

# Electron Beam Activated Cationic Curing

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## Background

Ultraviolet (UV) activated cationic curing is well known and has been used in commercial coating applications for more than 25 years. The technology uses photo-acid catalysts which generate strong acids upon UV irradiation. The most well known and widely used catalysts are diaryliodonium and triaryl-sulfonium salts. These salts use a weakly nucleophilic anion such as  $\text{PF}_6^-$  or  $\text{SbF}_6^-$  which facilitate the propagation step of the curing polymerization reaction.<sup>1</sup> The most well known and widely used curing systems are cycloaliphatic epoxies, most notably 3,4-epoxycyclohexyl methyl 3,4-epoxycyclohexane carbonate.<sup>2</sup> These systems often incorporate polyols which facilitate the reaction of the epoxies by a chain transfer mechanism.<sup>3</sup> Other curing systems including oxetanes<sup>4</sup> and vinyl ethers<sup>5</sup> are known as well.

UV cationic curing of epoxies is often selected because of advantages in cured coating properties compared to acrylate based free-radical cured coatings. The cationic curing of epoxies occurs through a ring-opening polymerization which produces considerably less shrinkage compared to free-radical curing of acrylate groups. Less shrinkage translates to better adhesion properties especially to rigid substrates such as metals where UV cationic curing of epoxies is commonly used.

Electron Beam (EB) curing of inks and coatings is well known and has been used in commercial applications for more than 25 years. The accelerated electrons have enough energy to break chemical bonds within the components of the coating producing free-radicals. This results in the polymerization (curing) of the acrylate based monomers and oligomers without the need for added photoinitiators. EB induced free-radical curing of surface inks and coatings is almost always conducted in an inert atmosphere (usually nitrogen) in order to displace oxygen which inhibits free-radical curing.

It is less well known that EB irradiation can be used to activate cationic curing. In this case an onium salt compound is needed for curing to occur. A proposed mechanism of EB induced cationic curing involves charge transfer from the onium salt to the free-radicals which are formed by EB irradiation. This is supported by the fact that iodonium salts which have a lower reduction potential are much more reactive compared to sulfonium salts in EB systems.<sup>6,7,8</sup> Since the propagating species is a cation rather than a radical, inhibition by atmospheric oxygen is not expected.

Drivers for considering EB activated cationic curing may include:

- Eliminates the need for inerting which is usually the largest operating expense associated with EB curing applications
- Allows curing of large items such as aircraft components constructed from composite materials which are difficult to inert<sup>9</sup>
- Allows curing of complex geometries which are difficult to inert<sup>9</sup>
- Allows production of materials with high temperature resistance associated with cationic cured epoxies<sup>9,10</sup>
- Allows curing of highly pigmented or filled coating layers that do not allow UV penetration
- Provides EB cured coating with excellent adhesion to difficult substrates including metals.

The purpose of this paper is to characterize the EB curing properties of cationic systems in order to facilitate the development of new applications.

## Experimental

Commercial raw materials were used and were weighed and blended to produce the desired formulations. The formulations were applied to BYK PA-2810 test cards with #3 or #8 wire-wound rods. The test cards with coating were attached to a carrier web and passed through the curing chamber of a BroadBeam EP series electron beam accelerator operating at 150 kV. The EB unit was operated in ambient air or with a nitrogen purge which produced a <200 ppm oxygen atmosphere. The web speed and beam current were adjusted to give the desired cure dose. The applied dose was confirmed using GEX B3 dosimeter films. Curing was evaluated by rubbing with the round end of a 32 ounce ball-peen hammer which was wrapped with 4 layers of paper towel material. Good curing was defined as no visible effect on the coating after 10 back-and-forth rubs with both dry and methyl ethyl ketone (MEK) saturated towel material. Coating adhesion was tested with Scotch brand 810 tape with and without cross hatch cutting of the coating. The amount of coating remaining after the tape test was recorded.

## Results and Discussion

### A. Design of Experiments to Identify and Optimize EB Curing Properties of Epoxies

Screening studies were conducted to identify various coating components including polyols and oxetane monomers. An acrylate monomer, pentarthritis triacrylate, was included to allow for hybrid cationic/radical curing. The materials shown in Table 1 were selected for optimization of the composition using a D-optimal mixture design. The testing included 16 compositions and 4 replicates to cover the range of compositions shown in the Table. The response studied was the EB cure dose needed to give good smudge and MEK rub resistance at various coating weights. Based on the analysis of the results the optimized composition shown in Table 1 was selected for further study.

Table 1. DOE Optimization of EB Cationic Cure Compositions

Component	Description	Range Low(%)	Range High(%)	Optimized Composition (%)
IGM Omniflex OC1005	3,4 epoxycyclohexyl methyl 3,4 epoxycyclohexane carbonate	47.5	95.5	65.5
Perstorp R3530	Alkoxylated TMP polyol	0	20	10
Sartomer SR444	Pentarithrotol triacrylate	0	20	20
Irgacure 250	4-methylphenyl 4-(2-methyl propyl) phenyl iodonium hexafluorophosphate	4	12	4*
BYK 307	Organosilicone	Fixed at 0.5		0.5

\*A slightly lower cure dose was achieved with higher catalyst levels; however, the 4% level was selected in order to limit the cost of the composition.

## B. Effect of Coating Weight and Curing Atmosphere on Cure Dose

The composition shown in Table 1 was applied to paperboard test cards with #3 and #8 wire-wound rods. The minimum EB cure dose required to give good curing was recorded. It was found that a cure dose of 100 kGy was needed when a #3 rod was used; however, good curing could be achieved at 60 kGy when a thicker coating was applied using a #8 rod. One possible explanation for the beneficial effect of the higher coating weight is that the thicker coating will reach a higher temperature due to the exothermic curing reaction. Cationic curing is well known to benefit from increased temperatures during the curing. There was no difference seen in the dose required for good curing when the EB was operated in air compared to inerting with nitrogen. This result was expected since oxygen is known to inhibit free-radical polymerization but does not affect cationic systems.

## C. Effect of Catalyst

A series of different catalysts were tested to determine the EB dose needed to cure the coatings. All compositions were tested with a catalyst concentration of 4% replacing Irgacure 250 in the optimized composition given in Table 1. The results with the different catalysts are summarized in Table 2. The results show a slight reduction in the dose needed for good curing using OPPI. This could be due to  $\text{SbF}_6^-$  counter ion which is known to give a stronger acid compared to the  $\text{PF}_6^-$  in Irgacure 250. It could also be a concentration effect due to the fact the Irgacure 250 is supplied as a solution (75% active) in propylene carbonate. Irgacure PAG 290 required a higher dose but could be advantageous due to low odor properties in applications where dose is not critical. Compositions with Irgacure 270 had poor curing even with dose levels up to 200 kGy which could be due in part to the incomplete solubility of this catalyst in the formulation.

Table 2. Effect of Catalyst on EB Cure Dose for Cycloaliphatic Epoxy Based Compositions

Catalyst	Description	Min. Cure Dose With #3 rod (kGy)	Min. Cure Dose With #8 rod (kGy)
Irgacure 250	4-methylphenyl 4-(2-methyl propyl) phenyl iodonium hexafluorophosphate	100	60
Irgacure 270	Proprietary low migration photo acid catalyst	>200	>200
Irgacure PAG 290	Triarylsulfonium borate	120	80
OPPI	(4-Octylphenyl)phenyl iodonium hexafluoroantimonate	80	40

## D. Cationic Curing of Vinyl Ethers

The cure dose of 40 to 120 kGy to cure the cationic epoxy coatings was relatively high compared to typical free-radical cured acrylates that cure in the range of 20 to 40 kGy. Modern low energy EB equipment can deliver 60 kGy at line speeds over 200 m/min; however, it is desirable to have systems that will cure at a lower dose for use in high speed converting applications that can run over 400 m/min. Lower cure doses may also be desirable when using substrates that may be adversely affected by high cure dose levels.

Faster reacting vinyl ether monomer based systems were evaluated in an attempt to lower the EB dose needed for curing. A representative test formulation is shown in Table 3.

Table 3. Vinyl Ether Based Composition of Cationic EB Curing

Material	Description	Composition (%)
DVE-3 (Ashland)	Triethylene glycol divinyl ether	92.5
CAB 381-0.5 (Eastman)	Cellulose acetate butyrate	5.0
BYK 307	Organosilicone	0.5
Irgacure 250 (BASF)	4-methylphenyl 4-(2-methyl propyl) phenyl iodonium hexafluorophosphate	2.0

The composition shown in Table 3 was applied with #3 and #8 wire-wound rods to test the effect of coating weight on curing. The effect of nitrogen and air curing atmospheres was also tested. The results are shown in Table 4. In contrast to the EB curing of the epoxy based formulations, the vinyl ether composition did show differences in curing with and with and without inerting. This effect of inerting appears to be coupled with the coating weight. When curing in a nitrogen atmosphere good curing was achieved with a dose at or below 5 kGy (0.5 Mrad). This is an extremely low dose compared to typical acrylate based systems. Curing in air was very dependent on coating weight. Coating applied at the heavier weight (#8 rod) was well cured at 10 kGy. At the lower weight (#3 rod) the coating required a dose of 40 kGy for good curing.

The fact that oxygen had an impact on the curing could be due to the ethylene glycol ether linkages in the DVE-3. The carbon alpha to ether linkages readily forms free-radicals by hydrogen abstraction. These radicals could be quenched by oxygen limiting subsequent activation of the iodonium catalyst. The testing was repeated under high and low ambient humidity conditions to confirm these were not moisture effects.

Table 4. EB Curing of Vinyl Ether Based Composition

Curing Atmosphere	Application Rod	Min. Cure Dose (kGy)
Nitrogen	#3	5
Air	#3	40
Nitrogen	#8	<5
Air	#8	10

#### E. Adhesion Properties of EB Cationic Cured Coatings

The cationic epoxy and vinyl ether compositions discussed above were tested for tape adhesions on tin-plate steel panels and 50 micron untreated polyester (PET) film. Adhesion is known to be a challenge for UV/EB systems with these substrates. Acrylate based coatings were also tested for comparison. A high  $T_g$  coating based on TMPTA and epoxy acrylate oligomer was used. A low  $T_g$  coating based on a urethane acrylate was also compared. All coatings were applied with a #8 rod. The results are shown in Table 5 below. The cationic epoxy had excellent adhesion to the steel and only failed on the PET with cross-hatch cutting of the coating. As expected the TMPTA/epoxy acrylate coating had poor adhesion under all conditions. The vinyl ether based coating was slightly better than the urethane acrylate in that it maintained adhesion to the PET in the case where the coating was not cross-hatched.

Table 5. Adhesion Properties of Cationic and Free-Radical Based Formulations

	Cure Conditions	Steel no x-hatch (adhesion %)	Steel x-hatch (adhesion %)	PET no cross hatch (adhesion %)	PET cross hatch (adhesion %)
Cationic epoxy	100 kGy air	100	100	100	0
Cationic vinyl ether	40 kGy air	100	0	100	0
Epoxy acrylate	40 kGy N <sub>2</sub>	0	0	0	0
Urethane acrylate	40 kGy N <sub>2</sub>	100	0	0	0

## Conclusions

Cycloaliphic epoxy based coatings were EB cured in air in the presence of an iodonium catalyst. The resulting coatings had excellent adhesion to difficult substrates. The main disadvantage of this system was the relatively high EB dose needed for curing. Vinyl ether based coatings cationic cured in nitrogen at an extremely low dose of less than 5 kGy (0.5 Mrads). This could be very useful in high speed applications or where a low dose is needed to prevent substrate damage. The EB dose needed to give good curing of both epoxies and vinyl ethers was reduced when higher coating weights were used.

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