



Cationic concentration effects on electron beam cured of carbon-epoxy composites

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ABSTRACT

Electron beam (e-beam) curing is a technology that offers advantages over the thermal curing process, that usually requires high temperature and are time-consuming. E-beam curing is faster and occurs at low temperatures that help reduce residual mechanical stresses in a thermoset composite. The aim of the present study is to analyze the effects of cationic initiator (diaryliodonium hexafluoroantimonate) ranged from 1 to 3 wt% in DGEBA (diglycidyl ether of bisphenol A) epoxy resin when cured by a 1.5 MeV electron beam. The specimens were cured to a total dose of 200.4 kGy for 40 min. Analyses by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) show that the e-beam irradiated samples with 2 wt% cationic initiator were 96% cured obtained a glass transition temperature ($\tan \delta$) of 167 °C. The same epoxy resin, thermally cured for 16 h with an anhydride hardener, reached a T_g ($\tan \delta$) of 136 °C. So, the irradiated sample had its T_g increased approximately 20% and the curing process was much less time consuming.

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1. Introduction

The properties of polymeric composites, such as chemical resistance and high strength, provide excellent material choices for structural applications previously reserved for metals.

Commercial epoxy resins, such as diglycidyl ether of bisphenol A and F, respectively, DGEBA and DGEBF, cycloaliphatics and NOVOLAC epoxy can be electron beam cured (Ohamad and McLaughlin, 1996; Crivello, 1999; Koleske, 2002; Nishitsuji et al., 2007), that result in polymeric matrix with high glass transition temperatures and mechanical properties similar or slightly lower than produced by thermal process. The electron beam curing process is carried out in a short time at room temperature (Crivello et al., 1997), but the exothermic heat of reaction can increase the temperature process up to 90 °C approximately.

Thermal curing of polymer matrix systems is time consuming and requires a well planned strategy to effectively use an oven or an autoclave, carefully matching the tool size to the size of the oven or the autoclave. For epoxy systems, anhydride curing agents are used in filament winding processes for a long working time (pot life); cure cycle times can be lengthy, e.g. 16 h is typical, at temperature generally between 100 and 200 °C.

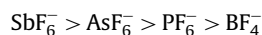
To manufacture structural polymeric composite, raw material, molds, electrical energy consumption and labor are important

factors of production costs. These ones lead to search of new production technologies for cost reductions while insuring material performance properties.

In the present work a carbon fiber/epoxy composite was cured by electron beam and oven heating. The glass transition temperature (T_g) of the composites cured by these two processes were measured and compared using dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC).

2. Mechanism of electron beam curing

Among the available commercial cationic initiators, diaryliodonium and triarylsulfonium salts are most frequently used in e-beam curing processes; but diaryliodonium salts are more effective than the triarylsulfonium salts of the same anion. The nature of the anion affect the effectiveness of the cationic initiator and it well known in the literature that it is inversely related to nucleophilicity of the anion and it proceeds the following order (Lopata et al., 1996):



3. Materials and methods

The samples were manufactured by a filament-wound process and the viscosity is an important variable affecting the resin wetting characteristics in the composite filament wound process.

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This way, a liquid TACTIX 123 (DGEBA) was chosen for this study. TACTIX 123 has low viscosity, high degree of purity, high cure reactivity and high glass transition temperature. Table 1 presents TACTIX 123 resin physical properties.

Unsize continuous carbon fiber (type AS4 12 k) with 12,000 filaments was used as reinforcement. Table 2 presents mechanical properties and technical data of the carbon fiber.

PC 2506 cationic initiator from Polyset was used to initiate the cationic polymerization. The active molecule (Fig. 1) is the diaryliodonium hexafluoroantimonate (Ar_2ISbF_6), which decomposes under electron beam irradiation, ultraviolet irradiation (240–300 nm range), or under thermal heating 170 °C.

Epoxy resin was dried using molecular sieves (Aldrich Chemical Company, Inc). The sieves were dried at 160 °C for 12 h prior to use. Such drying limits water concentration to below 0.1% in the reactants.

Three formulations named A1, A2 and A3 (Table 3) were prepared, respectively, with 1, 2 and 3 parts of initiator per hundred parts of resin (phr) of diaryliodonium hexafluoroantimonate.

The EB samples were homogenized for 20 min ranged from 70 to 80 °C and degassed in a vacuum oven for 20 min to remove air from the sample mixture. After that, they were stored in a desiccator shielded from ultraviolet light.

Table 1
TACTIX physical properties.

Physical properties	TACTIX 123
Resin type	DGEBA high purity
Viscosity (mPa s)	3200 at 27 °C
Epoxide equivalent (g eq^{-1})	172–176
Density (g cm^{-3} at 25 °C)	1.16
Manufacturer	Huntsman

Table 2
Carbon fiber mechanical properties and specifications.

Properties	AS4 12 K
Tensile strength (MPa)	4070
Elasticity modulus (GPa)	228
Elongation to rupture (%)	1.8
Fiber diameter (μm)	7.1
Volumetric density (g cm^{-3})	1.79
Linear density (g m^{-1})	0.80
Manufacturer	Hexcel

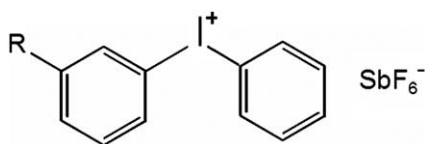


Fig. 1. Molecular structure of diaryliodonium hexafluoroantimonate.

Table 3
Electron beam resin systems.

Formulation	A1 (g)	A2 (g)	A3 (g)
TACTIX 123	100.00	100.00	100.00
PC2506	1.00	2.00	3.00

The advantages of electron beam curing process over thermal one generally mentioned in the literature (Lopata et al., 1999; Janke et al., 1997) are:

- (i) reduced matrix shrinkage in the range from 4–6% to 2–4%;
- (ii) the composites with metallic and ceramics substrates, i.e. different thermal expansion rates, can be joined together with adhesive that is e-beam cured;
- (iii) composite part size is not limited by curing vessel size, e.g. autoclave working volume or oven volume; large pieces or structures can be fabricated;
- (iv) glass transition temperature increases using e-beam curing compared to thermal curing;
- (v) reduction of internal stress because the process is carried out at room temperature;
- (vi) reduction of volatile production because hardeners and catalysts are not added;
- (vii) reduction of molds' fabrication cost because tool materials need not withstand high use temperatures;
- (viii) reduced electrical energy consumption because of short curing cycle time;
- (ix) resin stability leads to a long pot life. The resin formulation should just be protected against ultraviolet radiation; and
- (x) the resin system storage at room temperature for two years.

Normally the glass transition temperature (T_g) is one of the most important properties in a polymeric system and the choice of a resin system when designing a composite could be done in function of the temperature use. In order to allow a comparison with the EB cured matrix an experiment was performed with a thermally cured matrix, using the same resin in both process, but with different initiators. This comparison can be useful once the thermally cured resin is commonly used in the composite industry.

The thermally cured system was a TACTIX 123 epoxy resin, methyltetrahydrophthalic anhydride-based hardener (HY 917, Huntsman) and tertiary amine accelerator benzildimethylamine (DY 062, Huntsman); 100, 97 and 0.5 wt%, respectively, that were mixed at room temperature and vacuum degassed to eliminate air.

The carbon fiber was wound 90° to the longitudinal axis onto a rotating mandrel as shown in Fig. 2. Eight unidirectional fiber layers were laid down on the mandrel immediately after resin impregnation with each resin system. The samples were cut from the plates to a final dimension of 2 mm × 24 mm × 60 mm in size (Fig. 3). The thermal matrix system was cured under the followed cycle and took 16 h of heating:

- (i) 90 °C for 4 h,
- (ii) increase temperature from 90 to 180 °C in 4 h,



Fig. 2. Filament winding composite plates.

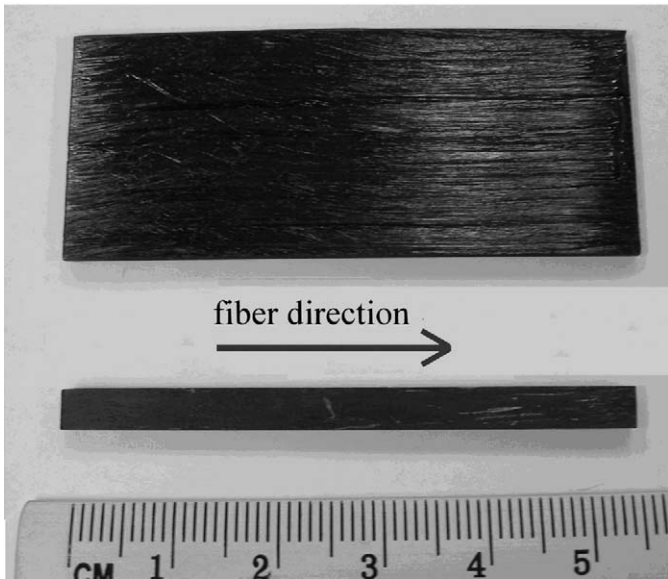


Fig. 3. Composite plate and sample for DMTA analysis.

- (iii) hold at 180 °C for 8 h, and
- (iv) cool to room temperature.

E-beam irradiated cured composites cured by electron beam with up to a 200.4 kGy total dose at the Instituto de Pesquisas Energéticas e Nucleares-IPEN (Energetic and Nuclear Research Institute) accelerator facility, in a Job 188 Dynamitron model accelerator, with 0.5–1.5 MeV energy, 0.1–25 mA current, 37.5 kW power and 60–120 cm scanning electron beam. The dose was calculated using a cellulose triacetate (CTA) dosimeter calibrated on the same machine conditions (current, energy and number of passes under the electron beam) according to the thickness and density of the material used for irradiation.

Due to the low energy of the IPEN's accelerator that causes a limited depth penetration, the maximum panel thickness of the samples was not more than 2 mm, considering composite density of the 1.55 g cm⁻³.

DSC analyses (Mettler Toledo DSC 823) were based on the ASTM D 3418-99 and ASTM AND 1356-98. Samples from 10 to 25 mg were analyzed at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

A dynamic mechanical analysis (Netzch DMA 242) was used to determine the glass transition temperature, according to ASTM 1640-99 standard. The analyses were carried out at a heating rate of 2 °C min⁻¹ and frequency of 1 Hz, in a three point bending device.

4. Results and discussion

To minimize temperature increase from exothermic heat of reaction a low dose rates in the first portion of the cure cycle are mentioned in the literature (Morgan et al., 2002). In the present study the samples were irradiated at a low dose rate of 0.8 kGy pass⁻¹ in the first 63 passes and after that the dose rate was increased to 25 kGy pass⁻¹ with six passes (2 min between passes). The temperature variation was continuously monitored in the samples and recorded during electron beam processing. So, the total accumulated dose was 200.4 kGy. As can be seen in Fig. 4, the temperature in the first portion of cure cycle was 50 °C.

For structural applications, the cure analysis of a polymeric matrix is a task that should be adopted as routine. In the present study, the DSC and DMTA techniques were used to analyze both the thermal and electron beam cured matrix.

DSC measures the temperature and heat flows associated with transitions in materials as a function of temperature or time in a controlled atmosphere and the glass transition temperature, exothermic cure reaction transition and degree of cure can be gotten by this technique.

The degree of cure of a polymeric matrix cured by oven heating or by electron beam can be determined by Eq. (4.1). This equation is a relationship between the residual curing heat (ΔH_a) of a partially cured material and the total curing heat (ΔH_t) for the same material, but completely cured. According to Raghavan et al. (1998), the total curing heat of a matrix in a determined process, for instance EB, could be considered as that of the same matrix completely cured by the DSC. So, in the present study, the total curing heat (ΔH_t) was determined by the DSC.

$$\text{Degree of cure} = \frac{\Delta H_t - \Delta H_a}{\Delta H_t} \quad (4.1)$$

The DSC results (Fig. 5) show that electron beam cured samples are partially cured. The exothermic peak on the curves of CFA1-EB,

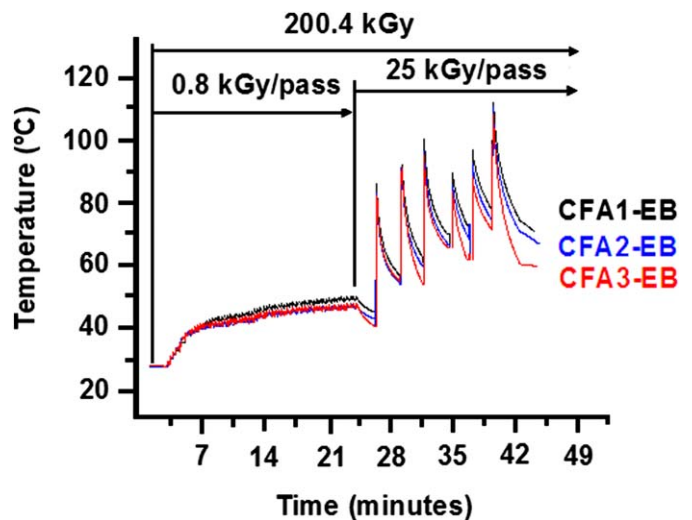


Fig. 4. Composite temperatures (CFA1-EB, CFA2-EB e CFA3-EB) along the electron beam curing process.

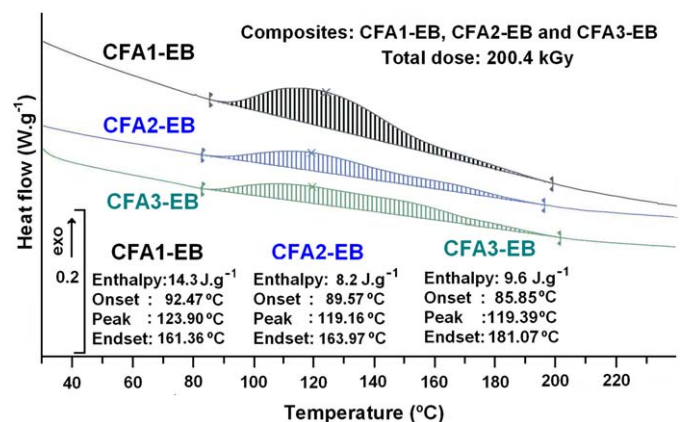


Fig. 5. DSC curves of CFA1-EB, CFA2-EB and CFA3-EB residual curing heat of the irradiated samples.

Table 4
Cure degree (DSC) and DMTA results of thermal and e-beam curing composites.

Composite Samplesample	Cure condition	Matrix	Cure degree (%)	T_g (°C), $\tan \delta$
CF-TC	4 h, 90 °C+4 h, 90–180 °C+8 h, 180 °C	DGEBA+ANHYDRIDE+BDMA (100:97:0.5)	100	136 ± 4
CFA1-EB	200.4 kGy	DGEBA+Ar ₂ ISbF ₆ (100:1)	87	165 ± 3
CFA2-EB	200.4 kGy	DGEBA+Ar ₂ ISbF ₆ (100:2)	96	167 ± 3
CFA3-EB	200.4 kGy	DGEBA+Ar ₂ ISbF ₆ (100:3)	96	162 ± 3

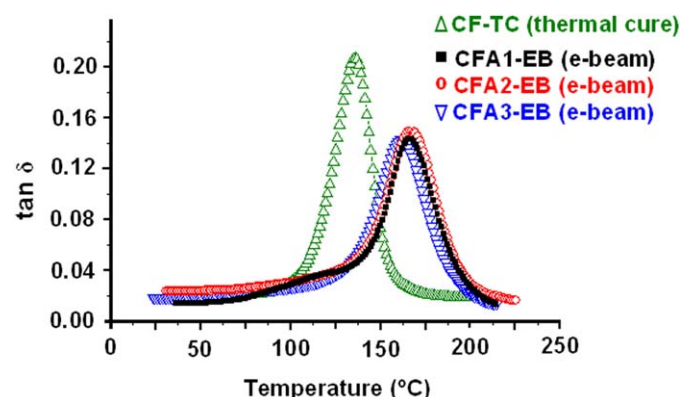


Fig. 6. DMTA composites curves ($\tan \delta$) cured by thermal and electron beam process.

CFA2-EB and CFA3-EB composites shows a residual curing heat that indicates a system partially cured (ΔH_a).

Glass transition temperature was measured at the maximum of $\tan \delta$ curve for thermal and electron beam cured composites and it was obtained by the DMTA. Table 4 shows the composites degree of cure and the T_g , where CF-TC means thermal cured composites and CFA1-EB, CFA2-EB and CFA3-EB means, respectively, electron beam cured composites with 1, 2 and 3 wt% cationic initiator.

Fig. 6 shows the DMTA $\tan \delta$ curves of the CFA2-EB and CFA3-EB composites that exhibit a dynamic mechanical behavior similar to a fully cured matrix, as that one obtained by the thermal process. In these curves, there were no secondary peak, although the DSC analysis showed that the composites cured by electron beam were not fully cured. For composite CFA1-EB, a secondary peak was observed in the $\tan \delta$ curve that indicates a material partially cured. This secondary peak suggests the presence of a residual curing enthalpy in the CFA1-EB matrix.

It was observed that the composite thermally cured (CF-TC) shows a dynamic mechanical behavior of a fully cured material due to the absence of a secondary peak in $\tan \delta$ curve.

The best concentration of the cationic initiator (PC2506) was 2 phr for the composite CFA2-EB that resulted in a T_g ($\tan \delta$ peak) greater than the composite CFA3-EB, although the last also reached a 96% degree of cure. Therefore, according to Lopata and Janke (1999), a study must be done for each cationic initiator in order to determine the best concentration optimizing the cost-to-benefit ratio. Also, according to Menard (1999), in some epoxy systems, the cure reaches a point where increased thermal post-cured time causes to no increase in either the T_g or E' modulus. In

some systems, this occurs starting from 94% of complete cure when measured by the residual curing heat in the DSC.

5. Conclusion

E-beam cured carbon/epoxy composite with 2 wt% cationic initiator and irradiated up to 200.4 kGy total dose has a glass transition temperature T_g ($\tan \delta$) of 167 °C, approximately 20% higher than thermally cured composites, that showed a T_g of 136 °C. The CFA2-EB composite sample was 96% cured by e-beam in approximately 40 min. By comparison, the thermally cured composite required 16 h for the heating portion of the thermal cure cycle plus additional cooling time.

Electron beam curing process is operated at room temperature. Lower process temperature offers an alternative for tooling materials selection other than steel and aluminum because temperatures are greatly reduced. Some of these alternative low-cost tooling materials are lighter, less expensive and faster to design, machine and deliver. Tool redesign and modification are also simplified. For all these reasons, room operating temperatures promotes the possibility of affordable tooling.

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