Chem. Mater. **1997,** *9,* 1273−1284

# Fabrication of Epoxy Matrix Composites by Electron Beam Induced Cationic Polymerization[1]

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*Received January 5, 1997*⊗

This paper describes the use of high-energy electron beam radiation to fabricate high-performance epoxy resin matrix composites. Employing catalytic amounts of diaryliodonium and triarylsulfonium salt photoinitiators, it was found that graphite fiber reinforced composites based on epoxy monomers could be efficiently e-beam cured at room temperature when exposed to e-beam irradiation. A mechanism involving the reduction of the onium salt initiators by e-beam induced free radicals has been proposed. Strong protonic acids generated during the course of this reaction initiate the cationic ring-opening polymerization of the epoxy resins. This chemistry was employed to fabricate high-performance carbon fiber reinforced composites. The mechanical properties of the composites were measured and effects of blends with other epoxy monomers and additional types of particulate fillers were evaluated using various testing methods.

## Introduction

At the present time, one of the main impediments to the use of high-performance composites for general purpose applications is their high cost. One major contributor, the use of expensive reinforcements such as carbon fibers is being addressed and it appears that significant cost reductions in this area will be realized soon. Another component of the high cost is the current use of composite fabrication techniques which are not suitable for automation. These include complex hand lay-up and preforming processes, long devolatilization, and thermal curing cycles involving high temperatures. It is in this latter regime that we are directing our attention in an attempt to bring new chemistry and processing techniques to the field of high-performance composites.

The use of electron beam (e-beam) radiation to carry out rapid, pollution-free, low-energy cross-linking polymerizations (curing) make it a highly attractive technique replacing complex, time-consuming thermal cures for many applications including composite fabrication.[2] "E-beam curing" as it is called has been applied chiefly to multifunctional monomers polymerizable by free radical mechanisms, i.e., monomers such as unsaturated polyesters and multifunctional epoxy acrylates and methacrylates. Although these monomers have been employed for the fabrication of composites,[3−8] the thermal and mechanical properties of such composites are notably deficient.

The direct, e-beam induced "free cationic" (i.e., without initiators) polymerization of epoxide monomers has been previously described and proceeds vigorously at room temperature.[9,10] However, these types of polymerizations are impractical for composite applications since the monomers have to be rigorously purified and the polymerizations carried out under scrupulously oxygen- and water-free conditions. Furthermore, the extremely high and rather impractical e-beam or $\gamma$-ray doses required to produce even small amounts of polymer have not attracted much attention from the scientific community.[11] In an attempt to reduce the radiation dose required to polymerize epoxy monomers, the use of catalytic promoters was investigated. In this laboratory, we have been exploring the UV and thermally induced cationic polymerizations of a wide variety of cationically polymerizable monomers including epoxides.[12,13] Scheme 1 shows the generalized mechanism of an onium salt photoinitiated cationic polymerization illustrated with triarylsulfonium salt photoinitiators. A similar scheme can be written for diaryliodonium salt photoinduced polymerizations.

Interaction of a triarylsulfonium salt with light affords the excited sulfonium salt which decays with either a homolytic or heterolytic rupture of a carbon−sulfur bond (eq 1). The resulting highly reactive species (cations, cation radicals, and free radicals) decay by a number of pathways through reaction with the solvent or monomer (RH, eq 2) to generate a variety of products and the acid, HX. If the HX generated is a strong

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⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

(1) Preliminary results were reported in: Crivello, J. V.; Malik, R.; Walton, T. C. *A. C. S. Polym. Prep. 35* (2), 890. Crivello, J. V.; Malik, R.; Walton, T. C. NASA Final Report for Phase 1 SBIR Program, NAS1-19876-ASP-2014, June, 1993.

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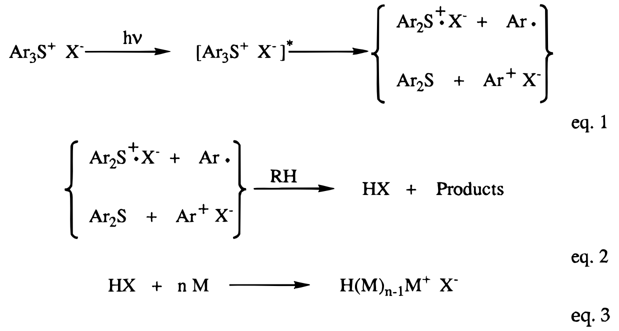
S0897-4756(97)00031-8 CCC: $14.00

**Scheme 1**



Brønsted acid, protonation of the monomer (eq 3) occurs rapidly to initiate cationic polymerization of epoxy as well as other types of monomers.

The main interaction of e-beam and $\gamma$-ray radiation with organic compounds is the cleavage of primary chemical bonds to form free radicals. It has been shown that certain free radicals can reduce onium salt photoinitiators to release acids in a similar manner as described in Scheme 1 for photolysis of these same compounds.[12] This suggested that onium salts could function as initiators or promoters for the e-beam and $\gamma$-ray induced cationic polymerization of epoxides. Further, we anticipated that the structure–reactivity relationships gathered from the onium salt photoinitiated polymerizations of epoxides might also apply to e-beam and $\gamma$-ray induced cationic polymerizations.

Initial work in this laboratory was directed toward the use of onium salt photoinitiators as rate-enhancing additives for the e-beam and $\gamma$-ray induced polymerization of epoxide monomers and gave very promising results.[1] Similarly, Russian workers[14,15] have employed sulfonium, diazonium, ferrocenium, and iodonium fluoroborate salts as cure adjuvants, while Davidson and Wilkinson[16] have used the hexafluorophosphate salts of the same onium salt compounds. Although it was clear from the data generated by these three groups that the use of onium salt promoters was effective in enhancing the rate of epoxide polymerization and lowering the required dose, dose levels remained much too high ($>$150 kGy) to be of practical use.

The objective of this effort is to develop epoxide systems that will polymerize rapidly and efficiently when exposed to e-beam radiation, requiring radiation doses comparable to existing acrylate or methacrylate monomers and yet having superior mechanical and thermal properties.

## Experimental Section

**Materials.** Epoxysiloxane difunctional monomer **I** and cyclic tetrafunctional monomer **II** were prepared as previously described from the corresponding silane and 4-vinylcyclohexene oxide (3-vinyl-7-oxabicyclo[4.1.0]heptane) using the hydrosilation reaction.[17,18] The resins were characterized by various techniques. Infrared spectra were obtained on a Buck Model 500 infrared spectrometer. $^1$H NMR spectra were recorded on a Varian 500 MHz nuclear magnetic resonance spectrometer. Elemental analyses were performed by Quantitative Analysis, Bound Brook, NJ. Other epoxy resins, Tactix 123, Epon resins (Epon 862, 825, 1031, and SU8), and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (UVR 6105) were obtained respectively, from the Dow Chemical, Shell Chemical, and the Union Carbide corporations and used without further purification. The onium salt initiators (4-(*n*-octyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC8**)[19] and *S*,*S*-diphenyl-*S*-(4-thiophenoxyphenyl)sulfonium hexafluoroantimonate (**SS**)[20] were prepared as previously reported. AG193P plain weave 3K (AS-4) carbon fiber fabric was supplied by the Hercules Corp. Other fillers, including carbon black (Colorblack S-160 and Printex U) and silica (Aerosil 380), were obtained from the Degussa Corp.

**Synthesis of Cyclic Epoxide III.** Into a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and an addition funnel were placed 24 g (0.1 mol) of 2,4,6,8-tetramethylcyclotetracyclosiloxane and 10 mg of tris(triphenylphosphine)rhodium(I) chloride. The reaction mixture was heated to 110 °C, and there were added 52.1 g (0.42 mol) of distilled 3-vinyl-7-oxabicyclo[4,1,0]heptane via the addition funnel at such a rate that to maintain the temperature at 110 °C. After 8 h, the reaction mixture was cooled to room temperature yielding viscous, colorless oligomer **III**.

**Synthesis of Cyclic Oligomer IV.** The above reaction was repeated decreasing the 3-vinyl-7-oxabicyclo[4,1,0]heptane to 37.2 g (0.30 mol) and combining this with 5.5 g (0.05 mol) of 1,7-octadiene. Reaction was conducted at 110 °C for 3 h, resulting in viscous oligomer **IV**.

**Synthesis of Oligomer V.** To a 100 mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, addition funnel, and nitrogen bypass were placed 99.2 g (0.80 mol) of 3-vinyl-7-oxabicyclo[4,1,0]heptane and 33.6 g (0.20 mol) of 1-hexene. There was added 10 mg of tris(triphenylphosphine)-rhodium(I) chloride, and the reaction mixture heated to 80 °C. Then, 60 g (1.0 mol repeating groups) of a poly(methylhydrogen siloxane) oligomer (General Electric Silicones SS4300C) dropwise over the course of 1 h. The reaction mixture was heated for additional 2 h at 110 °C. After cooling, the reaction mixture was transferred to a rotary evaporator, and the remaining starting materials were stripped off under reduced pressure. Oligomer **V** was obtained as a viscous, colorless oil.

**Synthesis of Oligomer VI.** To 20 mL of toluene in a 100 mL flask equipped with a magnetic stirrer and a reflux condenser there were added 3.0 g of poly(methylhydrogen siloxane) (General Electric Silicones SF-1229), 6.7 g of 3-vinyl-7-oxabicyclo[4,1,0]heptane, and 5 mg of tris(triphenylphosphine)rhodium(I) chloride. The mixture was heated at 100 °C for 3 days. After cooling, the product was isolated in quantitative yield by removing the solvent on a rotary evaporator and then removing the last traces of solvents in a vacuum oven at 50 °C.

**Preliminary Reactivity Evaluations.** Preliminary evaluations of the reactivity of the epoxy resins were obtained by dissolving 0.5 mol % (4-(*n*-octyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC 8**) in the resins and then irradiating 1 mil (25 $\mu$m) films of the liquid resins with a 200 W General Electric H3T7 medium-pressure Hg arc lamp mounted at a distance of 10 cm from the sample. Tack-free times were determined as a measure of the reactivity. All of the resins cured to a tack-free state within 12 s irradiation.

**Evaluation of Graphite Fiber Sizing.** Graphite cloth (Hercules AG193P plain weave 3K (AS-4) fabric) was placed in a Soxhlet apparatus and extracted overnight with refluxing acetone. The resulting acetone solution was placed in a rotary evaporator and the acetone removed under reduced pressure, leaving a pale yellow oil. Small portions of the oil were added

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**Table 1. Mechanical Properties of Filled and Blended E-beam Cured Resins**[a]

| sample | monomer | filler or epoxy resin | IOC8 (mol %/ total epoxy groups) | dynamic modulus[c] (*G′*, GPa) |
|---|---|---|---|---|
| F1 | 100 parts **I** + 2.73 parts GPS[b] | 4 parts Aerosil 380 | 0.5 | 0.7 |
| F2 | 100 parts **I** | 12.7 parts Printex U | 0.5 | 0.8 |
| F3 | 100 parts **I** | 8.4 parts Colorblack S160 | 0.5 | 0.8 |
| B1 | 100 parts **I** | 100 parts Tactix 123 | 1.0 | 0.9 |
| B2 | 100 parts **I** | 97 parts Tactix 123 + 43 parts Epon 1031 | 0.8 | 1.1 |
| B3 | 100 parts **I** | 57 parts Tactix123 + 43 parts Epon SU−8 | 1.0 | 1.1 |
| B4 | 100 parts **II** | 50 parts Tactix 123 | 0.9 | 1.3 |
| B5 | 100 parts **II** | 35 parts Tactix 123 + 15 parts Epon 1031 | 0.85 | 1.4 |
| B6 | 100 parts **II** | 35 parts Tactix 123 + 15 parts Epon SU−8 | 0.85 | 1.4 |

[a] E-beam dose: 80 kGy. [b] GPS: glycidoxypropyltrimethoxysilane. [c] 25 °C.

**Table 2. Composite Test Panel**[a] **Fabrication Parameters and Static Mechanical Property Test Results**

| composite resin matrix | initiator[b] | fabrication method | dose[c] (kGy) | flexural strength (MPa) | flexural modulus (GPa) | tensile strength (MPa) | tensile modulus (GPa) | in-plane shear strength (MPa) |
|---|---|---|---|---|---|---|---|---|
| control Tactix 123/H31 | | RTM | 1h @ 80 °C 2h @ 150 °C[e] | 711 | 42.8 | 455 | 63.0 | 34.2 |
| **Ia** | SS | RTM | 177.5 | 206 | 31.0 | 348 | 43.1 | 16.8 |
| **Ib** | IOC8 | RTM[d] | 76.5 | 338 | 29.4 | | | |
| **II** | SS | hot melt prepreg | 81.6 | 361 | 42.4 | 498 | 67.8 | 12.3 |
| **III** | SS | hot melt prepreg | 81.6 | 271 | 40.5 | 437 | 64.7 | 12.7 |
| **IV** | SS | hot melt prepreg[d] | 76.5 | 380 | 36.4 | | | |
| **V** | SS | R.T. lay-up[d] | 76.5 | 306 | 34.7 | | | |
| **VI** | SS | hot melt prepreg[d] | 76.5 | 293 | 27.4 | | | |
| **VII** | IOC8 | R.T. lay-up[d] | 76.5 | 84 | 14.9 | | | |

[a] Fiber volume for all test panels was approximately 50%; all test panels were eight plies except **Ib** which was 20 plies. [b] Initiator concentration 1.6%; SS used as 50% solution in propylene carbonate. [c] Cured using AECL 1−10/1 1 kW e-beam accelerator at 10 MeV. [d] Graphite fabric washed three times with acetone. [e] Thermal cure as recommended by supplier.

to a mixture of monomer **I** containing 1 mol % of **IOC8**. The inhibiting effects of the extracts was measured by determining the photogel times using a gel point instrument (Gel Pointe Scientific Instruments, Bellbrook, OH) as described previously[21] and comparing them to a standard mixture of **I** and **IOC8**. Carbon fiber composite samples prepared with and without removal of the sizing by extraction with acetone are listed in Table 2.

**E-Beam and $\gamma$-ray Irradiations.** E-beam irradiations were carried out using the Atomic Energy Canada Ltd. (AECL) Research 1-10/1 electron linear accelerator in Pinawa, Manitoba, Canada. A 10 MeV (electron energy) pulsed electron beam was configured with a vertical horn to scan over a 50 cm wide path onto a variable-speed conveyor belt. All irradiations were conducted behind a heavily shielded concrete and lead barrier. The electron beam was pulsed at 13−19 Hz with a pulse width of 4 $\mu$s. The beam is scanned at a repeat rate of 2−7 Hz with a circular spot size at the surface of the conveyor of approximately 10 cm. The dose rate delivered at the conveyor surface is 130 Gy/s (50 cm scan). This e-beam source was employed for the fabrication of bars for mechanical tests (Tables 1 and 2) and for the cure of carbon fiber reinforced composites (Table 2).

Similarly, $\gamma$-ray irradiations were made at AECL in a $^{60}$Co $\gamma$ cell at a dose rate of 98 Gy/min. Samples (3 g) were placed in small screw-cap vials and sealed. To the outside wall of the vials were attached a thermocouple connected to a recorder for direct temperature readout. The samples were ballasted against a cured sample to eliminate the thermal effects due to radiation-induced heating. The entire apparatus was insulated with polyurethane foam, and the samples were irradiated in the $^{60}$Co $\gamma$ cell for periods up to 80 min. The progress of the polymerizations was followed by continuous monitoring of the temperature of the sample with time using an *XY* plotter. Data gathered using this technique are displayed in Figures 1 and 2.

**Fabrication of Test Specimens and Mechanical Testing.** Graphite fiber composites were fabricated in a 0°,90° fiber orientation by standard vacuum bag techniques and by resin transfer molding methods. Vacuum assisted resin transfer molding (VARTM) was carried out using a 12 in. × 12 in. × 0.25 in. aluminum mold with a removable top plate for easy removal of the cured composite. The mold was prepared by coating with Frekote Sealer B-15 (Dexter Hysol Corp.) and baking for 1 h at 200 °F. This was followed by the spray application of a dry lubricant (Dexter Hysol Number 1 Release agent). Four layers (8 plys) of carbon fiber fabric was laid in the mold and the mold sealed. A vacuum was placed on the mold, and the liquid resin containing the initiator was drawn into the mold from a reservoir. Final consolidation was carried out after closing off the resin flow exit and reducing the pressure to 40 psi at the resin entry port for at least 10 min. The resin charged TRM preform panels were stored precatalyzed for up to one and a half days before irradiating. The filled molds and laid-up laminates were irradiated by placing them horizontally on a conveyor and passing them through the 10 MeV electron beam at such a rate as to produce a total dose of 75 kGys. All e-beam irradiations were conducted behind concrete shielded maze walls inside the accelerator room.

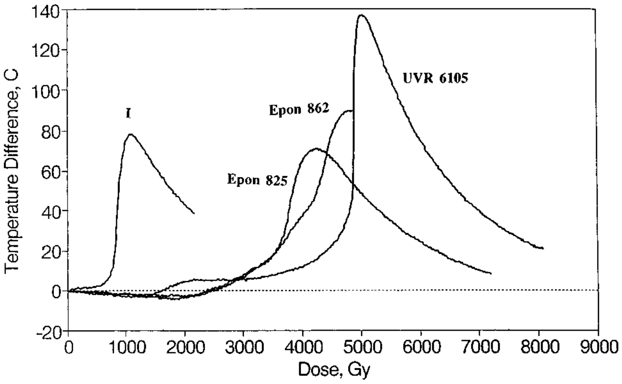

**Figure 1.** $^{60}$Co $\gamma$ cell monitoring of the polymerization reaction of various epoxy monomers exposed to $\gamma$-rays at a dose rate of 98 Gy/min in the presence of 0.5 mol % **IOC8**.

Measurements of the flexural and tensile strengths and moduli were determined in accordance with ASTM D790 and ASTM D638 procedures, respectively. In-plane shear strength (ASTM D3846) and dynamic mechanical properties (ASTM

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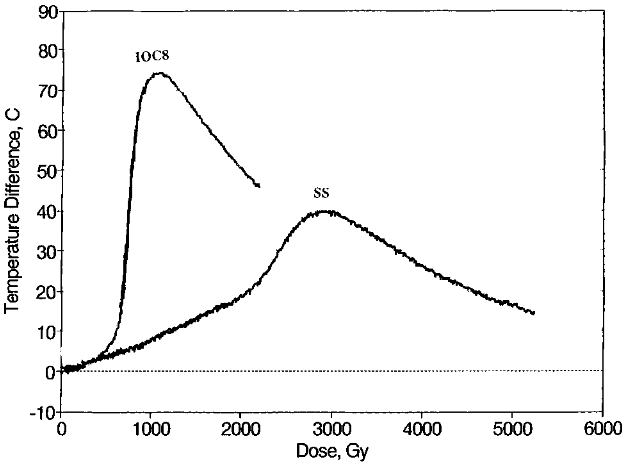
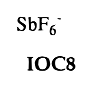


**Figure 2.** $^{60}$Co $\gamma$ cell monitoring of the polymerization reaction of epoxy monomer **I** exposed to $\gamma$-rays at a dose rate of 98 Gy/min in the presence of 1.0 wt % **IOC8** and **SS**.

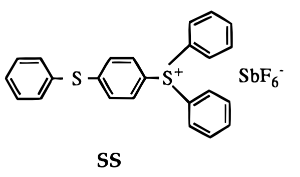
D4065) were measured in air on either a Rheometrics System IV instrument (NASA, LaRC) or a Rheometrics RSA dual cantilever instrument (AECL) in air at a heating rate of 10 °C/min.

## Results and Discussion

**Development of E-Beam Induced Cationic Polymerizations.** Since previous studies have shown that the mechanisms of the photo, $\gamma$-ray, and e-beam initiated cationic polymerizations in the presence of onium salts are similar, two major factors which determine the rate of polymerization are (1) the structure of both the anion and the cation present in the onium salt and (2) the structure and reactivity of the monomer. Accordingly, we decided to focus our initial investigations on the use of the most reactive onium salt photoinitiators as accelerators for e-beam induced epoxide polymerizations. Consequently, we elected to employ the two diaryliodonium and triarylsulfonium salts depicted below bearing the hexafluoroantimonate ($SbF_6^-$) anion. We reasoned that the e-beam induced decomposition of these onium salts containing the $SbF_6^-$ anion should result in the generation of $HSbF_6$, the strongest Brønsted acid known in chemistry and also the most powerful initiator of cationic polymerization.

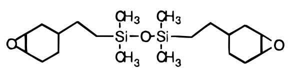


**IOC8**

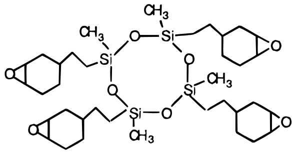


**SS**

The cationic ring-opening polymerization of all commercially available epoxy monomers generally takes place at rates that are much slower than the corresponding free radical polymerizations of acrylate or methacrylate monomers. Consequently, these monomers, by themselves, would not be sufficiently reactive to meet the low e-beam dose requirement set out as an objective for this research. However, it was recently discovered in this laboratory that certain silicon-containing epoxide resins undergo photoinitiated cationic polymerization at rates comparable to multifunctional acrylates.[23,24] The structures of two of these novel monomers are shown in **I** and **II**.



**I**



**II**

Monomers **I** and **II** contain siloxane linkages to which are attached highly reactive epoxycyclohexyl groups. The polymers derived from these monomers by UV-induced cationic polymerization have glass transition temperatures ($T_g$'s) as high as 180−200 °C and thermal degradation temperatures exceeding 300−350 °C in air.[22] Some preliminary mechanical tests have also shown that these materials possess flexural moduli measured in a three-point bend mode of 1.7−3.0 GPa. On the basis of the above photopolymerization results, a study of the behavior of monomers **I** and **II** in the presence of various onium salt photoinitiators under e-beam irradiation conditions was carried out.[25−27] It was observed that in the presence of photoinitiators **IOC8** and **SS**, the e-beam induced polymerization of thin (25−75 $\mu$m) films of pure monomers **I** and **II** took place rapidly to give cross-linked polymers at very low radiation doses (i.e., 10−30 kGy). In the absence of an onium salt photoinitiator, no polymerization was noted at doses below 100 kGy. In contrast, the same e-beam irradiations carried out using bisphenol A diglycidyl ether and either **IOC8** or **SS** as initiators did not display evidence of polymerization at the same doses. For comparison, the radiation dose required to cure acrylate monomers is approximately 20−23 kGy for a similar film thickness. The thermal and mechanical properties of the e-beam cured films of monomers **I** and **II** were essentially identical with those obtained by the photopolymerization of the same monomers.

Monomers **I** and **II** are comparatively low-viscosity liquids with viscosities of 65 and 10 000 cP, respectively. As such, these materials are highly suited for the fabrication of composites by resin transfer molding techniques in which the catalyzed monomer is caused to flow impregnate a woven fabric-filled mold under vacuum. Similarly, they are ideal for related composite fabrication techniques such as pultrusion and filament winding. However, their low viscosity does not allow them to be used for the fabrication of composites by traditional prepreg lay-up techniques. Accordingly, further modifications to monomers **I** and **II** were carried out and additional new silicon-containing monomers and oligomers were prepared. For example, it was observed that on prolonged heating at 110 °C, monomer **II** could be chain extended by reaction of the epoxy groups according to eq 4.

Using this process, the initial viscosity of **II** (10 000 cP) could be essentially doubled (20 000 cPs) after 8 h.

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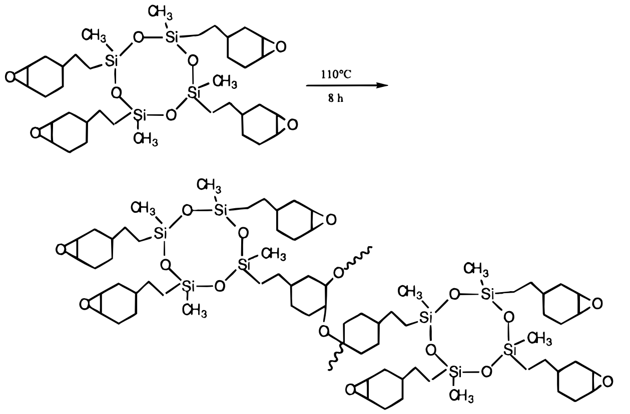
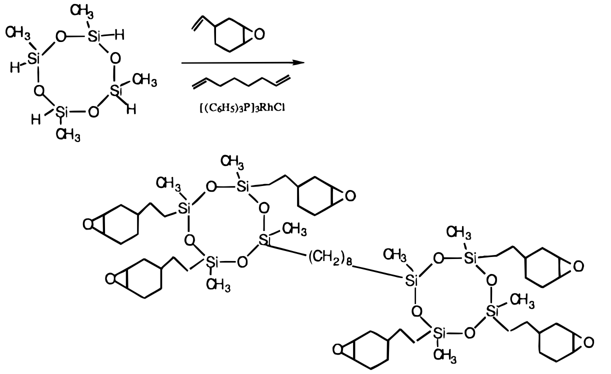


**III** eq. 4

This provided a material, **III**, with the ideal tack and drape necessary for the fabrication of hot-melt prepreg composites. An additional method of chemically modifying **II** was accomplished by coreaction of 1,3,5,7-tetramethylcyclotetrasiloxane with a small amount of 1,7-octadiene in the presence of 4-vinylcyclohexene oxide (eq 5).

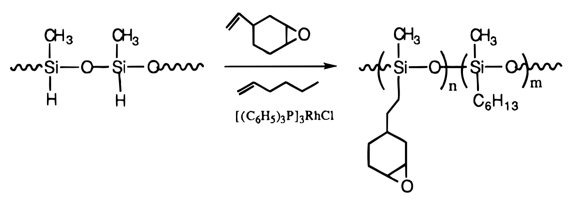


**IV** eq. 5

Thus, oligomer **IV** was produced with a viscosity of approximately 100 000 cP which could be employed for conventional layup by hot-melt prepreg techniques.

A further effective method of increasing the viscosity of highly fluid monomer **I** was to blend in 13% of a soluble high molecular weight butylene−ethylene−styrene terpolymer (Kraton 1650, MW = 80 000 g/mol, Shell Chemical Co.). The resulting homogeneous solution, **V**, had a viscosity of 1000 cP. Alternatively, **I** could be blended with 11% by weight epoxidized poly(isoprene) (MW = 250 000 g/mol, Elf-Atochem Corp.) to give solution **VI**.

Last, **VII**, a linear siloxane oligomer (1000 cPs) was prepared by the reaction depicted in eq 6.



**VII** eq. 6

Oligomer **VII** retains the highly reactive epoxycyclohexane groups and also includes *n*-hexyl groups which serve to consume all of the silicon−hydrogen bonds along the chain of the starting oligomer.

**Study of the Polymerizability of Epoxide Monomers with $\gamma$-ray Radiation.** The observation that silicon-containing epoxide monomers can be efficiently polymerized by e-beam radiation in the presence of onium salt initiators **IOC8** and **SS** and that the cross-linked polymers possess good mechanical and thermal properties suggested that these and other epoxy monomers could be employed for the fabrication of fiber-reinforced composites.[28] In the work reported here, we start out by addressing some of the basic issues associated with this new technology such as the effect of the initiator concentration and type and the effects of e-beam dose on the mechanical properties. Since the study of e-beam induced cationic polymerizations is at an early stage of development, we have again relied greatly on our closely related experience with the analogous UV-induced cationic polymerizations.

Preliminary studies[24−28] had shown that various epoxy monomers undergo e-beam induced polymerization as thin films in the presence of diaryliodonium and triarylsulfonium salts as accelerators. Most of these studies were carried out using very low intensity irradiation sources (e.g., Energy Sciences Inc. Electrocurtain Model CB-150 operating at 165 keV) which are not suitable for composite fabrication. Studies at higher radiation intensities in thicker samples of the silicone epoxy monomers had not been undertaken, nor had effective and simple means of monitoring these polymerizations been developed. For this reason, a study of the effects of resin structure on the polymerization rate was conducted using high-energy $^{60}$Co $\gamma$-ray irradiation in a $\gamma$ cell. The effects of $\gamma$-rays with respect to their ability to induce polymerization are very similar to e-beam irradiation and both involve bond-breaking reactions with resulting free radical formation. The advantage of using $\gamma$-ray irradiation for this study not only consists of the intrinsic highly penetrating nature of this radiation which makes possible the cure of thick samples but also the low dose rate which permitted us to accurately follow the course of the cationic polymerizations. These reactions were carried out in small vials to which thermocouples were attached. The progress of the exothermic polymerization could be directly followed by monitoring the increase of the temperature of the sample as a function of time.

The reactivities of various commercially available epoxide monomers were compared with that of monomer **I**, and these data are given in Figure 1. Each polymerization was conducted with bulk monomer containing 0.5 mol % of **IOC8**. Inspection of Figure 1 shows that a threshold radiation dose of 8−10 kGy is need to initiate polymerization in monomer **I**, whereas typical aromatic glycidyl ether resins; Epon 825 and Epon 862 required much higher threshold doses of 40−55 kGy to induce polymerization. It is interesting to note that in this experiment, the polymerization of the bisphenol A glycidyl ether-based epoxy resins are about as reactive as the biscycloaliphatic epoxy resin, UVR 6105 ((3,4-epoxycyclohexyl)methyl 3′,4′-epoxycyclohexanecarboxylate). It should be pointed out that the above samples had a mass of 4−5 g and a maximum thickness of 1 cm. E-beam induced cationic ring-opening polymerizations of epoxides are exothermic as noted in Figure 1 and are

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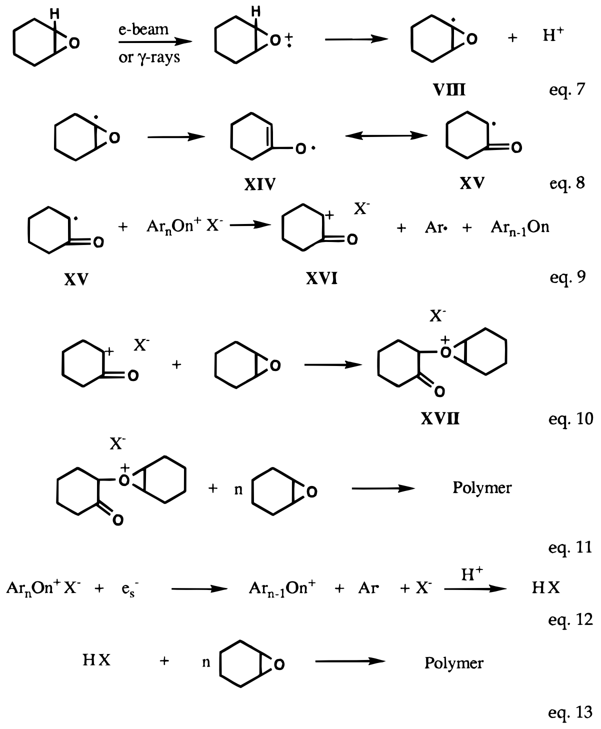
(28) Crivello, J. V. U.S. Patent 5,260,349, Nov 1993.

**Scheme 2**



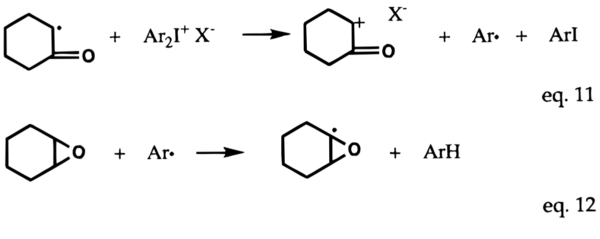
markedly autoaccelerated by the rise in temperature during the reaction. For this reason, differences in the monomer reactivities observed here may be somewhat different than those obtained in previous thin-film photo or e-beam induced polymerization studies.

The extraordinarily high reactivity of monomer **I** confirms earlier observations[22] made with respect to this monomer under UV irradiation conditions and once again, reinforces the conclusion that there is a close parallel between the factors that affect UV, $\gamma$-ray, and e-beam induced polymerizations. The high reactivity of monomer **I** under $\gamma$-ray and e-beam irradiation conditions can be best understood by a consideration of the mechanism shown in Scheme 2 which we have proposed for these polymerizations.[25]

In Scheme 2, the basic polymerizable epoxide unit of monomer **I** is represented by cyclohexene oxide. E-beam or $\gamma$-ray irradiation of the monomer (eq 7) initially produces free radical species by first ionization of the epoxide and then loss of the tertiary proton on the carbon adjacent to the epoxide oxygen. Next, cleavage of a carbon−oxygen bond (eq 8) is facilitated by the facile rearrangement of the initially formed carbon-centered radical **VIII** to the resonance-stabilized radicals **XIV** and **XV**. This reaction has considerable literature precedent and an analogous mechanism has been proposed by Gritter and Wallace[29] for the free radical induced ring opening of propylene oxide. This reaction is further driven by the relief of approximately 112 kJ mol$^{-1}$ ring strain from the opening of the epoxycyclohexane ring.[30] Radicals **XIII**, **XIV**, and **XV** can subsequently reduce the onium salt photoinitiator as illustrated in eq 9 for diaryliodonium salts. As depicted, the products are an aryl iodide, an aryl radical, and the cation **XVI**. Initiation of polymerization takes place either by direct attack by **XVI** on an epoxide oxygen to form an oxonium salt (eq 10) which undergoes subsequent cationic chain propagation (eq 11) or by interaction of **XVI** with trace amounts of water and other hydroxylic impurities to generate protonic acids which then initiate polymerization. Direct reduction of the onium salt by solvated electrons with subsequent initiation of polymerization by the protonic acid formed may also occur and this is shown in eqs 12 and 13 of Scheme 2.

Although 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate also bears epoxycyclohexyl groups, work in this laboratory[31] has demonstrated that the reactivity of this monomer in photoinduced cationic polymerization is markedly reduced due to side reactions involving the ester group. For this reason, 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate is much less reactive than monomer **I**.

**Effect of the Type of Onium Salt Initiator.** In Figure 2, is shown a comparison of the results of a $^{60}$Co $\gamma$ cell study of the polymerization of monomer **I** in which **IOC8** and **SS** were used as photoinitiators. Both of these photoinitiators those salts bear the $SbF_6^-$ anion. From the results given in Figure 2 it can be concluded that there is an additional effect on the rate of the reaction which is related to the type of onium salt cation which is employed and that the diaryliodonium salt, **IOC8** is considerably more effective as an accelerator than **SS**. These results can be best explained by again considering the mechanism depicted in Scheme 2 which is based on the reduction of the onium salt by the carbon centered free radicals **XIII**, **XIV**, or **XV**.[32] For this reaction to occur, the reduction potential of the radical should be lower than that for the onium salt. Further, the sum of reduction potential of the onium salt and the oxidation potential of the radical should be at least 10 kJ mol$^{-1}$ or higher for the electron transfer to occur with any appreciable efficiency. Since the reduction potential of **IOC8** is −14 kJ mol$^{-1}$ and that of **SS** is approximately −112 kJ/mol$^{-1}$, diaryliodonium salt photoinitiators are more reactive than triarylsulfonium salts in e-beam induced cationic polymerizations because they are more easily reduced by free radicals generated by e-beam irradiation of the epoxide resin substrate. Further, there is some evidence for the existence of a second mechanism which also contributes to the higher reactivity of diaryliodonium salts. Ledwith[33] has obtained a quantum yield of 3 for the photolysis of certain diaryliodonium salts in cyclohexene oxide. This suggests that the free radical induced catalytic cycle shown in eqs 11 and 12 may take place,



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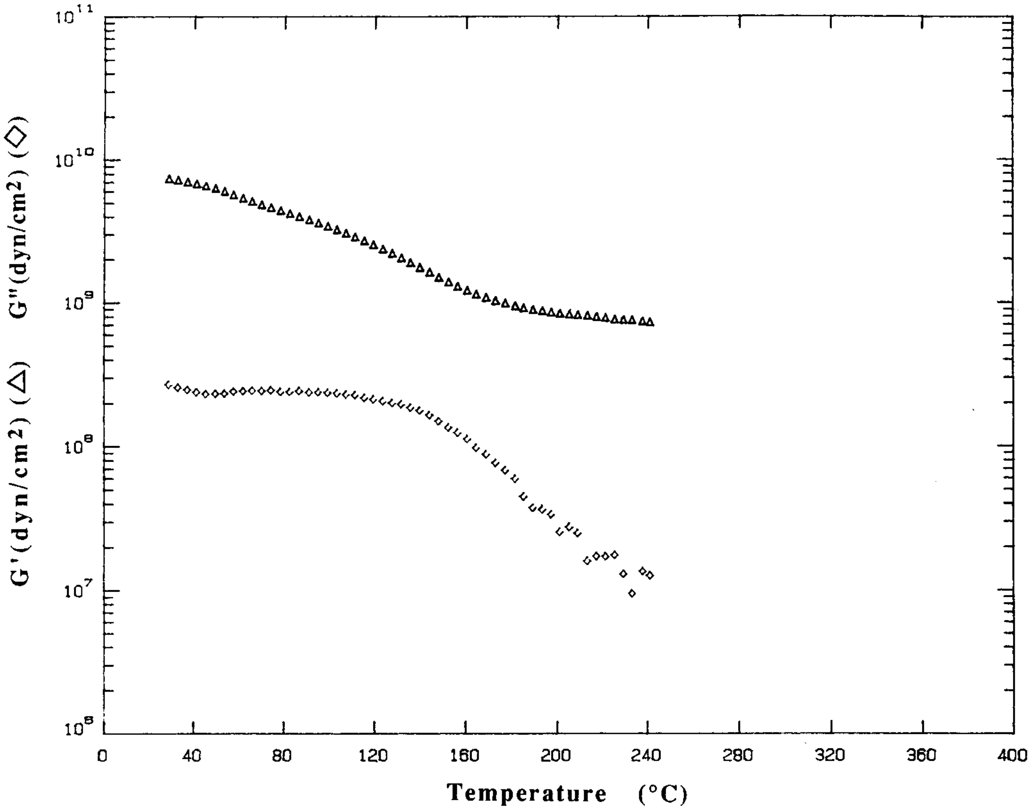

**Figure 3.** DMA of the polymer obtained from monomer **I** e-beam cured in the presence of 0.5 mol % of **IOC8** and at an irradiation dose of 80 kGy. (△), *G*′; (◇), *G*″.

which gives rise to decomposition of the onium salt with consequent enhanced initiation of polymerization. Again, diaryliodonium salts with their low reduction potentials would be expected to participate more readily than triarylsulfonium salts in this latter catalytic cycle.

Identical modulus profiles were obtained for polymers derived by initiating monomer **II** with 0.5 mol % **IOC8** or **SS** at 80 kGy which is much higher than the threshold dose for both onium salt initiators. Typical DMA curves for both monomers **I** and **II** cured in the presence of 0.5 mol % of **IOC8** and at an irradiation dose of 80 kGy are shown in Figures 3 and 4. It can be concluded from these results that despite the difference in the threshold doses between the two onium salts, once the threshold dose is exceeded, the ultimate mechanical properties are dependent primarily on the anion associated with the photoinitiator, i.e., the strength of the photogenerated acid, and on the type of monomer employed. This is because the rate of the initiation reaction is directly affected only by such factors as dose rate and onium salt concentration, while the polymer propagation reaction is primarily influenced by the reactivities of the monomer and the growing chain ends.

**Effect of Photoinitiator Concentration.** Earlier studies[12] of photoinduced cationic polymerizations showed that for any given multifunctional epoxide monomer system there is an optimum concentration of photoinitiator which gives the maximum conversion of the monomer within the shortest time. As the monomer conversion increases, the cross-link density correspondingly increases resulting in a higher modulus polymer. Accordingly, the moduli as determined from DMA measurements can be taken as a qualitative measure of the conversion. Real-time Fourier transform-infrared measurements have shown that monomers **I** and **II** attain their maximum conversions in photopolymerizations respectively, with 1.0 and 1.5 mol % of photoinitiator **IOC8**/epoxy group.[34]

The room-temperature dynamic moduli of e-beam cured polymers obtained from monomers **I** and **II** were 0.7 and 1.2 GPa irrespective of the photoinitiator concentration which was varied from 0.125 to 2.0 mol % **IOC8**/epoxy group. Thus, the moduli do not show any substantial variation with a corresponding change in photoinitiator concentration. Consequently, in all the subsequent model e-beam curing experiments a 0.5 mol % **IOC8** was arbitrarily adopted.

Udagawa et al.[35] have reported that photoinitiator fragments plasticized epoxy polymers obtained by UV curing resulting in low $T_g$'s. We have not observed any evidence of such plasticization in our DMA results even at 2.0 mol % loading of the diaryliodonium salt.

**Interpretation of DMA Data on Unfilled Polymers.** Given in Figure 3 is a DMA plot of the polymer derived from monomer **I** e-beam cured in the presence of 0.5 mol % of **IOC8** at an irradiation dose of 80 kGy. These measurements were made on a Rheometrics System IV dynamic mechanical spectrometer (DMA) in a torsion mode. Therefore, the *G*′ represents the shear modulus. It is seen that the shear modulus at room temperature is 0.7 GPa and that the modulus continuously falls as the temperature approaches the $T_g$ at approximately 160 °C. Unlike typical thermally cross-linked epoxy resins in which the modulus remains stable until it reaches the $T_g$ and then drops sharply

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(34) Crivello, J. V.; Bi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32* (4), 683.

(35) Udagawa, A.; Yamamoto, Y.; Inoue, Y.; Chujo, R. *Polymer* **1991**, *32* (15), 2789.

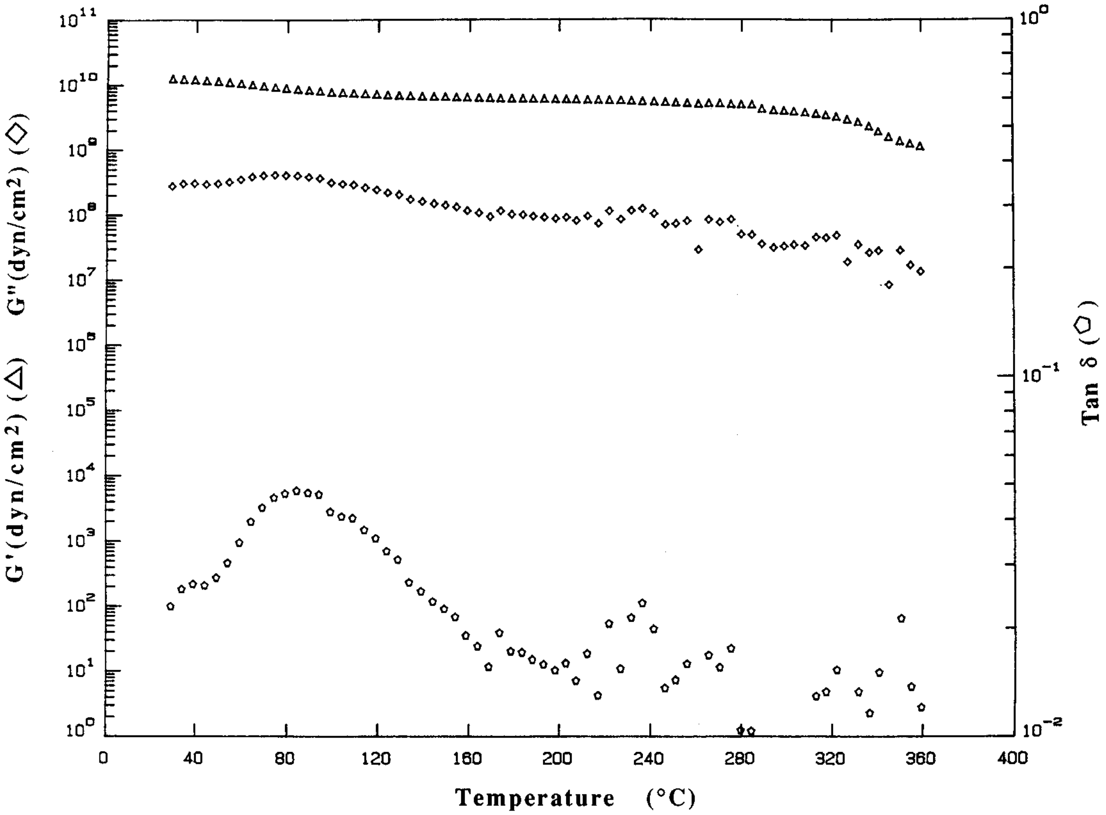

**Figure 4.** DMA of the polymer obtained from monomer **II** cured in the presence of 0.5 mol % of **IOC8** and at an e-beam irradiation dose of 80 kGy. (△), *G′*; (◇), *G″*; (⬡) tan *δ*.

until again stabilizing after reaching the rubbery region, the polymer from monomer **I** displays only a minor decrease in the modulus through the $T_g$. Similarly, Figure 4 gives the dynamic shear modulus of monomer **II** cured under identical conditions. The initial modulus (*E′*) is 1.2 GPa and shows a very minor decrease to 0.7 GPa after the $T_g$. In contrast, the typical decrease in modulus at $T_g$ for conventional epoxy thermosets is much greater and of the order of decades. The tan *δ* peak that is observed at about 80 °C in Figure 4 may not be indicative of the actual $T_g$ and could be indicative of a sub-$T_g$ transition due to localized deformations within the cross-linked matrix. Also, this system seems to be even more highly cross-linked than the one shown in Figure 3 since a rubbery region was not observed.

A number of factors may contribute to the mechanical behaviors which are shown in Figures 3 and 4. For example, the results can be explained as due to the presence of chemical heterogeneity in the overall chemical composition from one region to another. The results can be also explained on the basis of the presence of heterogeneities due to the presence of a tightly cross-linked microgel structure imbedded into a more loosely cross-linked matrix. At high cross-link densities, the tan *δ* peak broadens due to a wide distribution of molecular weight or a distribution of free volume between cross-links. Another possible explanation which has been proposed for this behavior may be that the cross-linking reaction may not be complete when carried out at room temperature and as the temperature in DMA instrument increases, the cross-linking progresses further. This latter explanation is unlikely since a second reheating of the sample produces the same DMA curve. Last, the shape of the curve shown in Figure 3 (i.e., monomer **I**) is typical of cross-linked photocured polymers, and it is believed that the rapid rate of photopolymerization rapidly freezes the difunctional monomers into a glassy state resulting in a large distribution of free volume. Also, in such photopolymerizations, the degree of monomer conversion obtained with epoxysilicone monomers reaches a value above 90%. Such a DMA profile is expected of a highly cross-linked matrix in which the modulus does not drop significantly after the $T_g$.

It can be seen in Figure 4 that the tan *δ* value at the peak is about 0.05. A value this low is characteristic of a very highly cross-linked polymer and further manifests itself in a low-impact resistance and a high notch sensitivity. The peak tan *δ* value for monomer **I** is about 0.1, which is only slightly higher than monomer **II** despite the fact that **I** is difunctional while **II** is tetrafunctional and the corresponding polymers from monomer **II** would be expected to be more highly cross-linked.

A DMA curve for the polymer obtained from monomer **I** was also obtained in a three point bending mode as is shown in Figure 5. The tan *δ* peak for this polymer is observed at about 150 °C. The elastic modulus ($E^*$) determined from this measurement is related to the shear modulus (*G′*) obtained previously by the following relationship where *ν* is the Poissons ratio:

$$E^* = 2\,(1 + \nu)G' \qquad (13)$$

The room-temperature shear modulus as read from Figure 3 is 0.7 GPa, and the elastic modulus from Figure 5 is 1.0 GPa. Using eq 3, the Poisson's ratio was calculated to be 0.29.

**DMA Study of Blended, Modified, and Filled E-Beam Cured Polymers.** Monomer **I** is a low-

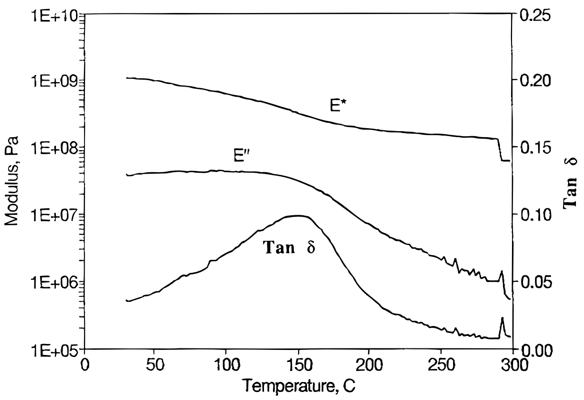

**Figure 5.** Three-point bend mode DMA of e-beam cured polymer obtained from monomer **I**.

viscosity fluid of 65 cP at 27 °C. While its low viscosity is an advantage for composite fabrication by resin transfer molding, this presented a problem for more conventional composite lay-up techniques. Accordingly, **I** was filled with various silica and carbon black fillers to modify the rheological properties of the monomers as well as the mechanical properties of the cured polymer. Addition of fillers to neat polymers also serve the purpose of reducing the monomer cost. The composition of the various filled polymers are given in Table 1 and are given the notations F1, F2, and F3, respectively. A DMA study of composition F1 showed that addition of 4 parts of fumed amorphous silica (Aerosil 380) does not bring about any change in either the modulus or the viscoelastic temperature profiles. Dispersing reinforcing silica filler did, however, impart appreciable thixotropy to the monomer. Figure 6 gives a DMA profile of carbon-black filled composition F3. Perceptible changes are seen in the DMA profile of monomer **I** after filling it with 8.4 parts of the reinforcing carbon black (Colorblack S160). There is also a slight improvement in the dynamic modulus of the polymer over the whole temperature range of measurement. The initial room-temperature dynamic modulus increases from 0.7 to 0.8 GPa (Table 1). A major change can be seen in the damping profile which becomes very broad and exhibits a shoulder at about 80 °C. Once again, this suggests that there are a minimum of two different environments in this system. The shoulder can be ascribed to the polymer fraction bound to the filler particles, and the main peak is due to the unbound polymer. The observed improvement in the mechanical properties of the polymer is brought about by the polymer fraction bound to the filler. A similar change in the DMA profile is also observed for the composition F2 which has 12.7 parts of reinforcing carbon black (Printex U). Therefore, particulate carbon fillers exhibit positive effects in reinforcement, reducing cost and increasing the viscosity of the monomer.

Monomers **I** and **II** were also blended with other commercially available epoxy and epoxy–novolac resins to enhance the mechanical properties obtained from neat monomers **I** and **II**. Table 1 presents the results of a study of several filled and blend systems that were made during the course of this project. Although it was earlier mentioned that commercially available glycidyl ether based epoxies required a higher e-beam irradiation dose, incorporation of epoxysilicone monomers into a blend with these monomers resulted in blends which cured extremely well.

The proportion of the monomer components in the blends was limited by the miscibility of various epoxy resins in monomer **I** and **II**. Although the blend compositions listed in Table 1 were completely miscible at room temperature, some degree of microphase separation did occur after the blend was e-beam cured as

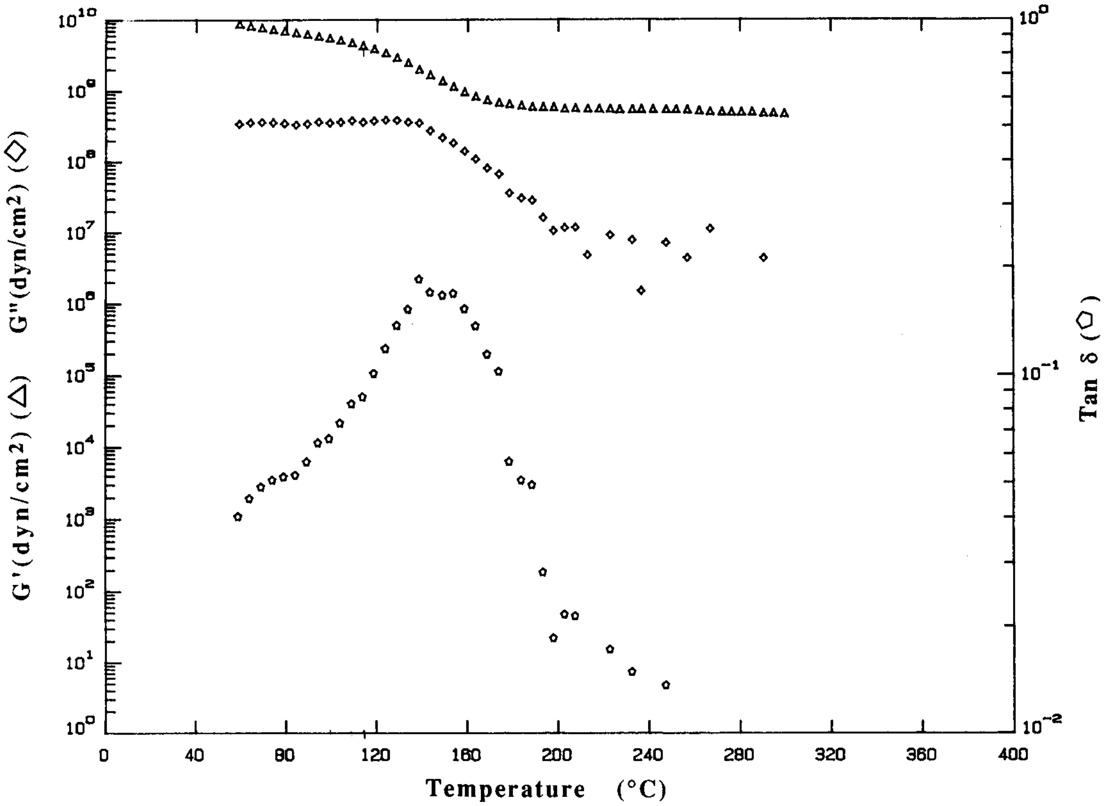

**Figure 6.** DMA of e-beam cured monomer **I** filled with Colorblack S 160 carbon black (F3).

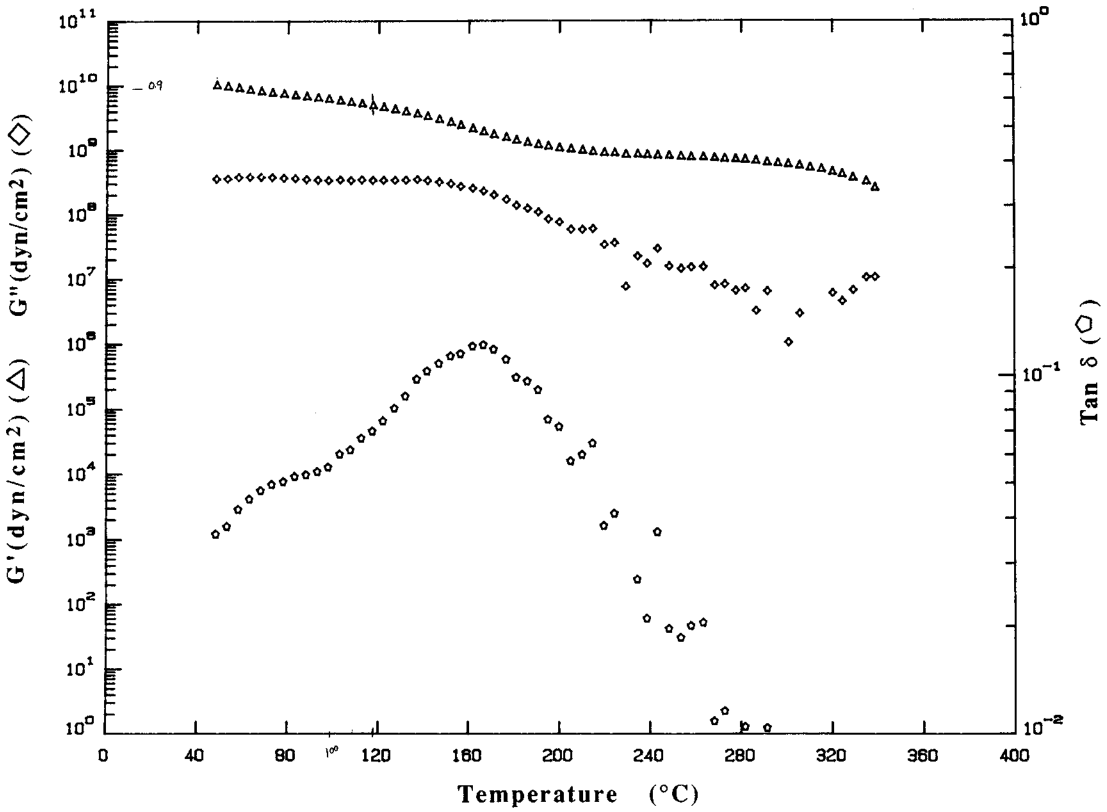

**Figure 7.** DMA of e-beam cured monomer **I** blended with Tactix 123 and Epon SU8 (B3).

evidenced by the presence of several peaks in DMA curves. The cured samples were optically clear, indicating that the phases were smaller than the wavelength of light. The DMA plot for blend B3 containing monomer **I** is shown in Figure 7. The presence of a shoulder at about 80 °C in the tan $\delta$ profiles of this and in all three blends is representative of a second phase. For comparison, the tan $\delta$ profile for neat monomer **I** (Figure 5) has a single peak. Blending with bisphenol A and novolac epoxy resins also increases the room-temperature dynamic modulus of monomer **I** from 0.7 GPa to a higher value as given in Table 1.

The DMA plots for B4 containing monomer **II**, given in Figure 8 is typical for those blends (B4-B6) containing monomer **II**. There is a significant difference in the tan $\delta$ profiles of these blends as compared to the neat monomer **II** (Figure 2). The tan $\delta$ profiles for the blends become much broader and possibly have two peaks possibly indicative of phase separation. The broad peaks further signify the presence of microheterogeneities and a highly cross-linked system. Blending with glycidyl ether-based epoxy resins also increases the overall modulus of monomer **II** at all temperatures of measurement. The room-temperature dynamic modulus increases from 1.2 GPa in pure monomer **I** to higher values in the blends as given in Table 1.

**Mechanical Properties of Carbon Fiber Reinforced Composit.** All fiber reinforcing materials employed in composites fabrication are treated with various sizing agents to improve handling, minimize fiber breakage during processing, and improve bonding to the polymer matrix resin. In many cases, the sizing agent must be tailored to the specific matrix resin to achieve maximum bonding and mechanical properties of the composite. Basic fiber sizing agents are commonly employed, and these agents could inhibit e-beam induced cationic polymerizations at the surface of the fibers. Accordingly, the graphite fiber cloth (Hercules AG193P) employed in these studies was extracted with acetone to remove the sizing, concentrated, and then monomer **I** was added. The photogel times of the mixtures were then determined in the presence of 1 mol % **IOC8**. It was found that in the presence of the extract, the photogel times were 4–8 times longer than in their absence. This indicates the presence of a basic inhibitor present in the sizing material on the surface of the carbon fiber fabric. These results suggested that some inhibition of e-beam induced polymerization is to be anticipated during composite fabrication using untreated fabric and further that the mechanical properties of the resulting composites will not be optimum.

Employing a variety of different monomers, modified monomers, and monomer–elastomer blends, eight-ply graphite fiber reinforced composites were fabricated in a 0°,90° orientation using conventional prepreg and lay-up (vacuum bag) methods and by vacuum-assisted resin-transfer molding techniques and cured using 10 MeV e-beam irradiation. Composites were prepared using both extracted and untreated carbon fiber cloth. The decision of which fabrication technique to use was made on the basis of the viscosity of the resin substrate. Those resins with low viscosities (<1000 cP) were fabricated into composites by resin-transfer techniques using a specially designed aluminum mold described in the experimental portion of this paper. Higher viscosity resins were used to impregnate carbon fiber cloth and then hand laid-up into composites and consolidated using standard vacuum bag techniques. After some preliminary investigations, it was determined that an optimum dose required to cure the resin transfer molded composites inside the aluminum mold was 70–80 kGy. Table 2 gives the epoxy resin formulations and the

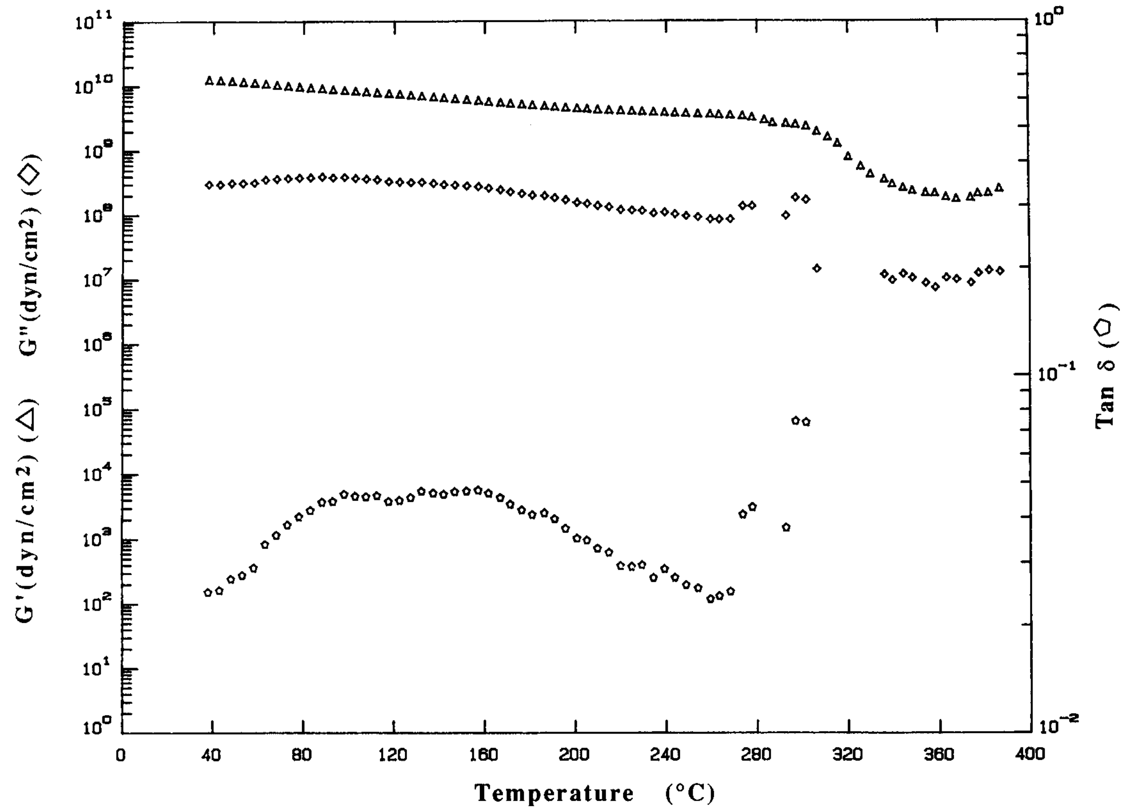

**Figure 8.** DMA of e-beam cured monomer **II** blended with Tactix 123.

fabrication parameters that were employed and gives the results of the mechanical testing procedures which were performed on the resulting composites.

These studies definitively demonstrate that graphite fiber reinforced high-performance epoxy composites may be readily fabricated and efficiently cured using e-beam irradiation. Mechanical properties were measured on the composites directly after irradiation without a thermal postcure. All mechanical properties reported in Table 2 are a statistical average of seven samples. A similar composite fabricated with carbon fibers but using a bisphenol A diglycidyl ether resin (Tactix 123) and thermally cured with an aromatic amine hardener (Dow Hardener H41) according to the manufacturer's recommendations served as a control with which to compare the mechanical properties of the e-beam cured composites.

Composites were readily prepared by both prepreg and lay-up and those fabricated by resin-transfer (RTM) techniques exhibited very low porosity by microscopic evaluation. The best room-temperature mechanical properties were obtained using prepreg and lay-up methods employing either monomer **II** or one of the modifications of that monomer (**III** or **IV**). The inclusion of thermoplastics such as Kraton 1650 or epoxidized poly(isoprene) (**V** and **VI**) appeared to markedly improve the flexural strength of composites based on monomer **I**.

Figure 9 gives the results of DMA measurements performed in a three-point flex mode on an eight-ply carbon fiber reinforced composite fabricated using monomer **I**. The room-temperature dynamic modulus for this composite is 16 GPa. A $T_g$ for the polymer matrix was observed at about 160 °C. It may be recalled that the room-temperature dynamic modulus for the neat **I** was 0.7 GPa (Figure 5). The increase in modulus to 16 GPa in the composite is due to the stiffness of the reinforcing carbon fibers. Table 2 shows that the static flexural modulus for this composite was 29 GPa. The composite begins to undergo thermal decomposition at about 280 °C.

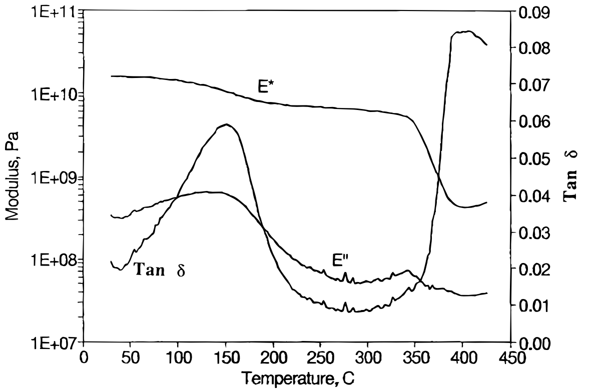

**Figure 9.** DMA of e-beam cured monomer **I** reinforced with eight plies of carbon fiber fabric.

Figure 10 gives the results of DMA measurements performed in a torsional mode on an eight-ply carbon fiber reinforced composite prepared from monomer **II**. For the sake of comparison, modulus (*G*′) curve B of the control resin has been overlaid. It is interesting to note that the shear modulus of the e-beam cured composite based on **II** remains nearly constant well past 300 °C indicating very high thermal stability. The damping peak (tan *δ*) has a value of approximately 0.08 which is characteristic of a very stiff material. This suggests that these composites are suitable for such structural, load-bearing composite applications as I-beams. As noted earlier in this paper, there is a very small transition seen in the DMA curve for this composite at about 80 °C. The high stiffness of the composite is also evident

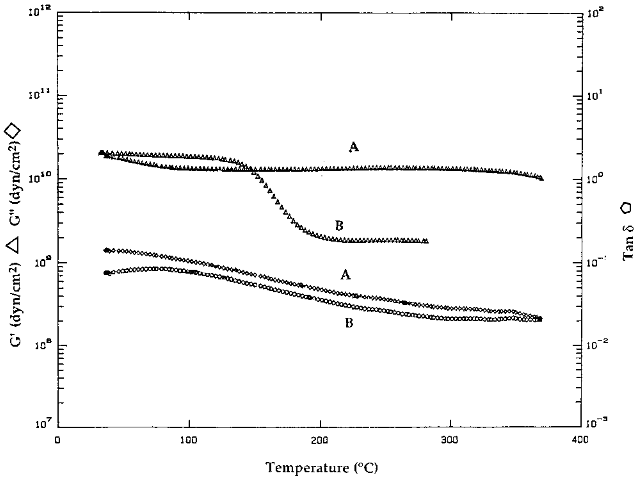

**Figure 10.** DMA of (A) e-beam cured monomer **II** reinforced with eight plies of carbon fiber fabric and (B) thermally cure Tactix resin reinforced with eight plys of carbon fiber fabric.

from an inspection of Table 2 where the static flexural modulus is 42 GPa (6.16 × $10^6$ psi).

A reviewer has pointed out that there are large differences in tensile and flexural moduli for composites with the same approximate fiber volume and that this is unusual since these are fiber-dominated properties. We have no explanation for these observations, but clearly more work is required to elucidate the reasons for the mechanical behavior of these e-beam cured composites.

Typical tensile moduli for e-beam cured acrylate-based composites are 35−38 GPa ((5.08−5.51) × $10^6$ psi).[7] The data of Table 2 show that the epoxy-based compounds of this work produced materials with better mechanical properties. With acrylate-based composites, there is a major decrease in the mechanical properties above 70 °C. E-beam cured composites can be fabricated with the new epoxy systems which retain their mechanical properties to 250 °C and beyond (Figures 5−9).

## Conclusions

Confirmation of the feasibility of using low dose e-beam radiation to cure fiber reinforced epoxy-functional silicone monomers to rapidly and efficiently fabricate carbon fiber reinforced composites has been demonstrated. Initial studies have shown that these nonoptimized epoxy-based composites display better mechanical and thermal properties than those obtained by e-beam curing acrylate or methacrylate monomers. Clearly, more work will be required to further optimize these properties to achieve full equivalence to conventional thermally cured epoxy resins. An especially attractive and unprecedented feature of the novel e-beam curable epoxy systems is their ability to cationically cure at high rates of speed at room temperature, while at the same time, obtaining high $T_g$ values. In addition, recent joint investigations[36] between this laboratory and NASA have shown that polymers prepared by photocuring monomers **I** and **II** have outstanding oxygen plasma resistance. These results suggest that composites based on epoxy functional silicones may have many potential aerospace applications.

**Acknowledgment.** The authors would like to acknowledge the financial support for this work from a NASA SBIR grant to the Aeroplas Corp.

CM9700312

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[36] Connell, J. W.; Crivello, J. V.; Bi, D. *J. Appl. Polym. Sci.* **1995**, *57*, 1251.