity focus (and or collimatic) regions are very different and can produce surprising results.

As the film moves into the first low-intensity foot, the photoinitiator creates radicals that are either trapped by ambient oxygen or initiate propagating chains, which can be terminated by oxygen before they attain a gel point.

Depending on the irradiance in the foot, oxygen may or may not be overcome before the high-intensity region is entered and it is possible that, at some level of foot irradiance, the formulation could run short of photoinitiator before it enters the high-intensity region. At this low level of irradiance, KCL is high, but rates of initiation are low.

As the moving web continues and begins to enter the high intensity region of the focused light source, irradiance and rate of initiator consumption increase dramatically and the KCL falls rapidly while the temperature of the film surface climbs.

When the moving film exits the high-intensity region and experiences the low-intensity foot for a second time, the irradiance decreases—causing a rise in KCL again and may promote continued strong propagation even if the photoinitiator is exhausted.

It is also clear to those with long experience in this field that physical properties of the final product will depend critically on where in the irradiance profile the major polymerization processes occurs. It is likewise clear that the behavior of the film depends critically on this prior history. At what point has photoinitiator run out if, in fact, this occurs? Are thermal effects and high concentration of free radicals at high-irradiance levels going to produce dark polymerization or has its LDCa already been achieved at some point during one of the three regions of exposure? How has this impacted the resulting KCL? Fortunately, today's formulators, manufacturers and product designers have access to powerful modeling techniques to support "seeing" what occurs and optimizing use of radcure solutions with greater speed and ease. ◗

—David Eaton, Glen Thommes and Jeff Thommes are with PrecisionCure LLC, Wilmington, Del.