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ELECTRON BEAM CURING OF EPOXY RESINS BY CATIONIC POLYMERIZATION

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ABSTRACT

A Cooperative Research and Development Agreement (CRADA) sponsored by the Department of Energy Defense Programs and 10 industrial partners has been established to develop high performance Electron Beam (EB) curable polymer matrix composites. EB curing of composites has a number of advantages over conventional thermal curing. Composites cured by EB have much shorter cure times, lower overall energy requirements, and reduced thermal stresses in the cured part. Furthermore, less expensive tooling can be used since the process occurs at lower temperatures. Preliminary investigations have determined that conventional epoxy resins can be cured at selectable temperatures with high glass transition temperatures (essentially the same as with thermal curing), while still exhibiting equivalent or comparable mechanical properties. A cationic photoinitiator at a concentration of 1-3 parts per hundred of the epoxy resin is required for this process. Gamma cell screening of cationic photoinitiators with bisphenol A, bisphenol F, and cycloaliphatic epoxies demonstrated that diaryliodonium salts of weakly nucleophilic anions such as hexafluoroantimonate are most effective. Diaryliodonium salts were also found to be the most effective initiators for the cationic polymerization of epoxy resins when a high energy/power electron beam accelerator was used as the source of ionizing radiation. For example Dow Tactix 123 (bisphenol A epoxy) containing 3 phr (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate was irradiated at a total dosage

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of 100 kGy. Glass transition temperature (tan delta) of the cured material as determined by dynamic mechanical analysis was 182°C as compared to 165°C thermally cured material.

KEY WORDS: Electron Beam Curing; Epoxy Resins; Cationic Photoinitiators

1. INTRODUCTION

As part of a Cooperative Research and Development Agreement (CRADA) sponsored by the Department of Energy Defense Programs, this project has the development of high performance Electron Beam (EB) curable matrix resins as one of its major objectives. EB curing of polymer matrix composites is a nonthermal curing method that uses high energy, high power electrons and/or X-rays at controlled rates to initiate polymerization and crosslinking. EB curing of composites offers substantially reduced cure times, lower overall energy requirements, reduced thermal stresses, and the use of less expensive tooling. Monomers and oligomers containing acrylate and methacrylate groups have been extensively used as EB curable coatings and adhesives. However, the polymers produced by crosslinking these materials are of little value for the high performance requirements of aircraft and aerospace composite applications. Limitations of such systems include low glass transition temperature (or low service temperature), low fracture toughness, and high shrinkage when cured. What is desired is a means by which higher performance resins can be processed at selectable temperatures, cured by means of EB radiation, and still achieve thermal and mechanical properties equal to or better than thermally cured resins.

A method of curing epoxy resins, which are widely used for aircraft and aerospace applications, by means of EB radiation would be extremely useful. Visible - ultraviolet curing of thin films of cycloaliphatic epoxies using cationic photoinitiators is well known (1), but these processes are limited to thin coatings due to the low penetration of visible-ultraviolet radiation. Thermal and mechanical properties of these materials are low and curing is incomplete. Crivello has recently disclosed a series of highly reactive cycloaliphatic silicone epoxies which are EB curable in the presence of certain cationic photoinitiators (diaryliodonium and triarylsulfonium salts) (2,3). These compounds are also known to be photoinitiators for visible - ultraviolet cured cationic epoxy compositions. However, it has been reported that examples of these same types of photoinitiators do not lead to complete EB curing of certain cycloaliphatic epoxies (4). It would appear that in some cases cationic photoinitiators react upon exposure to high energy EB radiation to produce cationic species which are capable of propagating cationic polymerization. Degree of curing appears to vary considerably. A systematic and reasonably comprehensive screening of possible photoinitators and commercially available epoxy resins was therefore the initial step in the effort to develop high performance EB curable epoxy resins. The initial screening was conducted using a ^{60}Co gamma cell. Promising photoinitiator-epoxy resin compositions were then cured using a high energy EB accelerator. Thermal and mechanical properties were determined and the data used to optimize the photoinitiator-epoxy resin system.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Epoxy Resins Samples of commercial epoxy resins were obtained from various manufacturers. These are described in Table 1.

2.1.2 Photoinitiators Samples of commercial photoinitiators were obtained from various manufacturers. Others were either purchased as research samples or synthesized (Table 1).

2.2 Gamma Cell Evaluation Initial photoinitiator resin screening was performed in an Atomic Energy of Canada Limited (AECL) Gammacell 220 ^{60}Co gamma cell (does rate: approx. 100 Gy/min.) at the AECL Whiteshell Laboratories, Pinawa, Manitoba. For preliminary determination of reactivity, a concentration of one part per hundred (phr) of active initiator was used. In many cases heating was required to dissolve the photoinitiator in the resin. Several milliliters of the mixture was placed in a vial to which a thermocouple was attached (Figure 1). An inert material (water or cured resin) was used as reference. Samples and reference were then placed in an insulated container and lowered into the gamma cell. In this manner up to eight samples were evaluated simultaneously. Data obtained and tabularized in Table 2 are: exothermic temperature increase (ΔT), dose at exotherm maximum, and physical state after gamma irradiation at maximum dose of approximately 10 kGy.

2.3 Electron Beam Accelerator All electron beam irradiation was performed at the Whiteshell Laboratories of AECL using the I-10/1 Electron Linear Accelerator (Energy, 10MeV; Power, 1kW).

2.4 EB Cured Specimens The epoxy-photoinitiator mixture was poured into an aluminum mold (specimen thickness, 3.1mm) which was treated with a release agent. Thickness of the side plates was 1.6mm. Specimens were irradiated in multiple passes of 50 kGy per pass.

2.5 Thermally Cured Specimens Control specimens were prepared by dissolving Elf Atochem ATO Boron Fluoride Monoethyamine Complex (boron trifluoride monoethylamine complex) in the epoxy resin at 3 phr concentration. The specimen in a metal mold (specimen thickness, 3.1 mm) was staged to a maximum temperature of 177°C for three hours.

2.6 Dynamic Mechanical Analysis Dynamic Mechanical Analysis (DMA) was carried out using a Rheometrics Solids Analyzer RSA. II. The sample was placed in a dual cantilever tool, with an initial stress and strain of zero. The strain used for measuring the rehological properties was set at 0.1%. The temperature was raised at 2.5°C per step with a dwell time of 12 seconds. The frequency of the applied strain was 6.28 radians per second. Sample size was normally 3 mm x 7 mm x 55mm. Measurements were obtained using the software provided by Rheometrics for the instrument.

3. RESULTS AND DISCUSSION

While a great variety of epoxy resins are available, Dow Tactix 123 (a high purity bisphenol A diglycidyl ether) and Shell Epon 862 (a bisphenol F diglycidyl ether) were chosen for use in preliminary photoinitiator screening because they are both low viscosity versions of widely used classes of epoxy resins. Various cycloaliphatic epoxies as well as a high viscosity epoxy novolac were subsequently evaluated with several photoinitiators. Most of the available cationic photoinitiators are diaryliodonium or triarylsulfonium salts of weak bases. Diaryliodonium salts were known to be more effective ultraviolet photoinitiators than triarylsulfonium salts of the same anion (5). From the data in Table 2 it is seen that DPI SbF_6 (diphenyliodonium hexafluoroantimonate) is more effective than 6974 (a triarylsulfonium hexafluoroantimonate), assuming the gamma cell exotherms (ΔT) to be a relative indication of photoinitiator effectiveness when samples are subjected to ionizing radiation. Alkyl and alkoxy substituted aryliodonium hexafluoroantimonates such as TBPI Sb F_6 and OPPI are even more effective in catalyzing the cationic curing of Epon 862. This general relationship holds for the various types of epoxy resins evaluated although the cycloaliphatic epoxies tended to be substantially less reactive than the diglycidyl ethers of bisphenol A or bisphenol F.

The nature of the anion also influences the effectiveness of the photoinitiator in catalyzing ultraviolet curing. The anion effect has been described in the literature and is inversely related to the nucleophilicity of the anion (5).

$$SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$$

The less nucleophilic anion is less attracted to the Bronstead acid (proton) generated by the photolytic degradation of the diaryliodonium or triarylsulfonium groups thereby resulting in very strong or "super" acids which initiate cationic epoxy curing. Additionally, these weakly nucleophilic anions cannot react with the growing polymer chain. From the ΔT data in Table 2 this trend holds when these photoinitiatiors are subjected to ionizing radiation. This trend is most evident with the diphenyliodonium salts of SbF_6^-, AsF_6^-, PF_6^-, and $CF_3SO_3^-$ when mixed at a concentration of 1 phr with Tactix 123 or Epon 862. The effect of the photoinitiator is dramatically illustrated in Figure 2.

The aryl groups of the cation can also have a profound influence upon reactivity. For example, with Epon 862 at 1 phr OPPI (aryl groups are 4-octyloxyphenyl, and phenyl) the reaction is more strongly exothermic than when TBPI SbF_6 (both aryl groups are 4-tert-butylphenyl) is used, which is more strongly exothermic than when DPISbF_6 (both aryl groups are phenyl) is used. From the data of Table 2 it is apparent that OPPI is by far the most effective photoinitiator when used with bisphenol A or bisphenol F based diglycidyl ethers.

OPPI and 6974 were chosen as the photoinitiators to be used for the EB curing studies. OPPI was chosen because it was the most effective photoinitiator evaluated in the gamma cell experiments and 6974 was chosen because it was the most effective triarylsulfonium salt and was readily available and widely used as an ultraviolet photoinitiator. The epoxy resins chosen were the same as for gamma cell evaluation so that gamma cell reactivity could be compared with degree of curing when irradiated by EB radiation. A range of photoinitiator concentrations were tried in order to find an optimal concentration. It was decided that amine cured resins would not be directly comparable to the EB cured resins since the amine becomes a substantial part of the polymer network. Properties are therefore highly dependent upon the particular amine used. The thermal curing mechanism most similar to EB curing is cationic curing with Lewis acids. Accordingly, control specimens were prepared using boron trifluoride monoethylamine complex. Specimens were stage heated to a maximum temperature of 177°C for three hours. Dynamic Mechanical Analysis (DMA) of the EB and thermally cured specimens provided a comparison of glass transition temperature (Tg), and retention of modulus at elevated temperature (initial service temperature: temperature at which the flexural modulus is 50% of its room temperature value).

From the results tabularized in Table 3, it is evident that OPPI is much more effective than 6974 as an initiator for the cationic EB curing of Tactix 123 and Epon 862. In this study, using Tg as the measure of cure, 6974 formulations do not achieve the cure of OPPI formulations regardless of concentration. Optimal OPPI concentrations appear to be 1 - 3 phr at 100 kGy. If OPPI is used as photoinitiator the Tg's of the bisphenol A and bisphenol F epoxy resins are higher than those of the corresponding thermally cured resins. Results obtained with 6974 do not equal thermally cured material. With Tactix 123 containing 3 phr OPPI the Tg (tan delta) was 17°C higher for EB curing versus thermal curing.

EB curing results correlate to gamma cell screening regarding effectiveness of OPPI versus 6974 and the effect of photoinitiator concentration. The properties of EB cured epoxies tend to degrade above 3-4 phr of either photoinitiator. In the gamma cell peak ΔT is reached at this level.

The high Tg's and degree of cure achieved by EB curing using cationic photoinitiators significantly contradicts previous reports. When $DPIPF_6$ at a concentration of 2% was used with a cycloaliphatic epoxy (3′,4′- epoxycyclohexylmethyl 3, 4- epoxycyclohexane carboxylate) a maximum cure of approximately 60% was achieved at 50 kGy (4). Continued irradiation was ineffective. It has also been reported that EB irradiation of this compound and conventional bisphenol A diglycidyl ethers in the presence of diaryliodonium and triarylsulfonium salts does not achieve curing at reasonable doses (2). Polymerization occurred only after massive doses (1000 - 3000 kGy) were applied. A possible explanation may be that both research groups utilized low energy/low power electron beam accelerators. Our results may only be applicable to EB curing using accelerators with energy and power in the order of 10MeV/1kW. Dose rate may be as important as total dosage. While this paper described only preliminary results, additional efforts are well underway to formulate higher performance EB curable epoxy blends, toughen these materials, and use these compositions to fabricate EB curable epoxy composites. A patent application on the cationic EB curing of epoxy resins has been filed.

4. CONCLUSIONS

Gamma cell screening of cationic photoinitiators with bisphenol A, bisphenol F, and cycloaliphatic epoxies demonstrated that diaryliodonium salts of weakly nucleophilic anions such as hexafluoroantimonate were particularly effective as catalysts for radiation induced cationic epoxy curing. This relationship corresponds well to results obtained using a high energy electron beam accelerator. Glass transition temperatures as high as 182°C (compared to 165°C for thermal cure) and good mechanical properties were obtained with bisphenol A based epoxy resins at a dose of 100 kGy.

5. REFERENCES

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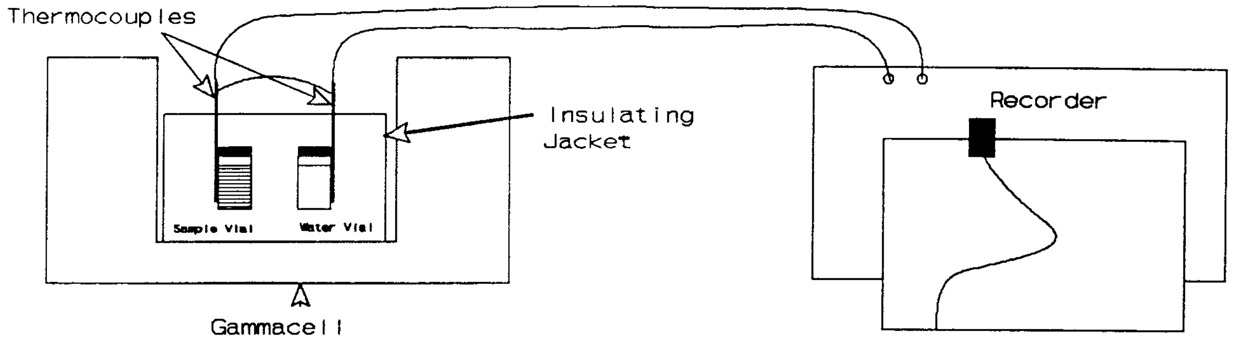

Figure 1. Experimental Setup for Gamma Calorimetry Experiments

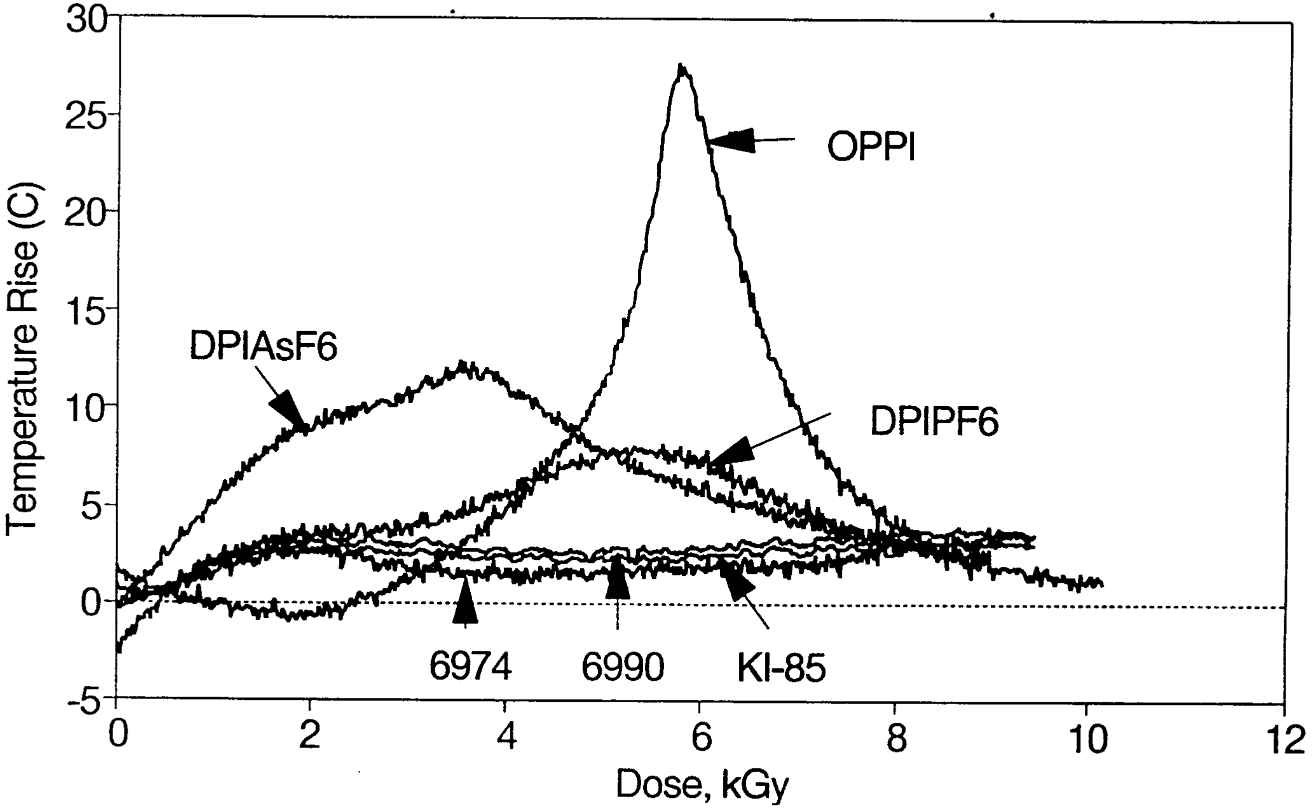

Figure 2. Gamma Cell Radiolysis of Tactix 123 with Various Photoinitiators (Concentration: 1 phr Active Photoinitiator; Dose Rate: 6 k Gy/h).

Table 1

Description of Materials

Epoxy Resins	**Description**
Tactix 123	Dow Tactix 123: High purity, low viscosity diglycidyl ether of bisphenol A; Epoxy Equiv. wt., 172-176; Viscosity at 25°C, 4400-5600 cps.
Epon 862	Shell Epon 862: Diglycidyl ether of bisphenol F; Epoxy equiv. wt., 166-177; Viscosity at 25°C, 3000-4500 cps.
ERL 2258	Union Carbide ERL 2258 (Discontinued): 50:50 blend of bis(2,3-epoxycyclopentyl) ether (ERL 4205) and diglycidylether of bisphenol A.

Cationic Photoinitiators	**Description**
OPPI	General Electric Aryl Fluoroantimonate, Product 479 - 2092 C: (4-Octyloxyphenyl)phenyliodonium hexafluoroantimonate; mp 55-60°C.
DPIAsF6	Diphenyliodonium hexafluoroarsenate: TCI America; mp 130°C.
DPIPF6	Diphenyliodonium hexafluorphosphate: TCI America; mp 142°C.
DPISbF6	Diphenyliodonium hexafluorantimonate: Prepared from diphenyliodonium chloride and sodium hexafluoroantimonate; mp 124°C.
DPITF	Diphenyliodonium trifluoromethanesulfonate: TCI America; mp 178°C.
TBPISbF6	Bis(4-tert-butylphenyl)iodonium hexafluoroantimonate: Midori Kagaku Co., Ltd.; mp 184°C.
6974	Union Carbide Cyracure UVI 6974: 50% solution of triarylsulfonium hexafluoroantimonate in propylene carbonate.
6990	Union Carbide Cyracure UVI 6990: 50% solution of triarylsulfonium hexafluorophosphate in propylene carbonate.
KI 85	Degussa Degacure KI 85: 50% Solution of triaryl sulfonium hexafluorophosphate in propylene carbonate.
Irg. 261	Ciba Irgacure 261: (n^5-2,4-Cyclopentadien-1-yl) n^6-isopropylbenzene) Iron(II) hexafluorophosphate; mp 85-88°C.

Table 2

Gamma Screening Studies for Various Photoinitiators and Epoxy Resins

Resin	Photoinitiator	PI Concentration (phr)	Gamma ΔT (°C)	Dose @ Peak Exotherm (kGy)	Effect @ RT after EB cure
Tactix 123	OPPI	1	27.8	5.8	H
	$DPIAsF_6$	1	12.4	3.5	H
	$DPIPF_6$	1	8.2	5.6	MH
	6974	1	4.2	9.9	S-H
	6990	1	4	8.7	NC-S
	KI-85	1	3.3	8.7	NC-S
	IRG.261	1	3	9.2	VI
	DPITF	1	1.8	6.1	NC
Epon 862	OPPI	1	57.4	6.4	H
	$TBPISbF_6$	1	14.2	7.2	H
	$DPISbF_6$	1	10.5	10	H
	6974	1	7.1	3.4	S-H
	KI-85	1	4.3	4.2	NC-S
	6990	1	3.4	4.2	NC-S
ERL 2258	OPPI	1	18.3	5.4	H
	6974	1	5.1	4.6	S

Note: H - Hard, MH - Medium Hard, S - Soft, VI - Viscosity Incease, NC - No Change, S-H - Soft after irradiation, then Hard next day, NC-S - No change after irradiation, then Soft next day.

Table 3

Electron Beam (EB) Cured vs. Thermal Cured Epoxy Resins

Resin	Photoinitiator	PI Conc. (phr)	Tg (°C) Tan Delta	Tg (°C) E"	Initial Service Temp.[1] (°C)	Weight Gain[2] (%)
Tactix 123	Thermally Cured[3]	NA	165	148	140	1.77
	6974	3	134	92	94	
	OPPI	3	182	164	156	1.41
Epon 862	Thermally Cured[3]	NA	153	138	125	1.78
	6974	3	149	102	104	
	OPPI	3	164	141	134	1.51[4]
ERL 2258	Thermally Cured[3]	NA	218	186	173	4.19
	OPPI	3	192	174	147	5.3

Note: 1 - Initial Service Temperature defined as temperature at 50% of 25°C Flexural Modulus; 2 - Weight gained after 48 hour water boil; 3 - Thermally Cured with 3 phr of boron trifluoride monoethylamine; 4 - PI Conc. of 2 phr. EB Dose: 100 kGy

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