Curing performance for non-traditional implementations of low energy electron beams

Mikhail Laksin, Subh Chatterjee, Joshua Epstein

Introduction

Electron Beam (EB) curing is being deployed increasingly to address the high performance curing requirements of a broad range printing, packaging, and industrial coating applications. The economics of EB curing have improved with technological advances in energy curable chemistries and with the evolution of low voltage EB curing equipment. While EB curing traditionally has been relegated to wide web offset printing and high speed coating lines, the industry increasingly is considering EB for a wider range of applications. With new EB technology configurations and applications, it is necessary to study the effects on the kinetics of EB curing. This article summarizes and explores the implications of the research conducted in this regard by Mikhail Laksin and Subh Chatterjee from Ideon LLC, who found that these approaches offered equivalent if not superior curing performance to traditional energy curable configurations. This information will be presented formally at the April 2008 UV/EB Conference in Chicago, Illinois.

Overview of Advances in EB Technology and Applications

EB curable formulations and raw materials have advanced rapidly over the past several years. Converters, formulators, and raw material suppliers have sought to develop solutions that offer enhanced product performance and that can be applied to a wide range of printing and coating techniques. In particular, flexible packaging applications have benefited from advances in EB coatings, laminating adhesives and printing inks that comply with food packaging regulation. Building on this success, EB increasingly is considered for a wide range of potential printing, packaging, and industrial coating applications (see figure 1).

Just as EB curable chemistries are advancing, so is EB curing equipment. Traditional large, high voltage systems have given way to smaller lower energy systems that are both more cost effective and more readily integrated into a wide range of production applications. One design tradeoff that is often considered is sacrificing power output (typically referred to as dose-rate and measured in Kilogray-feet-per-minute) in favor of providing smaller EB emitters. Lower power output translates to lower curing speeds. This can be overcome by designing systems with multiple low power emitters in series to deliver a cumulative system dose rate that meets printers' press speed targets. The curing efficiency of "multi-step EB" has not been adequately studied in order to be properly compared to the curing efficiency of traditional electron beam configurations.

In addition to these novel implementations of EB curing equipment, there is growing interest in combining EB curing and traditional Ultraviolet (UV) curing technology.

While it is well known that EB energy will cure a UV curable formulation, there is little documented analysis regarding the performance of a "UV/EB hybrid" implementation. While substantial research on UV polymerization kinetics has been performed by Decker and others[1], there remains a lack of understanding regarding how a UV curable formulation reacts to multiple exposures from energy – whether it be UV or EB energy.

The general lack of understanding of the reaction kinetics seen in cumulative curing of energy curable formulations has been a cause of concern for those considering investments in multi-step EB curing or UV/EB hybrid approaches. The Ideon study examined curing efficiency for multi-step EB and UV/EB hybrid vs. traditional approaches and found reassuring results, which are discussed below.

Experimental evaluation of multi-step EB curing and UV/EB hybrid curing

Formulation

While the Ideon study focused on the effects of different energy curing technology configurations, it must be acknowledged that the efficiency of energy curable polymerization is highly sensitive to the formulation. This study used a single clear coat formulation and three ink formulations (cyan, magenta, yellow) – all of which are commercially available products and representative of modern formulation technology. The results were analyzed by measuring the degree of cure relative to other measurements of the same formulation. The intent of the study was not to discuss strategies for creating formulations optimized for multi-step EB of for UV/EB hybrid curing applications.

Measuring degree of cure

Historically, it has been challenging for the industry to agree on appropriate measures of "degree of cure." It has been shown [1-3] that monitoring acrylate double bond conversion at 810 cm^{-1} by FTIR spectroscopy is likely the most reliable, available method for assessing the degree of cure. Conversion of double bonds tends to be the indicator of cure performance that correlates with limiting monomer migration, an important factor in complying with food packaging regulation.

While conversion of double bonds is a helpful measurement, it is not always a predictor of product performance criteria such as chemical and abrasion resistance, coefficient of friction, or flexibility. The industry has historically used solvent resistance of the cured product as a practical quality control tool. While it is not appropriate to compare solvent resistance across multiple products, it can be useful for evaluating the cure of the same product, with the same film thickness, under multiple curing conditions. The Ideon study measured solvent resistance by recording the number of double rubs with isopropyl alcohol (IPA) required to remove the full ink layer from the substrate.

The study employed both FTIR spectroscopy and solvent resistance to evaluate the degree of cure seen in a controlled set of formulated products under differing configurations of EB and UV curing conditions.

Lab Setup

To accommodate the range of experimental factors, the Ideon study was carried out in a laboratory setting. Coating and ink systems were applied consistently, as shown in figure 2. EB curing was performed using Advanced Electron Beams Application Development Unit, with the parameters shown in figure 3.

Multi-step EB curing

Modern, low energy EB emitter technology has the advantage of being more compact, easy to integrate, and easy to service. While higher power output systems may still be the most practical solution for applications such as wide web printing, there are many applications in which the configuration complexity requires the flexibility provided by low energy emitters. The limitations of power output related to these smaller devices can be overcome by configuring curing systems with multiple emitters in series.

Positive effects from small, cumulative EB doses on conversion of acrylate functional blends have been reported in several publications.[2-4] An extremely high conversion rate of an acrylate-based system at relatively low EB dose was demonstrated by C.Patacz et al.[2], who observed a very steep initial slope of the acrylate conversion curve with a gradually increasing irradiation dose at the levels below 10 kGy. The same authors noticed an unexpectedly high conversion rate with multiple small EB doses in contrast to the conversion achieved with a single, larger dose. These effects were not influenced by the functionality of the acrylate compounds used in curing experiments. Rather, these results are attributed to the smaller thermal effects, lower inhibition and less pronounced post-polymerization effects associated with small, incremental irradiation doses.

In the Ideon study, the curing efficiency of multi-step EB curing was evaluated by comparing the degree of cure seen in a given formulation exposed to a given dose while varying the number of exposures to achieve that dose. The experimental design is shown in figure 4.

Figure 5 compares the double bond conversion seen in the clear coating sample under different EB configurations. The results indicate that multi-step EB exposure generates conversion values equal to or greater than those achieved by a single exposure at the same overall dose level.

Figure 6 compares the solvent resistance seen in the three ink samples under different EB configurations. The three charts illustrate the observed improvement in solvent resistance when exposed to a given dose level with multiple passes vs. a single pass. As can be seen for all three colors, there was a slight decrease in performance at 30 kGy and a significant improvement at 60 kGy. While these results are mixed, it there are sufficient datapoints to motivate the need for additional study

UV/EB Hybrid Curing

There are many applications where complete replacement of UV curing technology with EB curing technology is either not possible or not economically viable. While EB can offer many benefits, UV curing technology continues to be smaller in scale, cheaper, and easier to integrate. Many printing applications require curing between each color station in order to prevent any smearing of colors as the product passes through subsequent print stations. Hybrid UV/EB approaches offer novel curing solutions to common challenges faced by traditional UV curing approaches. UV curing can be used to provide adequate surface cure after each or every other color station, while an EB curing system can provide a final end-of-line cure. This configuration offers several advantages including:

- Better “through-cure”
- Better adhesion to substrate
- No “post-curing”
- Lower amount of photoinitiator required
- Less migration risk
- Increased line speeds
- Lower intensity UV lamps generate less heat

In order to evaluate the combined effects of UV and EB curing, a full factorial design of experiments examined and compared the relationship of photoinitiator concentration, UV dose, and EB dose with the degree of cure. Figure 7 outlines the experimental approach used. The total number of experiments performed is 39, including 3 points at zero PI, 3 EB dose levels (10, 20 and 30 kGy), and 9 points for UV curing only (3 PI levels x 3 UV dose levels). EB curing was performed at < 200 ppb of oxygen.

Solvent resistance was tested 24 hours after curing was completed in order to minimize any possible post-cure and polymer network conformational effects. The number of IPA rubs was normalized by the print optical density, which varied in the range between 1.50 and 2.00.

The results summarized in figure 8 clearly show that EB curing has an additive effect to the initial UV curing. A target minimum cure level identified by 18 IPA rubs was arbitrarily selected for illustrative purposes. In the case of UV curing only (0 kGy line in figure 8), a substantial amount of photoinitiator and a relatively high UV dose were required in order to reach the minimum cure requirement. Exposure to 10, 20, and 30 kGy of EB dose (10, 20, 30 kGy lines in figure 8) showed that a minimum cure can be achieved with substantially less photoinitiator and lower UV dose. These results support the notion that UV/EB hybrid approaches could deliver performance advantages over pure UV lines.

Conclusions

There is sufficient experimental evidence to suggest that the cumulative application of a small EB dose is a viable alternative to a single large dose. This concept could potentially be used in designing EB curing systems based on an approach of delivering multiple, low dose exposures with multiple filaments or, alternatively, with modular EB emitters.

Hybrid combinaton of UV and EB curing may also prove beneficial to various commercial applications, helping to reduce the amount of photoinitators and enhance cure at elevated press speeds.

Aknowledgments

The authors express their gratitude to Mr. Mark Mitry for performing ATR measurements.

References

1. Anseth, K.S., Decker, C., Bowman, C.N. Real time infrared characterization of reaction diffusion during multifunctional monomer polymerization. Macromolecules 38, 1995, 4040.
2. Patacz, C., Defoort, B., Coqueret, X., Electron-beam initiated polymerization of acrylate compositions 1: FTIR monitoring of incremental irradiation. Radiation Physics and Chemistry 59 (2000), 329-337.
3. Cojocaru, G., Martin, D., and others. Electron Beam applications in chemical processing. ICPE – Electrostatica, Bucharest, Romania, 1998
4. G.M. Miasik. Development of radiation-curable coatings for repainted strip. British Steel, Final Report, December 1990-May 1994.