

Effects of Oligomer and Diluent Selection on the Performance of EB-Cured Coatings

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Electron beam (EB) curing is a growing market due to low odor and extractables for food packaging applications, speed of cure, and the recent lower cost of the EB equipment. However, the number of EB-cure applications is less than for ultraviolet light cure and the formulation variables are, therefore, less well understood. This remains a challenge for EB ink and coatings formulators.

Radiation induced in situ polymerization offers significant advantages compared to conventional thermal cure processes, as well as some UV-cure applications.

A wide range of oligomer chemistries was evaluated for cure response and adhesion at various dose and oxygen concentration in the process zone at low operating voltage. Chemistries included urethane, polyester, polyether, epoxy, and amine-modified acrylates; specialty backbones; and diluents with varying degrees of ethoxylation and propoxylation. Results were analyzed and presented so formulators have a better understanding of raw material performance in EB-cured coatings.

Introduction

Radiation induced *in situ* polymerization offers significant advantages compared to conventional

thermal cure processes, as well as some UV-cure applications. Since the introduction of EB equipment in the 1970s, the ability of electrons to initiate free radical polymerization without addition of photoinitiators or photosensitizers was of interest to the graphic arts market, in particular. Packaging applications were some of the first areas to successfully commercialize EB curing because of the high rate of cure offered by EB processing. Food packaging was a particular focus because EB-processed products result in:

- High degree of conversion (low migration).
- Highest gloss and scuff/abrasion resistance.
- Good quality control by National Institute of Standards and Technology (NIST)-traceable dosimetry techniques.
- No issues on cure of highly pigmented inks.
- Low temperature for thermally sensitive films.

Large food packaging converters adopted the technology for these reasons. Paper and folding carton products dominate this technology due to increased productivity. But the technology failed to penetrate broader markets, such as the general flexible packaging market. The reason for the restricted growth of

the higher-voltage EB equipment of the past was:

- **Size**—EB equipment was too large.
- **Cost**—EB equipment was too expensive.
- **High voltage**—damaged some radiation labile films used in flexible packaging.

Introduction of low-voltage EB equipment in the 90-110kV range in

early 2000 addressed all of the limitations of the higher-voltage EB equipment. Since its introduction, these types of low-voltage EB equipment have been seeing excellent growth in packaging as a curing option for:

- Offset and flexo inks.
- High gloss and abrasion-resistant oligomer p-phenylenevinylenes (OPVs) replacing film laminations.

- Curing laminating adhesives replacing moisture-cured polyurethane (PU) adhesives.

Flexible packaging is a \$60 billion market globally and growing at a rate of 3-4% annually. The most important reasons for this sustained growth in flexible packaging are high speed of production and low cost. The market is demanding even higher speeds, with

TABLE 1

Acrylate functional materials used in EB cure study

#	Description	<i>f</i>	Molecular Weight, g/mol	Typical Use
EA1	Standard neat Bis-A epoxy acrylate	2	800	Litho inks, OPVs
EA2	Modified epoxy acrylate	2	>EA1	Flexo & litho inks
EA3	Highly modified epoxy acrylate	2	>EA1	Flexo & litho inks
EA4	Modified epoxy acrylate	2	>EA1	Flexo & litho inks, OPVs
PE1	Low MW amine modified polyether acrylate	3	900	Flexo inks, OPVs
PE2	Medium MW amine modified polyetheracrylate	4	2300	Flexo inks, OPVs
PE3	High MW amine modified polyether acrylate	4	5700	Flexo inks, OPVs
PE4	Polyester acrylate	3	5000	Flexo & litho inks, OPVs
UA1	Aliphatic urethane acrylate	2	5500	Litho inks
UA2	Aliphatic urethane acrylate	3	3600	Litho inks
UA3	Aliphatic urethane acrylate	3	5900	Litho inks
UA4	Aromatic urethane acrylate	6	920	Litho inks, OPVs
CR1	Chlorinated polyester co-resin	0	NA	Litho inks
CR2	Inert adhesion co-resin	0	NA	Litho inks
CR3	Sucrose benzoate	0	NA	Litho inks, OPVs
RD1	Low viscosity aliphatic urethane acrylate	1	215	Flexo & litho inks, OPVs
RD2	2 mol propoxylated neopentyl glycol diacrylate	2	328	Flexo & litho inks, OPVs
RD3	PEG200 diacrylate	2	308	Flexo inks, OPVs
RD4	PEG400 diacrylate	2	508	Flexo inks, OPVs
RD5	PEG600 diacrylate	2	708	Flexo inks, OPVs
RD6	Trimethylolpropane triacrylate	3	296	Flexo & litho inks, OPVs
RD7	3 mol ethoxylated trimethylolpropane triacrylate	3	428	Flexo & litho inks, OPVs
RD8	6 mol ethoxylated trimethylolpropane triacrylate	3	560	Flexo inks, OPVs
RD9	9 mol ethoxylated trimethylolpropanetriacrylate	3	692	Flexo inks, OPVs
RD10	3 mol propoxylated glycerol triacrylate	3	428	Flexo & litho inks, OPVs
RD11	Alkoxyated pentaerythritol tetraacrylate	4	572	Flexo & litho inks, OPVs
RD12	Di-trimethylolpropane tetraacrylate	4	467	Flexo & litho inks, OPVs

TABLE 2

Co-resin formulation used in EB cure study

Component	Weight %
Co-Resin	35
Highly modified epoxy acrylate (EA3)	35
TMPTA	30

flexo presses and laminators operating now in excess of 500 mpm. Because of this requirement for faster and faster cure rates, this paper presents data for improved curing at a faster rate (lower dose), allowing for higher production speed. A range of different acrylate functional chemistries was evaluated for cure response and also for cure response under higher oxygen atmosphere concentration (lower nitrogen consumption). This would result in lower operating costs while maintaining the demands of low migration and high-end product requirements.

Experimental

A broad range of acrylate functional materials was tested and can be found in Table 1. These were selected as products typically used in EB-curable inks and OPVs. All materials were tested as is and will be referred to in subsequent text by their abbreviation: EA=epoxy acrylate, PE=polyether or polyester acrylate, UA=urethane acrylate, CR=co-resin and RD=reactive

diluent. Molecular weight (MW) reported is GPC MW.

The oligomers (EA1 through UA4) were diluted 70:30 with trimethylolpropane triacrylate (TMPTA) for ease of application. The co-resins (CR1-3) were formulated as shown in Table 2. This is a typical basic ratio used in offset ink formulations. The reactive diluents (RD1-12) were tested as is.

All materials and formulations were drawn down onto Laneta Form 2A opacity charts using a #3 wirewound drawdown bar to give 5m wet coating weight. The coated charts were taped onto the PET film web and passed through the EB cure unit at 10 mpm.

The EB equipment used for this testing was the pilot line at ESI. This pilot is older generation EB equipment and the voltage condition chosen was 135 kV. This voltage is equivalent to 110 kV for the new generation low-voltage EB equipment. The higher speeds being run on some production lines can result in more oxygen being

dragged into the curing chamber which can result in slower cure. Nitrogen inerting is also not an insignificant running expense for EB cure production lines—so materials that can be effectively cured at high O₂ levels can result in cost savings as well. Therefore, all of the above materials were tested at full nitrogen inerting as well as lower levels (resulting in more O₂ exposure) and these testing parameters are listed in Table 3.

Lower settings were also tried (2.83 m³/hr Window, 2.83 m³/hr Baffle, 5.66 m³/hr Inboard Knife) but this resulted in too much oxygen-inhibiting cure. Slower curing materials would not cure at even 4 MRads, making the data inconclusive. Cure was evaluated using powdered graphite where a small amount of graphite is rubbed gently onto the surface of the coating and then wiped off. Cure was assessed visually where no graphite means full cure, a slight amount means borderline cure, and a dark gray stain means a very poor cure.

Results

All results can be found in Table 4. Results are reported from 1 to 4, with 4 meaning fully cured (no graphite residue left), 3 meaning borderline cure (very slight graphite residue), 2 meaning not fully cured (significant graphite residue), and 1 meaning poor or no cure (dark gray graphite stain). These results are also displayed graphically in Figures 1 and 2.

TABLE 3

EB inerting settings

Nitrogen Inerting System	Full Inerting Settings, m ³ /hr	Low Inerting Setting, m ³ /h
Window	11.33	4.25
Baffle	11.33	4.25
Inboard Knife	8.5	5.66

Discussion

Starting with the results from the fully nitrogen-inerted testing (Table 4 and Figure 1), it can be seen that distinct variations are obvious. If one takes the individual product classes as a set (EA, PE, UA, CR and RD), trends within each class are apparent, as are trends between each class of material.

Starting with the epoxy acrylates, it would be expected that EB-cure

response would be primarily dependent on MW and functionality. This is also usually true of UV-cured processes. However, this is not the entire story, particularly when the epoxy acrylate results are compared to the other classes of oligomers. In fact, epoxy acrylates should not be expected to cure very effectively under EB radiation since they have a high concentration of benzene rings.

Benzene rings are known to absorb electrons and reduce cure due to lower concentrations of available electrons to polymerize the acrylate double bonds.

Since EA1 (standard Bis-A epoxy acrylate) shows the fastest cure response of any material tested, it is theorized that the resonance states of the high-energy epoxy acrylate are conducive to cure in this low MW material. The low MW means that the

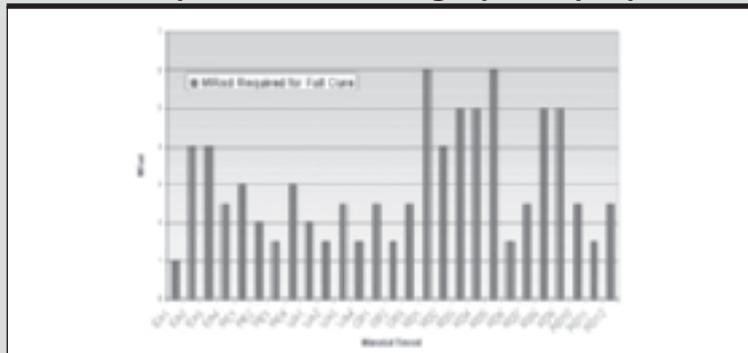
TABLE 4

EB setting

Material	Full Nitrogen Inerting				Low Nitrogen Inerting		
	0.5 MRad	1 MRad	2 MRad	3 MRad	1 MRad	2 MRad	3 MRad
EA1	2	4	4	4	2	4	4
EA2	2	2	2	3			
EA3	1	2	2	3		2	4
EA4	1	2	3	4		2	3
PE1	2	2	3	4	1	2	3
PE2	1	2	4	4	1	3	4
PE3	2	3	4	4	2	3	4
PE4	1	2	2	4		2	2
UA1	2	2	4	4		2	2
UA2	2	3	4	4	1	3	4
UA3	2	2	3	4	1	2	3
UA4	2	3	4	4	1	3	4
CR1	1	2	3	4		2	
CR2	2	3	4	4		2	
CR3	2	2	3	4		2	
RD1	1	1	1	1			
RD2	1	1	2	3			
RD3	1	1	2	2			
RD4	1	1	2	2			
RD5	1	1	1	2			
RD6	2	3	4	4		2	
RD7	1	2	3	4		1	
RD8	1	2	2	2			
RD9	1	1	2	2			
RD10	1	2	3	4		1	
RD11	1	3	4	4		1	
RD12	1	2	3	4		2	

FIGURE 1

UV dose required to fully cure raw materials tested (some extrapolation done for graphical purposes)



acrylate functionality is in close proximity to both the benzene rings and the secondary hydroxyl groups off the epoxy backbone. The hydroxyl groups should also help to draw the electrons out to the acrylate functionality, effectively increasing cure.

Once the epoxy acrylates are modified or chain extended (EA2-4), the cure is decreased since they are higher MW, but also because the proximity of the acrylate groups is much further away from the benzene rings and hydroxyl groups. EA4, for example, is much lower MW (better than 1/2 the MW) than the difunctional UA1 so it should cure faster, but cures quite a bit slower. It does cure faster under UV cure conditions, for example, showing that other effects are reducing the cure rate under EB exposure.

If the polyether acrylates (PE1-3) are examined, it is interesting to find that the higher MW materials cure with less dose than the lowest, despite only minor increases in functionality. Again, acrylate equivalent weight should be very important to the cure response of these materials under EB exposure. However, the higher MW polyethers also have more amine modification. This helps in two ways. One is that

there is always some oxygen dissolved in the raw materials so amines act as oxygen scavengers, preventing the oxygen from interfering in the chain propagation mechanism or by quenching the radical species as it forms after absorption of the electron. The second is that nitrogen stabilizes radicals. Stable radicals have longer half lives so they can participate in polymerization more effectively.

The urethane acrylates cure surprisingly quickly under EB exposure considering their relatively

high molecular weights. They are known to be widely used in EB-curable applications. Generally, this can be explained by the nitrogen in the urethane linkage stabilizing radicals. The fact that UA3 cures more slowly than UA1 is likely due to UA3 having a very soft, almost tacky, surface in the first place. However, the fast cure response of all the aliphatic UAs is quite interesting and should be of interest to the formulator. The very high functionality, aromatic UA probably is hurt in cure response since the benzene ring will retard cure (as described above) when explaining the epoxy acrylate results. While fast curing, it was not as reactive as might be expected given its ~150 g/mol acrylate equivalent weight. Use of urethane acrylates in EB formulations is also advantageous in that they will give excellent all-around physical performance—such as flexibility, scratch resistance, adhesion, etc.

Another surprise is the co-resin results. Despite being non-functional and formulated with a slow-curing modified epoxy acrylate (EA3), the cure response was quite reasonable. CR1 is chlorinated and this may assist

FIGURE 2

Investigation of lower nitrogen versus higher nitrogen inerting and EB dose required to fully cure raw materials tested (some extrapolation done for graphical purposes)

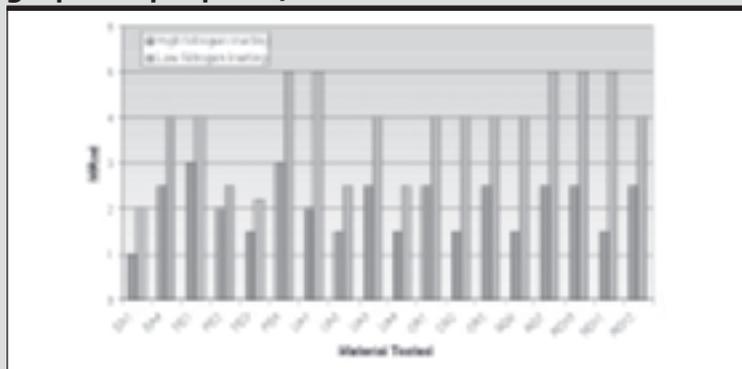
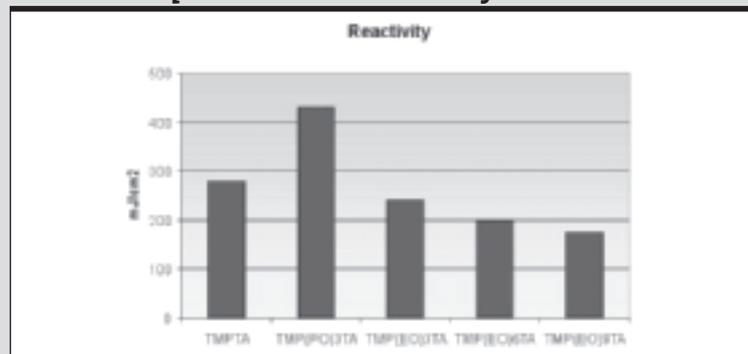


FIGURE 3

UV dose required to cure TMP acrylate derivatives



with cure. Chlorine can absorb electrons, but obviously does not affect the ability of those absorbed electrons to participate in the polymerization mechanism. CR2 has a unique proprietary backbone; this obviously contributes to the fast cure. It is not clear why CR3 (sucrose benzoate) cures rapidly under EB exposure, but the fact that it is a hard crystalline material means that relatively few crosslink reactions are required to achieve a hard film.

Lastly, it is surprising how many of the reactive diluents showed no cure response at all under EB exposure. Out of the difunctional diluents, only RD2 (propoxylated neopentyl glycol diacrylate) exhibited any cure and it was not very fast. The PEG diacrylates (RD3-5) showed very poor cure response. An interesting series is the TMP derivatives (RD6-9). Under UV cure conditions, some degree of ethoxylation helps cure response, as shown in Figure 3. However, this is due to the hydrogen abstraction potential of the EO linkages when cured with Type II photoinitiators. Here, 6 mol and 9 mol do not cure at all. In fact, the only reactive diluents exhibiting any reasonable degree of cure are the higher functionality materials with little or no

ethoxylation, such as RD6, RD7, RD10, RD11 and RD12.

When the nitrogen inerting was reduced, allowing for higher oxygen levels in the curing chamber, all of the material classes exhibited reduced cure response as shown in Figure 2. EA3 actually shows a reduction in cure response, but this is thought to be experimental error, possibly due to a much higher film weight being applied to the substrate. Higher film weights result in less oxygen sensitivity because radicals are available from the lower levels of the coating to replenish those quenched at the surface by oxygen.

However, the oligomers (meaning all materials tested except the RD materials) show lower reduction in cure compared to the reactive diluents. If the ratio of the dose needed to cure for full nitrogen inerting versus lower nitrogen inerting is examined, virtually all the oligomers cure at less than twice the dose at low nitrogen inerting versus high. Almost all of the monomers, however, cure under low inerting with a dose more than twice that seen with maximum nitrogen inerting. It is thought that the high concentration of oxygen in the backbone of the reactive diluents makes oxygen more soluble and,

therefore, can interfere in curing to a greater degree. The amine-modified polyethers show the least reduction in cure response, which is expected since the amine will act as an oxygen scavenger as discussed above.

Conclusions

The results here lead to definite formulating techniques to optimize for maximum cure rate in EB-curable systems. These can be summarized as follows:

- 1) Urethane acrylates are excellent oligomers to utilize as the backbone of any EB-cured formulation. Not only do they cure rapidly, but they will also give an excellent balance of other properties, such as flexibility, adhesion, scratch resistance, etc.
- 2) Unmodified epoxy acrylates have excellent cure, but are somewhat limited due to lack of flexibility and adhesion on plastics and metallized films. They are also very high in viscosity, meaning that high concentrations of slow-curing reactive diluents have to be used for correct application viscosities.
- 3) Amine-modified polyethers are very fast curing and also have an excellent balance of other properties. They tend to be very low viscosity, and can result in label-free inks and coatings.
- 4) Use of co-resins to help adhesion is recommended since they do exhibit very good cure rate.
- 5) Use of monomers should be limited to those that are high functionality and are not ethoxylated. This is fine for offset inks, but does limit the choices for lower viscosity ink and coating systems.

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