

# Low-Energy Electron Beam-Induced Cationic Polymerization with Onium Salts

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**ABSTRACT:** Demand for higher polymer performance with very short cure times has resulted in the development of low energy electron beam processes. This article presents the results of such a process for curing two epoxy systems, namely 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate and di-glycidyl ether of bisphenol A (DGEBA), using the cationic photoinitiator salts, triarylsulfonium hexafluoroantimonate, and diaryliodonium hexafluoroantimonate, respectively. Glass transition temperature measurements were done using a modulated DSC method while the degree of conversion was measured using FTIR spectroscopy. Results indicate that for both epoxy systems a relatively low dosage of not more than 5 Mrad was sufficient to achieve up to 60% conversion, with up to 80% conversion achievable using 30 Mrad. The diaryliodonium salt appeared to be more effective than the sulphonium salt in the above study. The effect of varying photoinitiator concentration and the resulting glass transition temperature has been studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3099–3108, 2001

**Key words:** electron beam; degree of conversion; glass transition; cationic polymerization

## INTRODUCTION

Thermoset resin formulations based on epoxies<sup>1</sup> have been widely used in microelectronic packaging and inert coating materials to protect, insulate, and conceal circuits or components of electronic devices. Epoxies, silicones, and some polyimides are examples of thermoset polymers widely used in electronic packaging. Most thermosets require heat and pressure for curing.<sup>2</sup> The demand for higher performing systems has also led to systems with correspondingly longer cure times. In particular, for the microelectronics/elec-

tronics industry, the curing process has become the bottleneck of the whole production process. Although increasing the temperature of cure would increase the cure rate, this is limited by the fact that the maximum rate of reaction for any given curing system is already determined for a constant temperature. Heating it at a higher temperature would not increase its rate of reaction, but instead lead to thermal degradation.

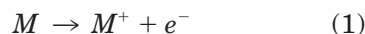
More recently, cationic polymerization induced by radiation has drawn interest for applications such as passivation coatings, printing inks, and for photolithography. Radiation curing sources include ultraviolet light, gamma rays, laser, and electron beam. UV light has limited application due to its poor penetration ability and limited dose rate. Gamma rays are from naturally radiating sources such as Cobalt-60, with enormous

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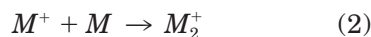
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radiation hazards and environmental issues. Laser irradiation requires that the material to be cured be nonreflective. Application of an electron beam as a source of curing is not new,<sup>3-6</sup> and more recently,<sup>7-9</sup> the use of an electron beam has been found to be a more viable process for curing thermoset polymers, with the advantage of a very short cure time, minimal residual stresses due to the room temperature curing, and low operating and process costs. Radiation-induced ionic polymerization proceeds via the three basic steps of initiation, propagation, and termination, which are analogous to free radical polymerization.

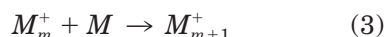
1. In initiation, generally monomer ions are formed by the interaction with radiation.



Although the generated electrons can react with other species subsequently, the positive ions can initiate polymerization by adding to the monomer.



2. Leading to the general propagation reaction.



3. Termination is usually brought about by an impurity, such as  $X^-$

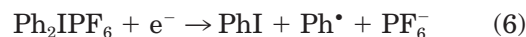


The termination may occur by charge transfer, proton transfer, or addition of an ion to a base. However, if the amount of impurity is extremely low and the ions are regarded separate, termination would occur by reaction between the propagating ion and the counterion.



In the case of the cationic mechanism, the process is more complex. As epoxides are unaffected by radicals and low dosages of high-energy electrons, a catalyst that generates hydrogen ions is still required. Available cationic photoinitiators, such as sulfonium salts, can be used as catalysts. The coatings absorb energy from high-speed electrons, and ionization occurs to produce slow electrons. These slow electrons will interact with any neighboring photoinitiator molecule, causing dissociative electron capture.

The use of onium salts as photoinitiators is typically with the presence of a counteranion, which dissociates upon being radiated, thus allowing the curing rate to increase significantly. As such, an appropriate combination of radiation source, epoxy resin, photoinitiators, and counteranion is required for optimal curing of the coating. It is known that the reduction of iodonium and sulfonium salts leads to their decomposition:



Meanwhile, the ionized resin can abstract reactive hydrogen radicals from adjacent molecules, thus producing cations, stabilized by the  $\text{PF}_6^-$  anion. These cations can attack epoxide functionality, causing polymerization.

To date, EB-cured polymer systems include monomers and oligomers containing acrylate and methacrylate groups, such as coatings and adhesives.<sup>10,11</sup> Electron beam curing of epoxy resins with various onium salts as photoinitiators have also been investigated recently for cycloaliphatic epoxy monomers<sup>12-14</sup> and other cationic epoxy systems.<sup>15</sup> In these cases, it has been found that knowing the optimal concentration of photoinitiators to be used is critical, due to plasticization effect of unreacted salt initiator fragments left behind.<sup>16</sup> In particular, diaryliodonium salts have been shown to be more effective photoinitiator than triarylsulfonium salts of the same anions, for a UV curing source.<sup>17</sup>

Although thermal analysis of bulk resins has been extensively performed using conventional DSC systems, similar analysis of radiation coatings often does not achieve consistent results. Modulated DSC has been shown<sup>18</sup> to give accurate and consistent results. Determination of the degree of conversion for the irradiated coating has been shown to be more accurately performed using an FTIR method.<sup>19-22</sup>

The use of onium salts as photoinitiators is typically in the presence of a counteranion, which dissociates upon being radiated, thus allowing the curing rate to increase significantly and spontaneously. As such, an appropriate combination of radiation source, epoxy resin, photoinitiators, and counteranion is required for the optimal curing of the coating. There has, however, been a lack of data relating the glass transition temperature to the applied EB dosage, and also to the percentage

conversion of the resins after electron beam radiation. This article is thus an attempt to investigate the use of a low-energy electron beam to cure epoxy coatings with an onium salt as the photoinitiator, and study the resulting glass transition temperature as well as the optimum concentration of the photoinitiator that should be used for different monomers, and lastly, the percent conversion of E-beam-cured coatings by FTIR.

## EXPERIMENTAL

### Materials and Methods

Two epoxy resins were used in this study: a difunctional cycloaliphatic epoxide monomer 3,4-epoxycyclohexylmethyl-3', 4'-epoxycyclohexane carboxylate (ERL 4221E, obtained from Union Carbide Asia Pacific, Inc.), and diglycidyl ether of bisphenol A (DGEBA, Epikote 828 obtained from Shell Chemical). Two photoinitiators (with the same counterion but different cations) were used, namely, triarylsulphonium hexafluoroantimonate (UVI6974, obtained from Union Carbide Asia Pacific, Inc.) and (2-hydroxytetradecyloxyphenyl) phenyliodonium hexafluoroantimonate, (CD1012, obtained from Sartomer Co, Inc.). Formulations of the epoxy resins were made with the photoinitiators at varying weight percents of 0.5–5.0. In the case of sulphonium salt, which was a liquid, an homogeneous mixture was obtained by stirring at room temperature. On the other hand, the mixture with the iodonium salt (white solid) was to be stirred at 40°C, to obtain an homogeneous solution. FTIR-grade potassium bromide (KBr) was purchased from Nicolet Corporation, USA.

The epoxy formulations were coated onto clean glass slides of dimension 80 × 30 × 1 mm. A K-Bar handcoater was used to apply the films with a wet film thickness of 50 μm. The electron beam accelerator used was an Electrocurtain® EB System Model CB175 from Energy Science Inc., USA, with an accelerating voltage range between 150 and 175 keV and a beam current range of 0–10 mA. The coated glass slides were passed through the electron beam accelerator at an acceleration voltage of 175 kV and a beam current of 5 mA, with the conveyor speed set to 19.3 m/min. The dose per pass was 5 Mrad under these conditions. Samples that needed higher dosages were irradiated by multiple passes through the accelerator. All irradiated samples were dark cured at room temperature for 45 min before storing at

–20°C to arrest the process of postpolymerization and its effect on subsequent properties of the cured resin.

Two different Differential Scanning Calorimeters were used for the measurement of the glass transition temperature of the cured products. The standard DSC used was a Perkin-Elmer DSC 7. Cured samples of 10–15 mg, each crimped into standard aluminum pans, were subjected to a temperature program of 30 to 250°C at 10°C/min. The Modulated DSC used was provided by TA Instruments (modulated DSC 2910 with Refrigerated Cooling System, RCS). The samples were subjected to a heating program of 0–250°C at 5°C/min, with a modulation of ±1 degree per 60 s. The corresponding temperature on the X-axis at half  $C_p$  was accepted as the  $T_g$ .

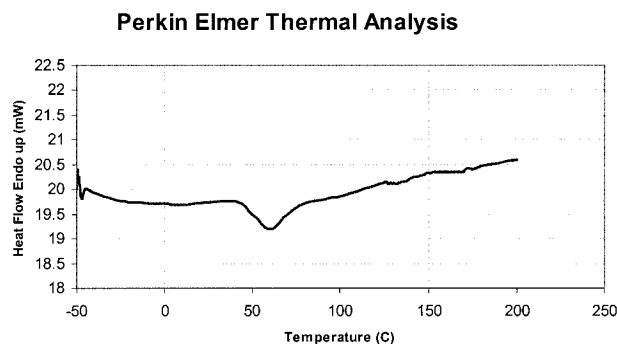
A Nicolet Magna 560 FTIR bench was used to measure the percent conversion of cured samples. KBr pellets of 13-mm diameter were prepared using a hydraulic hand press. The epoxy resin formulations were coated onto the KBr pellets (approximately 20 μm thick) and EB cured directly at an acceleration voltage of 175 kV and a beam current of 5 mA. Care was taken to limit the film thickness on KBr pellet so that the absorbance was within the limit of Beer's law. Spectra of the cured film on KBr pellets were recorded at a resolution of 4 cm<sup>-1</sup> and a total of 100 scans were signal averaged to obtain an enhanced signal-to-noise ratio. Ratio of peak heights was determined at constant peak position and baseline using the quantitative analysis software of the instrument. Percent conversion was calculated using the following relationship:

$$\text{Percent Conversion}(\alpha) = 1 - \frac{(A_{\text{peak}})_t (A_{\text{ref}})_0}{(A_{\text{ref}})_t (A_{\text{peak}})_0}$$

where  $(A_{\text{peak}})_t$  is the height for the active functional group after exposure to the E-beam and subsequent dark cure;  $(A_{\text{ref}})_t$  is the height of the reference peak after curing after exposure to the E-beam and subsequent dark cure;  $(A_{\text{peak}})_0$  is the height for the active functional group in the uncured sample; and  $(A_{\text{ref}})_0$  is the height for the reference peak in the uncured sample.

## RESULTS AND DISCUSSION

Although reports have been published relating to the determination of  $T_g$  for radiation-cured ep-



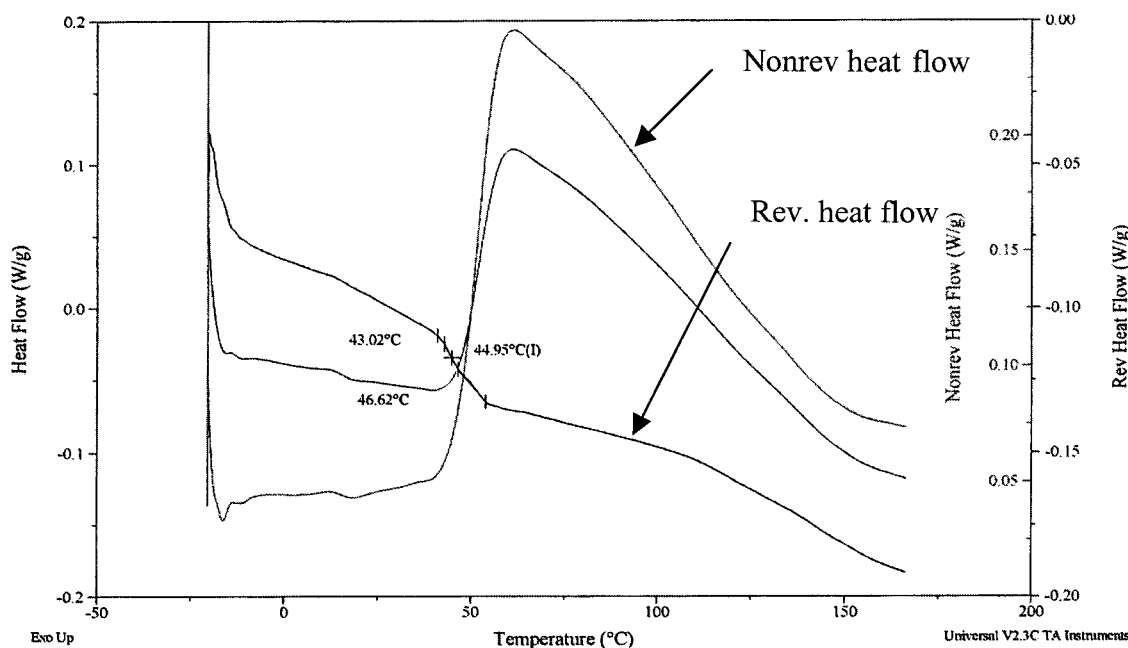
**Figure 1** DSC curve for DGEBA with 3 wt % of UVI6974 Sulphonium Salt system (125- $\mu$ m coating) over the temperature of 30 to 220°C, cured at 20 Mrad.

oxies using normal DSC analysis,<sup>19,23</sup> the modulated DSC technique (MDSC) has been shown to be a more accurate method of analysis particularly for high-density crosslinked systems.<sup>7</sup> Figure 1 shows the DSC curve of the DGEBA cured with 3% of sulphonium salt at 20 Mrad, using the Perkin-Elmer DSC 7. The glass transition is not clear from the curve. On the other hand, Figure 2 shows the MDSC results of the same sample. The instrument measures the reversible heat flow, the nonreversible heat flow, and the total heat flow, which is a combination of the former two components. The glass transition region, which is a reversible phenomenon, is clearly apparent as a

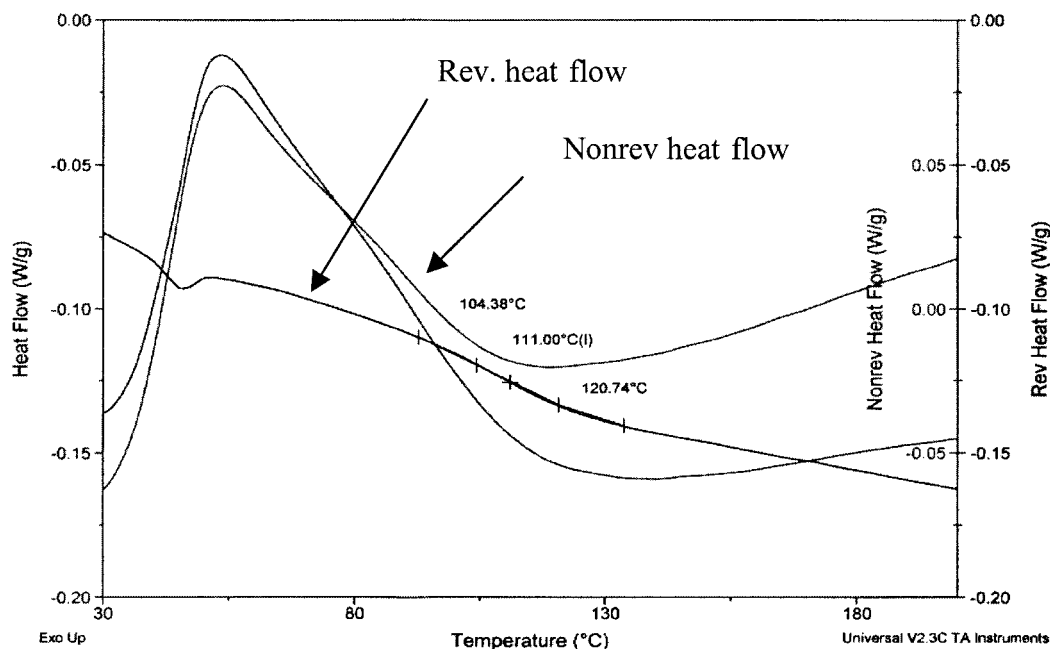
step change on the reversible heat flow signal. The broad change in slope at around 40 to 60°C for the reversing heat flow curve probably reflects the broad range of  $T_g$  values obtained for the coating. The reason for this is because the electron beam is attenuated across the thickness of the coating, resulting in a higher dose received for the surface compared to the bottom. An exothermic peak also appears from 45 to 60°C in the nonreversing heat flow curve, similar to the DSC result in Figure 1. It is interesting to note that the  $T_g$  signal in the normal DSC is not evident because the exothermic peak could overlap the  $T_g$  signal. In the MDSC scan, the  $T_g$  signal could be detected clearly because of the split signals of the total heat flow.

### Dark Curing

One of the interesting postcuring phenomenon observed for electron beam-cured cationic polymerization systems, is that curing seems to take place spontaneously even after exposure to the electron beam has ceased. A plausible explanation for this phenomenon could be due to the ions generated during radiation. Unlike the case for free radical polymerization, these ions cannot recombine to terminate the reaction, but have to react with terminating nucleophilic species to



**Figure 2** The MDSC curves for DGEBA with 3 wt % of UVI6974 Sulphonium Salt system (125- $\mu$ m coating) over the temperature of -30 to 180°C, cured at 20 Mrad.



**Figure 3** MDSC curves of 125  $\mu\text{m}$  Cycloaliphatic Epoxide (ERL4221E) coating with 3 wt % photoinitiator UVI6974, cured with 5 Mrad and dark cured for 1 h with no refrigeration.

terminate the curing process. Because the systems used was without solvent, chain transfer would most likely occur with the reactive monomers to terminate the propagating chain.<sup>7</sup> However, this mechanism also generates a reactive species to further propagate polymerization. The polymerization can, therefore, proceed for a considerable time even after the irradiation has stopped. This phenomenon has been commonly referred to as dark curing.<sup>2--26</sup> This explains why cationic polymerization is not inhibited by oxygen, and as such, dark curing can occur even in the presence of oxygen.

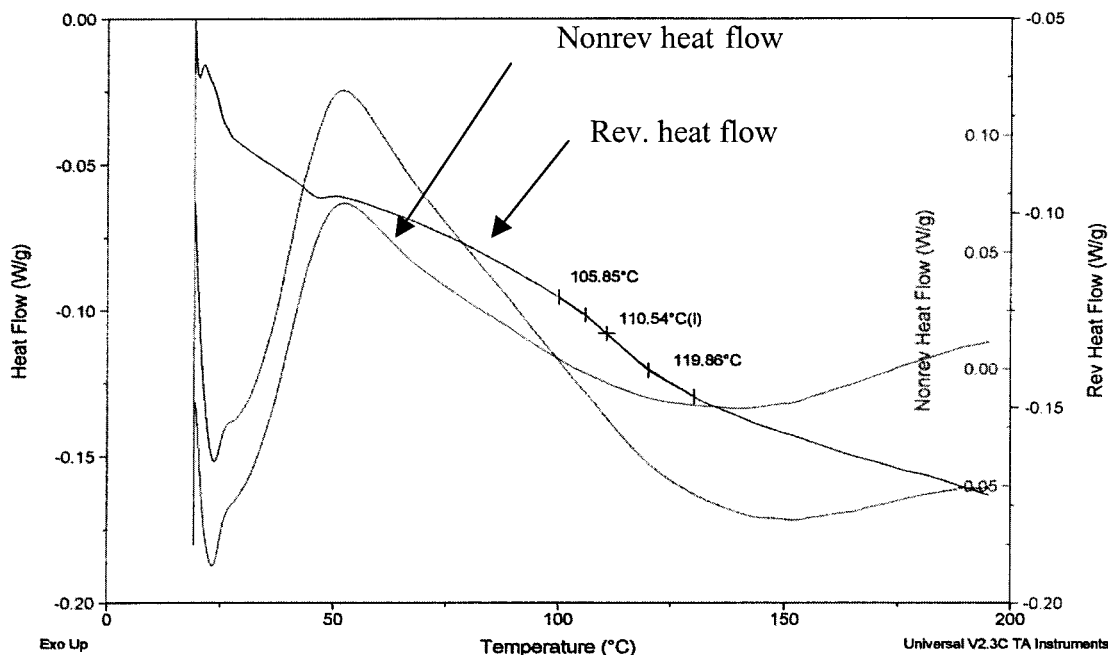
Care was taken to minimize the variation in the degree of dark curing among samples, after exposure to the electron beam. This was necessary to accurately establish the level of degree of cure and glass transition reached for an applied dose. To characterize the associated dark curing phenomenon, each of the EB-irradiated samples was left to dark cure at room temperature for 45 min before putting into the freezer at  $-20^\circ\text{C}$  to arrest further curing. Figure 3 shows the MDSC scan of a cycloaliphatic epoxy with sulphonium salt after irradiation to 5 Mrad and dark cured at  $25^\circ\text{C}$  for 1 h. Figure 4 shows the MDSC scan for the same sample, but which was frozen at  $-20^\circ\text{C}$  for 5 days after irradiation and retrieved to dark

cure for 1 h at  $25^\circ\text{C}$ . Both samples were found to have comparable  $T_g$  values of 104 and  $106^\circ\text{C}$ , respectively, indicating that freezing was fairly effective in termination of the dark curing process.

### $T_g$ vs. Dose Relationship

For three-dimensional polymer network systems, similar to ones under the present study, complete curing of the system is usually not achieved. This is because the onset of curing itself becomes a hindrance to further intermolecular movement, leading to residual unreacted functional groups. Inevitably, the unreacted functional groups become entangled and trapped within the matrix, with a corresponding drop in the maximum  $T_g$  achieved. This explains why the maximum limiting  $T_g$  is not always close to 100%.

Figure 5 shows the  $T_g$  values vs. the radiation dosage for the cycloaliphatic epoxy coatings with 3 wt % of both sulphonium and iodonium salts. As observed, for both the photoinitiators, the initial increase in glass transition temperature of the cured resin for the first dosage of 5 Mrads is quite high, reaching a limiting maximum at 10 Mrad. Subsequent exposure to obtain higher dosages, does not achieve much of an increase, albeit, a



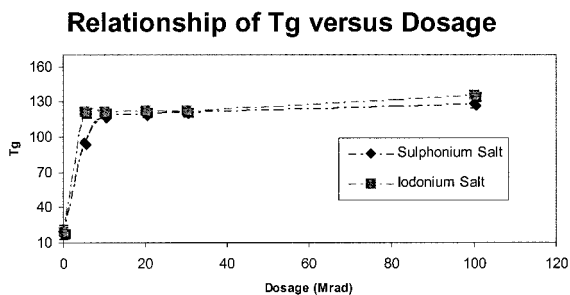
**Figure 4** MDSC curves of 125  $\mu\text{m}$  Cycloaliphatic Epoxide (ERL4221E) coating with 3 wt % photoinitiator UVI6974, cured with 5 Mrad, refrigerated, and dark cured for 1 h.

small increase at excessive dosage of 100 Mrads. Evidently the initial dose of the E-beam was sufficient to dissociate the  $\text{SbF}_6^-$  (hexafluoroantimonate) counterion, thus immediately allowing the fast cure rates to occur. These results agree with reports that  $\text{SbF}_6^-$  is more effective than salts with other counterions in producing an optimum cure at low doses.<sup>25–27</sup> The marginal increase in the glass transition above about 30 Mrad could be due to the dosage applied, which is high enough to initiate the crosslinking of the free monomer functions remaining in the system after the initial dose. Results in Figure 5 also indicate that the coatings with iodonium salt as the pho-

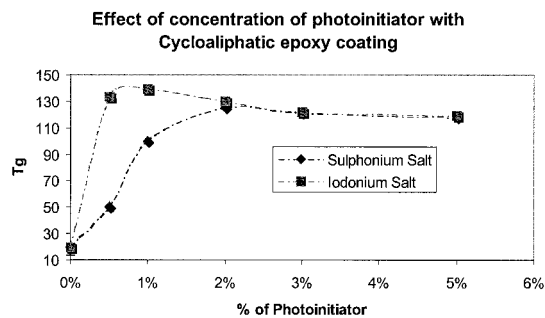
toinitiator had higher glass transition values than those with sulphonium salt, for all doses.

#### Optimum Concentration of Photoinitiator in the E-beam-Cured Epoxy Coating

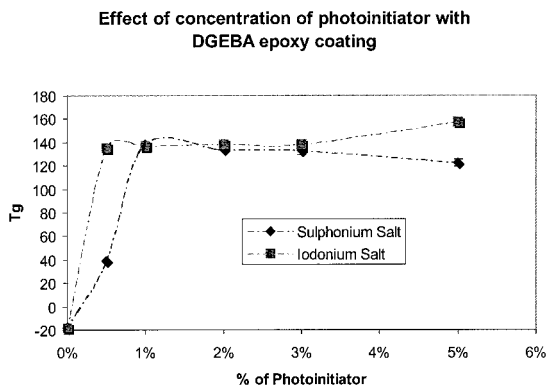
Figures 6 and 7 show the  $T_g$  values against the wt % of photoinitiators used for both cycloaliphatic epoxy and DGEBA coatings after they have been electron beam cured at 30 Mrad. For the cycloaliphatic epoxy system with iodonium salt, the  $T_g$  value increased up to a maximum value at 1 wt % and then actually decreased with further addition, probably indicating that the excess salt has



**Figure 5** Relationship between  $T_g$  and dosage for electron beam-cured cycloaliphatic epoxy with 3 wt % of sulphonium salt and iodonium salt as photoinitiator.



**Figure 6** Effect of concentration of photoinitiator with electron beam-cured cycloaliphatic epoxy coating.



**Figure 7** Effect of concentration of photoinitiator with electron beam-cured DGEBA epoxy coating.

an adverse plasticizing effect on the property. The addition of the sulphonium salt increased the  $T_g$  to a limiting maximum value at about 3 wt %, after which the increase was not significant, as observed from Figure 6. Evidently, unlike the iodonium salt, the excess amount of sulphonium did not appear to have the plasticizing effect. In both cases, the optimum concentration of about 3 wt % of photoinitiator appears corroborative of the results obtained by Udagawa for an E-beam-cured cycloaliphatic epoxy with TPSHA (Triphenylsulphonium Hexafluoroantimonate) as the photoinitiator analyzed by DMA.<sup>16</sup>

Figure 7 shows similar plots for the DGEBA system. The  $T_g$  value increased to a maximum at 1 wt % of sulphonium salt and then decreased with further addition up to 5%, indicating that, unlike the case for cycloaliphatic epoxy, the excess sulphonium salt did have a plasticizing effect for the DGEBA system. The addition of iodonium salt conversely gave a limiting maximum but  $T_g$  did not drop in value with further addition, indicating that excess of iodonium salt in DGEBA did not have an adverse plasticizing effect.

#### Percent Conversion Analysis by FTIR

One significant advantage of using the FTIR approach is that the method works easily for a thin coating of irradiated film.<sup>20</sup> Typically, an IR spectrum<sup>28–30</sup> has two major regions: the near IR that covers approximately the interval between 14,000 and 4000  $\text{cm}^{-1}$  and the mid-IR that covers the region between 4000 and 400  $\text{cm}^{-1}$ . Whereas the mid-IR is mainly concerned with characteristic fundamental bands (hence known as the fingerprint region) of organic compounds, the near-IR

region is associated with fewer bands, which are mostly the harmonic overtones of the fundamental and combination bands (of mid-IR region) associated with hydrogen atoms.

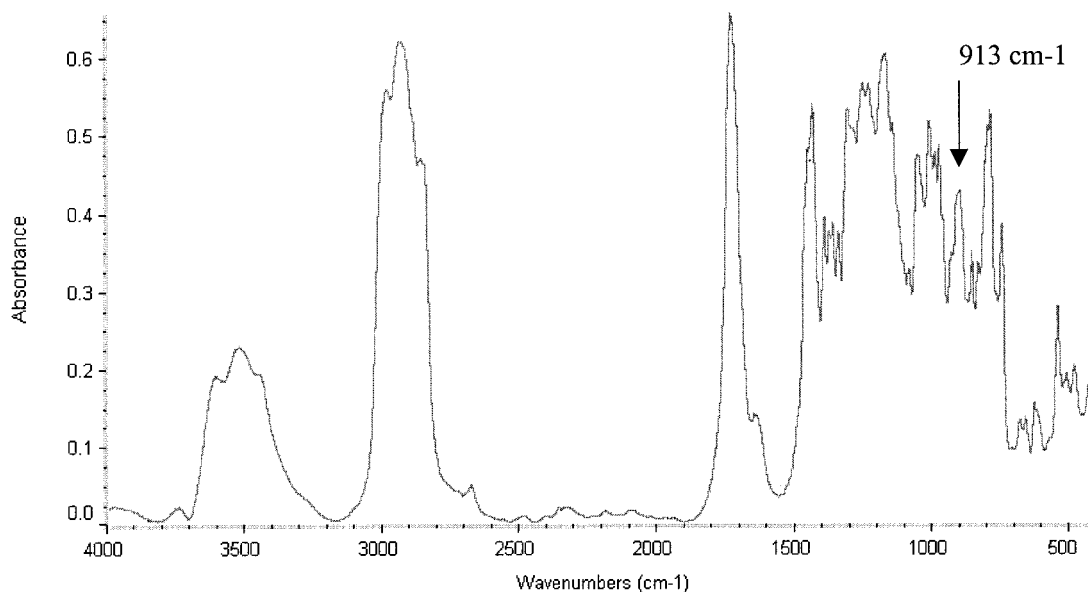
The small ring epoxy compounds usually absorb at three positions in the mid IR region: a medium-intensity symmetric stretching vibration in the range of 1280–1230  $\text{cm}^{-1}$ , a strong asymmetric band between 950 and 815  $\text{cm}^{-1}$ , and a strong band between 880 and 750  $\text{cm}^{-1}$ . Most of the studies pertaining to epoxy resins have been done at the mid-IR region by following the disappearance of the asymmetric C—H<sub>str.</sub> of the small ring epoxy group at 910–915  $\text{cm}^{-1}$ . However, a few studies have also been carried out by following the disappearance of the peak at 4530  $\text{cm}^{-1}$  (epoxy combination band, stretching and bending) in the near IR region.

Figure 8 shows the FTIR spectrum of an uncured epoxy formulation. We evaluated the peak height (instead of peak area) both before and after curing of the resin at 913  $\text{cm}^{-1}$ . The reactive peak heights at constant peak position (913.16  $\text{cm}^{-1}$ ) and fixed baseline (946.89–877.47  $\text{cm}^{-1}$ ) were normalized against the reference peak (CH<sub>2</sub> str.) at 2936.2  $\text{cm}^{-1}$  (baseline positions at 3187.8–2699.9  $\text{cm}^{-1}$ ). Software was used for the calculation of the peak height ratio, and the degree of conversion was obtained from the relationship described above.

Figure 9 depicts the IR spectra of cured samples (3 wt % iodonium salt) at different exposure levels. As expected, the absorption maximum at 913  $\text{cm}^{-1}$  goes on decreasing with increasing E-beam dosage, a result of diminishing epoxy functional groups.

Figure 10, on the other hand, shows the combined IR spectra of epoxy samples exposed at a fixed E-beam dose (30 Mrad), but at different photoinitiator concentrations (iodonium salt). Increasing photoinitiator concentration does affect the extent of curing, as is evident from the peak absorption of epoxy functionality.

Figure 11 shows the plot of the percent conversion vs. the radiation dosage for the cycloaliphatic epoxy for both photoinitiators at a concentration of 3 wt %. As for the results from the MDSC of cured resin, the increase in  $T_g$  for dosages above 10 Mrad was very small. This was indicative of the resins attaining a near ultimate degree of conversion that changes significant little upon further exposure. As observed from Figure 11, both resins achieved a conversion of close to 60% at a dosage of 5 Mrad. However, the percent conversion does increase until about 30 Mrad, at



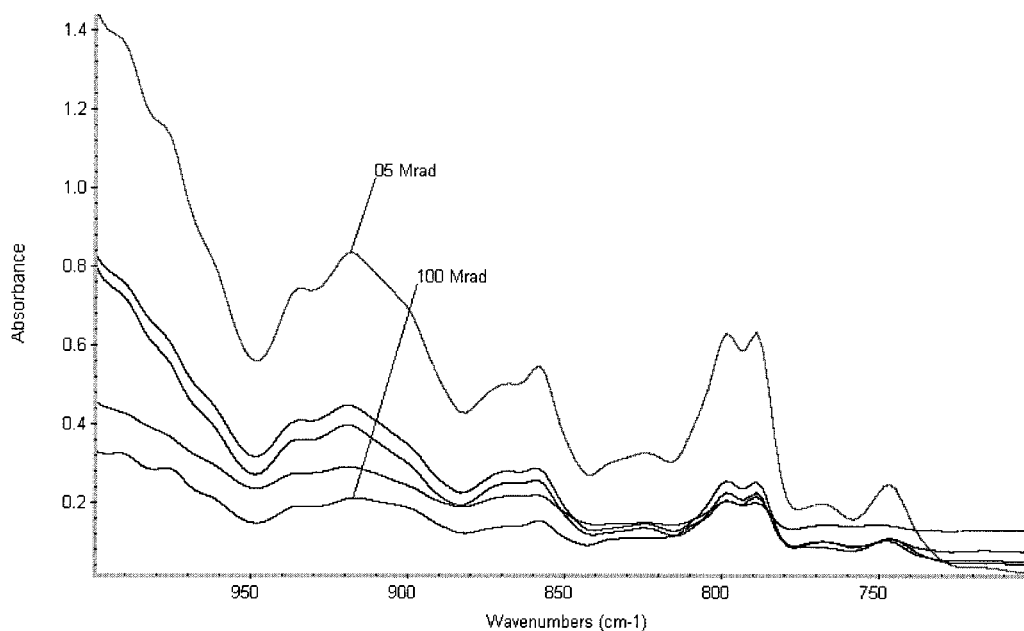
**Figure 8** An illustration of the FTIR spectrum of an uncured epoxy formulation.

which point it reaches a maximum under the experimental conditions.

Figures 12 and 13 show the plots of the percent conversion vs. concentration of photoinitiators for both cycloaliphatic epoxy and DGEBA at a dosage of 30 Mrad. The percent conversion for both coatings incrementally reached 60% at about 3% concentration of photoinitiator and then leveled off.

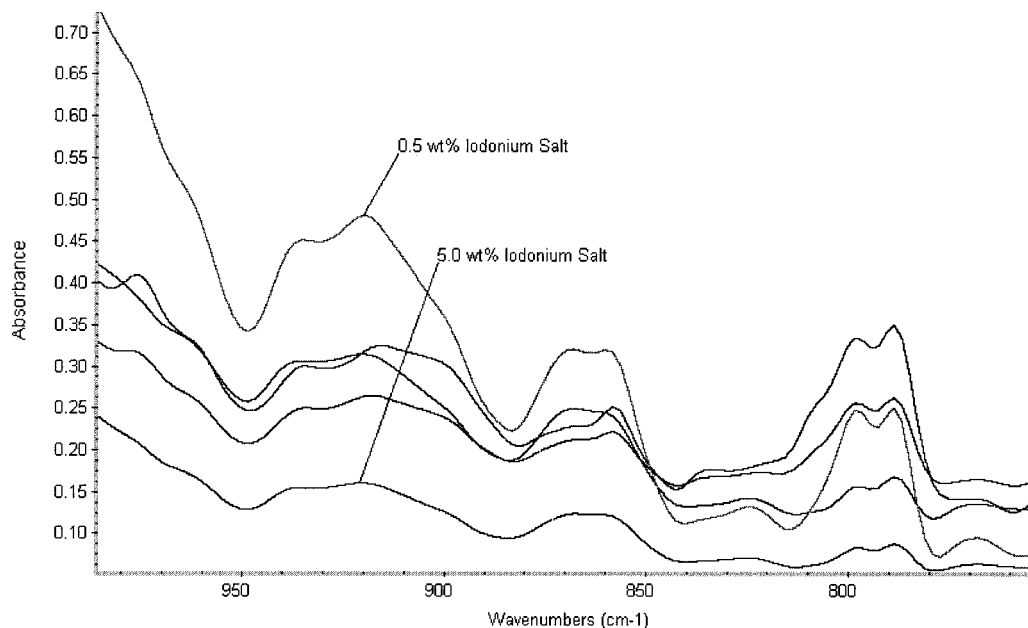
This indicates that the coatings had reached optimum percent conversion with just 3% concentration of the photoinitiator.

The percent conversion for both coatings incrementally reached 80% at about 100 Mrad, indicating that an increase in the degree of conversion after the initial dosage could only be achieved after excessive dosage.<sup>18</sup> Comparatively, the iodo-



**Figure 9** Variation of epoxy absorption peak at  $913\text{ cm}^{-1}$  with increasing exposure to E-beam (iodonium salt as photoinitiator).





**Figure 10** Effect of photoinitiator concentration (iodonium salt) on epoxy absorption at constant exposure (30 Mrad).

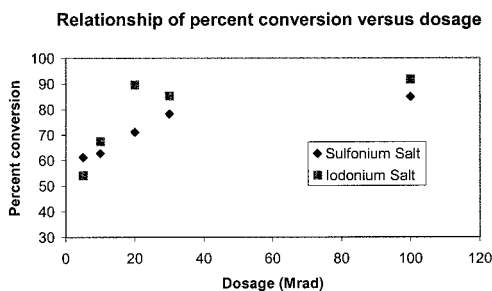
nium salt coating gave higher conversion results than did the coatings with sulphonium salt as the photoinitiator.

**CONCLUSION**

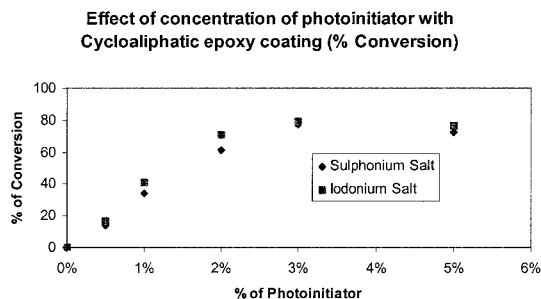
Two conventional epoxy systems, namely a cycloaliphatic and a DGEBA type epoxy, were successfully cured with a 175-keV electron beam, using both diaryliodonium and sulphonium as radiation initiators. Optimal curing was achieved after only a 5-Mrad dose exposure at room temperature, yielding glass transition temperatures suitable for microelectronics applications. The dose–glass transition relationship and the dose–conversion relationships were obtained using

modulated DSC and FTIR techniques. The diaryliodonium salt appeared to be more effective than the sulphonium for cationic polymerization under electron beam initiation. The optimal photoinitiator concentration for the two epoxy systems, using both initiators, was shown to be about 3 wt %.

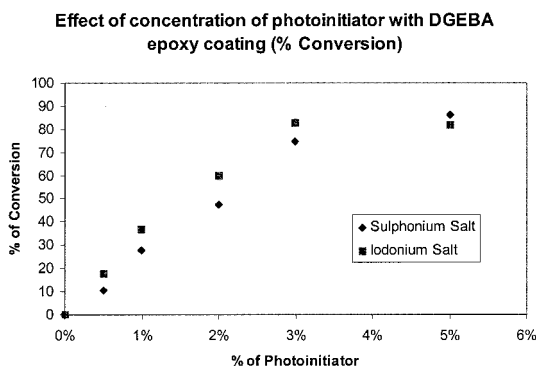
The authors would like to acknowledge Union Carbide Asia Pacific Inc. for providing the monomer and sulphonium photoinitiator, and also Sartomer Co. Inc. for providing the iodonium salt photoinitiator. We would also like to thank S.C. Low of Union Carbide Asia Pacific Inc. and K.T. Yeo of Sartomer Co. Inc. for their assistance in providing the materials for use.



**Figure 11** The relationship between the percent conversion vs. dosage.



**Figure 12** Effect of concentration of photoinitiator vs. % conversion of electron beam-cured Cycloaliphatic epoxy coating.



**Figure 13** Effect of concentration of photoinitiator vs. % conversion of electron beam cured DGEBA epoxy coating.

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