

Study of electron beam curing process using epoxy resin system

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Abstract

Polymeric matrix composite (PMC) has been used in engineering applications instead of metal in the last few years, due to its corrosion resistance and excellent relation between tensile strength/density and elastic modulus/density. However, PMC materials cured by thermal process require high temperature and are time-consuming. The electron beam (EB) curing technology allows its use at room temperature and reduced curing times, and this is one of the main advantages over thermal technology. The aim of this work is to investigate electron beam curable epoxy formulations to use in filament winding processes to produce composite material with similar or better properties than thermal curable composites. The study has been made with commercial epoxy resins and cationic initiators. The epoxy resin samples were irradiated for few minutes with total dose of 150 kGy. The glass transition temperatures (T_g) were determined by dynamic mechanical analyzer (DMA) and the result was 137 °C. The thermal process was carried out in a furnace following three steps: 4 h at 90 °C, increasing temperature from 90 °C to 130 °C during 4 h and 12 h at 130 °C. The total process time was 20 h. The T_g of this sample was 102 °C.

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1. Introduction

The competition among the industries has demanded systematic cost reduction without affecting the final quality of the product. This fact has encouraged the use of new technology applications on productive process, especially on polymeric composites, in order to assure the competitiveness.

Raw material, molds, energy consumption and hand labor are important factors to be considered in the production of advanced polymeric composites, because they can increase the products final cost of the products. The polymeric composites cured by thermal process (furnace or

autoclave) are an example of long curing cycles, which demand time and energy. For instance, it may be necessary about 24 h to cure an epoxy resin system in the filament winding process.

The use of radiation process is an alternative to reduce the curing time and energy consumption. More specifically, the electron beam curing technology is done at room temperature in a shorter time interval and these are the main advantages over thermal cured epoxy system.

The study involving polymeric composites cured by electron beam with addition of cationic initiator, consists on the optimization of the radiation process parameters (dose and dose rate), the addition of modifier in order to assure tenacity and as well as to study the fiber/matrix interface.

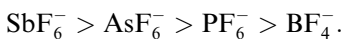
The aim of this work is to compare thermal properties between electron beam and thermal curing processes.

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2. Mechanism of electron beam curing

The commercial epoxy resins, such as diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF), cycloaliphatics and epoxy NOVOLAC added with 1 phr up to 3 phr of cationic initiator can be electron beam cured, resulting in matrix with high glass transition and mechanical properties similar to thermal cured matrix. The polymerization is carried out with controlled dose rate and at room temperature [1,2].

Among the available commercial cationic initiators, the diaryliodonium salt is known as more effective initiator than the triarylsulfonium salt of the same anion, which also affects the effectiveness of the cationic initiator utilized in radiation cure processing. The anion effect is inversely related to the nucleophilicity of the anion. Within a given cationic initiator family, the anion reactivity in the cure process is as follows:



When the cationic initiator is activated by electron beam radiation, as shown in Fig. 1, it occurs a strong acid formation (Bronsted acid) that is responsible for the polymerization initiation. The presence of amines and other basic materials can inhibit the cure reaction of the matrix [3,4].

3. Materials and methods

One of the main advantages in electron beam curing process is the fast and single cure cycle and being done at room temperature, without intermediate cycles [5]. This process requires only a few minutes instead of hours, as in the thermal curing process.

Other advantages of using electron beam curing over thermal curing are [6,7]:

- Lower shrinkage has been measured in the range from 2% to 4%, while the values for thermally-cured epoxies are generally in the range from 4% to 6%.
- Increase of glass transition temperature.

- Reduction of internal stress because the process is carried out at room temperature.
- Reduction of volatile production because hardeners and catalysts are not added.
- Reduced tooling cost.
- Reduced of electrical energy consumption.
- Resin stability leads to an almost infinite resin pot life. The resin formulation should just be protected against ultraviolet radiation and moisture.

The samples, in this present work, were irradiated at the Instituto de Pesquisas Energéticas e Nucleares-IPEN (Nuclear and Energetic 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 partial view of this accelerator is presented in Fig. 2.

To manufacture the samples, it was used as reinforcement unsized carbon fiber with 12,000 filaments. Among the resins available, the one chosen for this study was

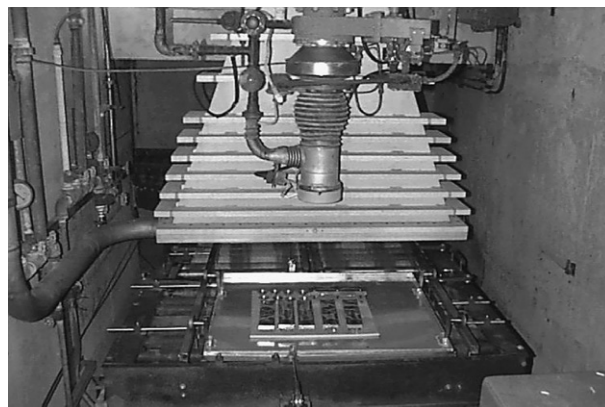


Fig. 2. Samples to be irradiated at JOB 188 accelerator facility.

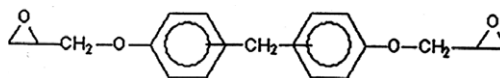


Fig. 3. Molecular structure of DGEBF epoxy resin.

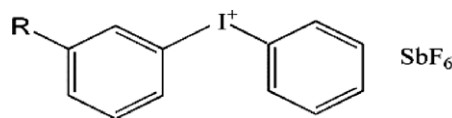


Fig. 4. Molecular structure of diaryliodonium hexafluoroantimonate.

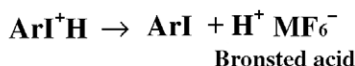
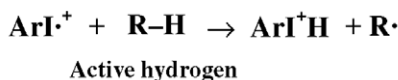
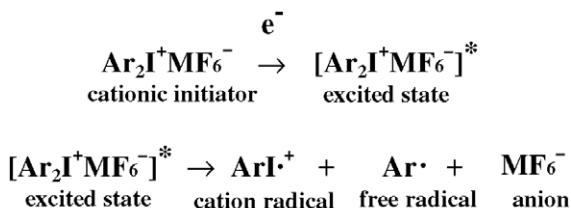


Fig. 1. Cationic initiator activation.



Fig. 5. Irradiated sample.

Table 1
Glass transition temperature for the electron beam and for the thermal curable matrices

Process	Electron beam	Thermal
Formulation	DGEBF + Ar ₂ ISbF ₆ (100:3)	DGEBF + ANHYDRIDE + BDMA (100:102:0.5)
Cure condition	150 kGy	4 h, 90 °C + 4 h, 90–130 °C + 12 h, 130 °C
Glass transition temperature (°C), tan(δ)	137	117

DGEBF resin (GY281, Huntsman) whose viscosity is 5000–7000 mPa at 25 °C. The molecular structure of this resin is shown in Fig. 3.

For most epoxy resins the optimum initiator concentration is between 2 and 3 phr, regardless of the initiator used [8]. The cationic initiator used in this study was the UV9390C (solution of a bis(4-alkylary)iodonium hexafluoroantimonate salt plus photosensitizer in a glycidyl ether reactive diluent) with 3 phr from GE Silicones. It was mixed with epoxy resin (DGEBF) at 70 °C and irradiated at 150 kGy dose at room temperature. The total cycle time took only a few minutes. The molecular structure of the initiator is shown in Fig. 4.

Samples were molded in bar measuring 2 × 4 × 50mm, respectively thickness, width and length. Dynamic mechanical analysis (DMA) was used to determine the glass transition temperature, according to ASTM 1640–99 standard. The analyses were carried out at a rate of 2 °C min⁻¹ and frequency of 1 Hz. In Fig. 5 it is shown a sample that was irradiated at the electron beam accelerator.

For the thermal process, one used an epoxy resin (DGEBF), methyltetrahydrophthalic anhydride and benzildimethylamine (BDMA), 100, 102 and 0.5 parts, respectively. The thermal process was carried out in a furnace in three steps: 4 h at 90 °C and an increasing temperature from 90 °C to 130 °C during 4 h and 12 h at 130 °C. The total process time took 20 h.

4. Results and discussion

The results of both electron beam and thermal curing process are presented in Table 1. The T_g was determined by tan(δ) and these curves are presented in Figs. 6 and 7.

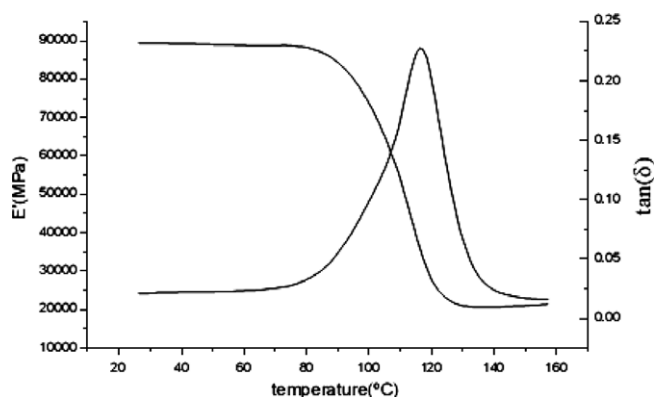


Fig. 6. E' and tan(δ) curves of thermal cure matrix versus temperature.

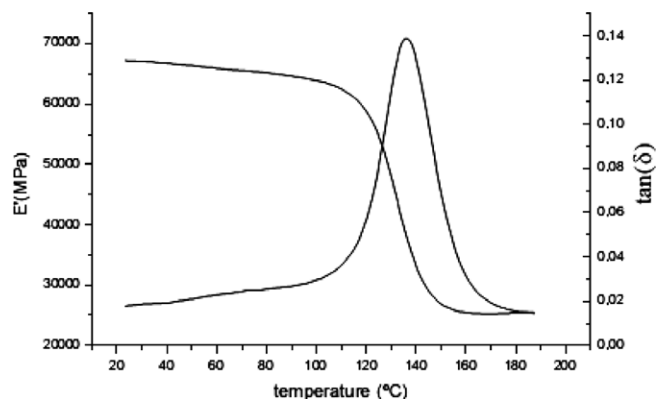


Fig. 7. E' and tan(δ) curves of electron beam cure matrix versus temperature.

The glass transition temperatures (T_g) of the irradiated samples were higher than that of the thermal curable resin (see Table 1). This increase in the T_g , is due to the higher density crosslinking which provides higher polymeric matrix rigidity [9]. As a consequence, it can be necessary to add a modifier or tenacity agents, as engineering thermoplastics [10] or elastomers [11], to increase the fracture toughness.

The T_g of the electron beam curable resin was 137 °C, 17% higher than the T_g obtained in the thermal process.

5. Conclusion

The electron beam curing process time was reduced for more than 20 h in relation to the thermal curing process. The glass transition temperatures (T_g) of the irradiated samples were higher than those of the thermal curable resin. Therefore, it allows the composite structures cured by electron beam to be used at higher temperatures than that obtained by thermal curing process.

Acknowledgement

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