Enhanced Conversion of EB Curable Systems with Low Dose Irradiation

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Abstract

Significant benefits from curing various electron beam (EB) curable coating & ink systems under multiple exposures to low dose Electron Beam irradiation have been demonstrated. Higher conversion rate and chemical resistance of the EB curable system may lead to increased product performance benefits, such as broader compliance with Food Law regulations and enhanced product resistance. Multiple exposures to low dose EB irradiation can open up new opportunities for EB curing system designs, reduce nitrogen consumption and create other processing benefits. Additionally, hybrid Ultraviolet (UV) / EB curing may offer significant product performance enhancements in applications which are traditionally limited to UV curing only.

Introduction

Electron beam (EB) curing has rapidly advanced in the Graphic Arts markets over the past several years, offering enhanced product performance and meeting the broad regulatory compliance requirements of the food packaging industry. Several new applications, including EB coatings, laminating adhesives and EB curable printing inks, successfully have been introduced to flexible packaging printing and converting applications as viable, and in many cases preferred, alternatives to conventional solvent and water based product applications. Building on this success, the time is right to identify new applications in printing that will benefit from EB curing.

Expanding the use of EB curing requires a better understanding of its capabilities and the substantial benefits it would bring in product performance. Ideally, these benefits would outweigh the cost considerations associated with investing in EB curing equipment. One of the key factors in selecting EB curing equipment is the equipment's ability to deliver the desired irradiation dose at high press speeds. In reality, though, there is very limited scientific evidence of what the optimum EB curing dose should be for various practical applications.

Just as EB curable chemistries are advancing, so too is electron beam curing equipment. Traditional large, high voltage EB systems have given way to smaller, lower energy systems, which are both more cost effective and more readily integrated into a wider range of production applications. One often considered design tradeoff is to sacrifice power output (typically referred to as dose-rate and measured in kilogray-meters -perminute) in order to use smaller EB emitters. Traditionally, lower power output translates to lower curing speeds. However, this can be overcome by designing systems with multiple low power emitters in series in order to deliver the cumulative system dose rate needed to meet printers' press speed targets. The curing efficiency of multiple low dose exposures has not been adequately studied which complicates comparing these modern configurations to traditional electron beam curing systems.

Interestingly, there is a similar lack of understanding regarding the analogous problem in UV curing, which is a much more widespread and accepted curing technology than EB curing. While substantial research on UV polymerization kinetics has been done by Decker and others[1], this research is not easily translated into practical applications. Total UV energy received by printing inks and coatings varies widely due to the varying spectral outputs generated by UV lamps from different manufacturers, the pigment interference, the press speeds and, finally, the cumulative effects of consecutive exposures to multiple sources of UV light. It becomes more difficult, if even possible, to predict the curing results of a hybrid, UV/EB curing process.

The general lack of understanding regarding the reaction kinetics seen in cumulative curing of energy curable formulations leaves industry with certain material questions that may affect the adoption rate of novel curing technology configurations:
1. Is it possible that cumulative EB curing can be generated by applying multi-step incremental irradiation using low voltage modular EB source available on the market today?
2. Can this type of curing offer any product performance benefits?
3. Do hybrid UV/EB approaches offer superior results to UV alone?

It appears that some of these questions may be answered, or at least addressed, by assessing the cumulative effects of EB and UV doses delivered under controlled laboratory conditions.

Experimental Conditions

Degree of Cure

The degree of cure, one of the most important factors in radiation curing, has never been addressed to the satisfaction of practical users of energy curable technology. Monitoring acrylate double bond conversion at 810 cm^{-1} by FTIR spectroscopy has shown to be [1-5,,] perhaps the most reliable scientific method to assess degree of cure. The most accurate conversion data reportedly can be acquired in the transmission mode using a NaCl crystal.

This method is not always practical for industrial use. It requires special sample preparation, which is quite difficult to accomplish with many curable products, including printing inks, coatings and adhesives, which vary greatly in viscosity. Typical application film thicknesses for UV and EB curable inks, coatings and adhesives are in the range of

.5 and 2 micron. As such, it is difficult to apply these products on top of the NaCl crystals at similar thicknesses.

Sample preparation can be simplified if conversion measurements are performed in the reflection mode. Since film thickness is critical for even semi-quantitive analysis of conversion, some control of the applied film weight is required and can be achieved using most common laboratory printing and proofing techniques.

Still, conversion of double bonds is not always helpful for assessing the performance of the cured products and their fitness for final use, which may be affected by chemical and abrasion resistance, coefficient of friction, and flexibility. For that reason, monitoring the solvent's resistance to the cured ink or coating film has always been the most common and practical quality control tool[6]. Solvent resistance is a very product specific factor and depends on the total film thickness, acrylate functionality of the formulation, presence and solubility of the non-reactive components and free volume of the cured film. It is not recommended to use a solvent resistance test as a comparative evaluation of different products or of the same product when applied at different film weight. However, solvent resistance is still an indicator of cure and, if the same or various formulations are applied to the same film weight, the solvent resistance of the cured film can be accepted as a measure of cure that correlates fairly well with applied curing dose.

In this work, both FTIR spectroscopy and solvent resistance test are employed in order to understand the effects of single and cumulative curing doses on various commercial and model UV and EB curable compositions.

Experimental Approach

Nicollete FTIR spectrometer was used to evaluate the double conversion of the model EB coating compositions in reflective mode (ATR). A clear coating composition was applied with #10 Mayer bar (approximately 5 micron film thickness) over aluminum foil. Percent conversion was determined by comparing the 810 cm^{-1} peak area of cured samples with that of an uncured layer.

In order to ensure uniform thickness throughout each experiment, the same drawdown film was cut into multiple samples and irradiated with various EB doses. All EB curing experiments were conducted using Advanced Electron Beams' Application Development Unit at 100 kV of accelerating voltage and with 50 feet/min table speed.

For the purpose of testing printing inks, various ink systems were applied via a Little Joe offset proofing press. Film thickness was controlled volumetrically (3 notches on the ink measuring plunger) and, to target the print optical density, with X-Rite reflective spectrophotometer.

Cumulative EB Curing

Several EB curable compositions were selected in order to assess the effects of cumulative exposures from EB irradiation:

> An EB curable clear coating model was characterized by the following simple blend: Photomer 3016-40T, a blend of Bis A-epoxyacrylate and TPGDA from Cognis - 20%, DPGDA from Cognis -80%.
>
> Three distinctly different EB ink formulations (acrylate functionality, presence of noncreative components, etc.) with three different colors, identified as: **A** - Yellow, **B -** Magenta, **C** - Cyan. The cure rate at each EB dose was calculated on the percentage base, selecting the highest number of IPA rubs within each experimental series as 100%.

Hybrid UV/EB Cure

In order to evaluate the combined effects of UV and EB curing, a full factorial design of experiment was created (**Table 1**). A model litho offset blue ink was chosen to run the full factorial design experiment outlined in **Table 2**. The same composition free from photoinitiator was tested with EB curing only.

Table 1

Experimental Factors		**Factorial Levels**		
		-1	**0**	**1**
A	PI concentration, %	3	6	9
B	UV dose, mJ/cm^2	38	140	240
C	EB Dose, kGy	10	20	30

Table 2 – Test Ink Composition

	Factorial Levels, %		
Components	**-1**	**0**	**1**
G49-6044 Blue Dispersion, Sun Chemical	40	40	40
Ebecryl 657, Cytec	43	43	43
TMPTA, Cognis	15	15	15
Photoinitiator package - Omnirad Cure All 2500, IGM	3	6	9
Total	101	104	107

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 in < 200 ppm of oxygen.

Solvent resistance was tested 24 hours after curing 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. Design Expert 7.1.3 software was used for statistical analysis.

Results and Discussion

Cumulative EB dose

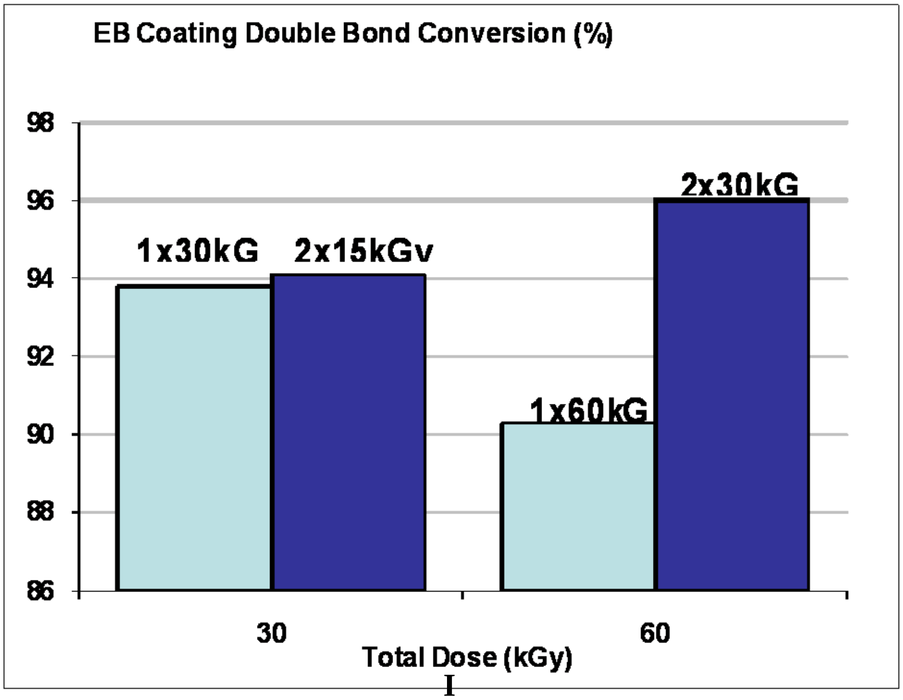
Positive effects from small, cumulative EB dose on conversion of acrylate functional blends have been reported in several publications [2-5,7]. An extremely high conversion rate of an acrylate-based system at relatively low EB dose was demonstrated by C.Patacz et al.[2], who observed a very steep initial slope of the acrylate conversion curve with a gradually increasing irradiation dose at the levels bellow 10 kGy.

The same authors noticed an unexpectedly high conversion rate with multiple small irradiation 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. Instead, these results are attributed to the smaller thermal effects, lower inhibition and less pronounced post-polymerization effect associated with small, incremental irradiation doses.

Similar observations are presented in [3] and [4]. Depending on chemical composition, conversion coefficients were found to decrease at higher absorbed EB dose rates. Some conversion/dose curve profiles are strikingly similar to those found in this work, demonstrating rapid increase in conversion at lower irradiation doses and then falling off as irradiation dose increases.

The most interesting results of EB curing with low cumulative doses are reported by Berejka in[7]. Polymerization of mono-funcional acrylate monomer was achieved after incremental exposure to several small EB irradiation doses but the same monomer remained liquid after irradiation with first single and then double 45 kGy EB dose, receiving total of 90 kGy.

Results of all curing experiments are presented in **Graphs 1** and **2.** This data was obtained with several formulations, from clear coatings to various inks systems (different chemistry and color), and supports most of the previously reported findings. The data suggests that there is some significant benefits of the cumulative effect of smaller, incremental EB exposures rather than a single large dose of EB irradiation.



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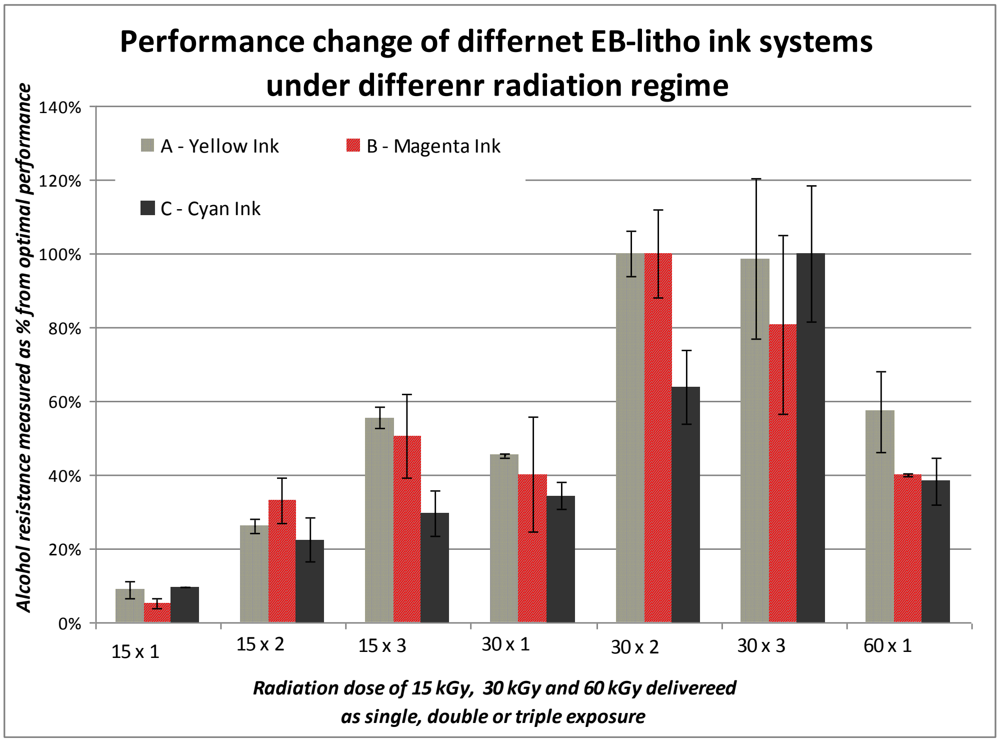
Graph 1



Graph 2

Graph 1 presents the conversion rate of acrylate double bonds in a simple EB coating, comprised of a blend of acrylated di-epoxide and two monomers – TPGDA and DPGDA. The coating was cured with several combinations of smaller EB doses, 15 and 30 KGy, as well as with a significantly higher single dose – 60 kGy. It appears that a relatively high cure rate can be achieved with small cumulative EB doses. In some cases, just two exposures to small, 15 kGy or 30 kGy doses can lead to a conversion that is equal to or higher than what is achieved with a significantly higher single dose of 60 kGy. Two 30 kGy of EB dose gave the highest conversion of the coating.

In this experiment, ATR measurements were performed with a relatively simple EB coating blend. In the next set of experiments, very complex, multi-component ink formulations were tested, using a very simple solvent resistance technique. However, the general trends and effects of small cumulative doses vs. larger doses appear to be similar (**Graph 2**).

The cumulative effects of small EB doses are high for each ink system/color. General trends are also similar despite significant difference in solvent resistance between individual colors. The solvent resistance of the blue ink in this experiment was significantly lower than that of the yellow and magenta inks, suggesting that this formulation has lower average acrylate functionality in comparison to other colors.

The best cure was achieved with the double 30 kGy dose for both yellow and magenta inks. Third additional exposure to 30 kGy did not show any benefits in curing of these two inks. Much less reactive cyan ink achieved the highest cross-linking density at 3x30 kGy dose. Two very small 15 kGy doses generated slightly lower cure than single 30 kGy dose for all colors. Finally single 60 kGy has been very ineffective in respect to cure in all cases.

Based on these experiments, it is fair to conclude that the area of cumulative EB irradiation merits further investigation. Additional findings would support the argument in favor of curing systems based on multiple, low energy, modular EB emitters.

Hybrid UV/EB Cure

Combining UV and EB curing in the same application can bring additional benefits to the printing and converting processes. Such a hybrid UV/EB curing process is known in the Graphic Art industry, but has been limited to a few specific applications in the label and folding carton market segments.

One can suggest that there are many more applications that will benefit from the combination of these two curing methods. In such a hybrid approach, UV curing is used for intermediate solidification of the inks and coatings required to move printed media through the printing press without physical damage to the printed image. This process is typically known as “interstation curing”. A final and more complete cure is achieved with EB irradiation. In this case, one can expect a significantly broader operation window, new opportunities in chemistry selection, such as photoinitator free systems and polymeric photoinitiators (both are not quite competitive in cure efficiency with traditional photoinitiators), and a possible reduced need for total UV irradiance and EB dose.

These assumptions require experimental confirmation, which were, in part, addressed by performing the experimental design, combining UV and EB cure in a broad range of total UV output (from 38 to 240 mJ/cm^2), and controlling EB dose (10 to 30 kGy).

Statistical analysis of the design's model implies that it is significant because the F-value is equal to 25.47, suggesting that there is only a 0.01% chance that a "Model F-Value" that is this large could be due to noise. Several other statistical check points (for instance, a signal-to-noise ratio of 18 is much higher than the desired minimum of 4) also point out to significant terms of the model.

Graphical interpretation of the model is presented on four graphs that can be found in the Appendix. A target minimum cure level, identified by 18 IPA rubs, was arbitrarily selected for illustrative purposes. In the case of UV curing only ("0" EB dose graph), a substantial amount of photoinitiator and a relatively high UV irradiance are requred in order to reach a desirable cure level, illustrated in light area above the "18 Rubs" line. Exposure to only 10 kGy of EB dose (second graph in the Appendix) significantly increases the area of desirable cure on the plot, shifting it into the lower photoinitator and UV irradiance regions.

When applying 20 kGy of EB dose (third graph), targeted cure response can be achieved with less then 6% of the photoinitator package and with an even lower UV dose. Finally, 30 kGy (fourth graph) expands targeted cure even farther, achieving a cure of over 18 IPA rubs and with just 4% of photoinitator and less than 50 mJ/cm^2 of UV irradiance. Cumulatively, these results indicate that the introduction of hybrid UV/EB cure may allow a significant reduction of the photoinitiator's concentration while printing at much higher press speeds.

Conclusions

There is sufficient experimental evidence to suggest that the cumulative application of a small EB dose may significanly enhance the total cure of various EB curable inks and coatings. 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

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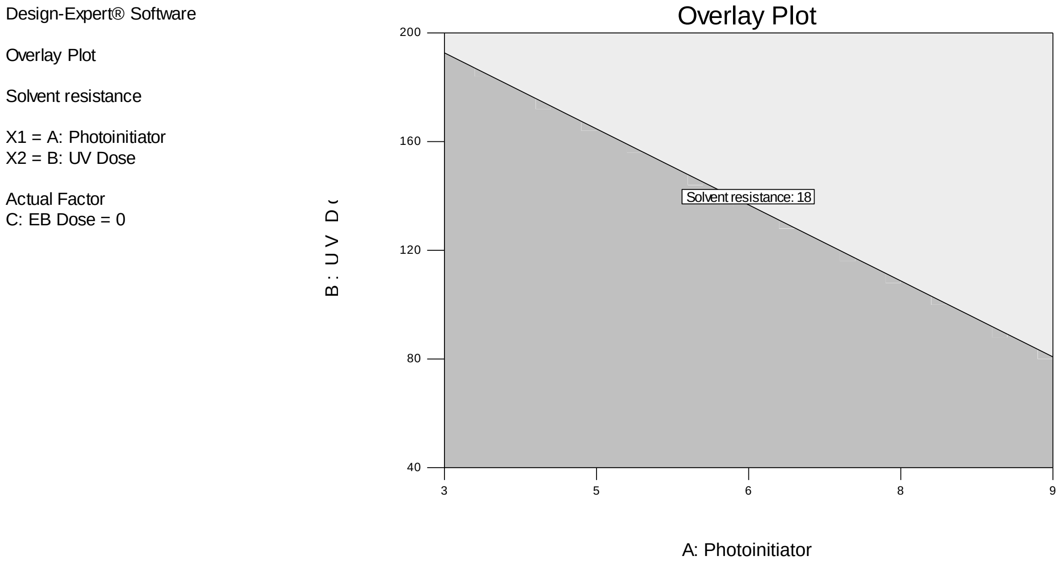
References

1. 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 crylate 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.
5. X. Coqueret, B. Defoort, J. M. Dupillier and G. Larnac, Polymerization kinetics of acrylate monomers under UV/EB radiation: from labscale monitoring to the modelling of industrial curing EADS SPACE Transportation
6. ASTM D-7244 – Standard Test Method for Relative Cure of Energy-Cured Inks and Coatings
7. Anthony J. Berejka RADIATION PROCESSED MATERIALS: DOSE-RATE EFFECTS, 2007

Appendix

Effect of EB Dose on Cure of Blue UV Ink



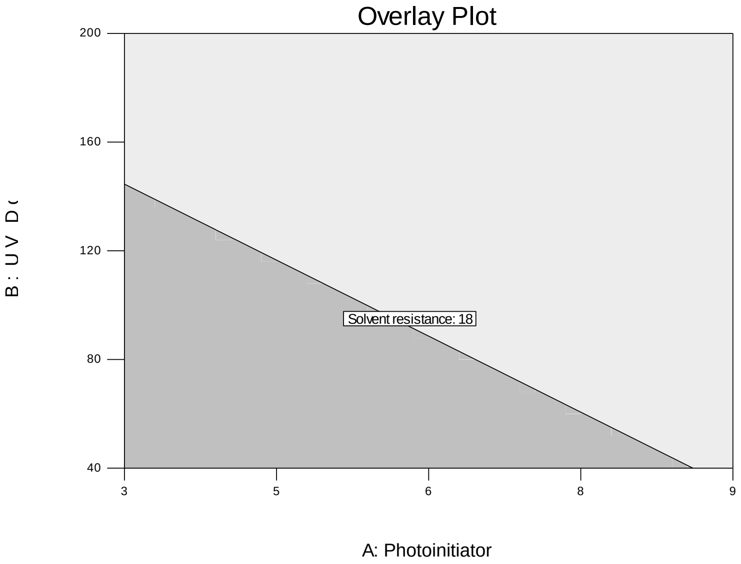
Design-Expert® Software

Overlay Plot

Solvent resistance

X1 = A: Photoinitiator
X2 = B: UV Dose

Actual Factor
C: EB Dose = 10



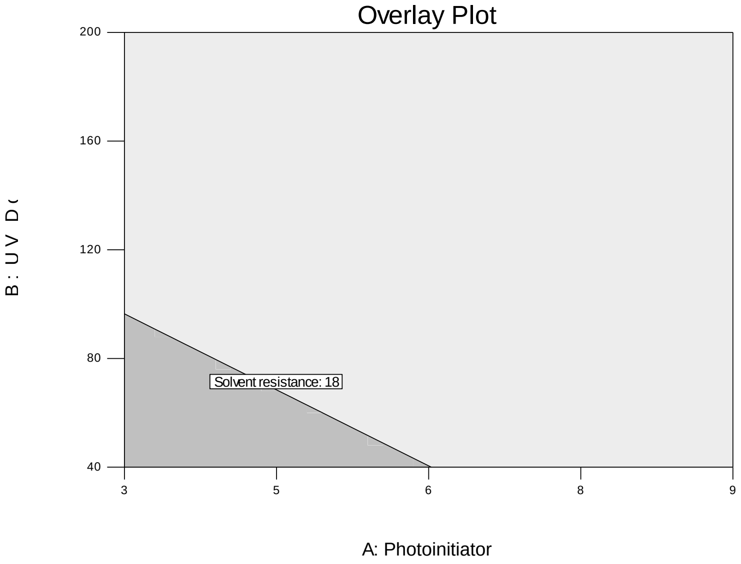
Design-Expert® Software

Overlay Plot

Solvent resistance

X1 = A: Photoinitiator
X2 = B: UV Dose

Actual Factor
C: EB Dose = 20



Design-Expert® Software

Overlay Plot

Solvent resistance

X1 = A: Photoinitiator
X2 = B: UV Dose

Actual Factor
C: EB Dose = 30