

HEAT-RESISTANT COMPOSITES CURED BY ELECTRON BEAM*

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Abstract Electron beam (EB) curing of composites has many advantages. Heat-resistant EB-curing composites could substitute polyimide composites used in aeronautical engines. In this paper, the effects of catalyst and dose on the cured resin were investigated. The heat-resistance of the resin cured by EB was evaluated by dynamic mechanical analysis (DMA). The experimental results show that the mechanical properties of the composites cured by EB could meet the specifications of aeronautical engines at 250°C.

Keywords Electron beam curing, Composites, Epoxy, Heat-resistance

INTRODUCTION

Electron beam (EB) curing of polymer matrix composites is a novel manufacturing process having the merits of low-cost and no pollution. It is a nonthermal, nonautoclave curing process that potentially offers many special advantages compared to thermal curing methods^[1-4] such as:

Curing at ambient temperature; this can eliminate dimensional changes in both the product and the tooling, thus reducing the thermal stresses in the final product.

Curing time is reduced; the production speed of EB curing far exceeds that of thermal curing with a typical autoclave.

The stability of resin is improved, most EB curable resin would not cure at room temperature, so it is unnecessary to store the resin at low temperature.

EB curing process offers better material handling, it includes the manufacturing of the prepreg and the curing of the composites.

The EB process is suitable for manufacturing large composite parts.

The curing area is selectable during EB-curing, so it is very suitable for repairing composites.

The volatiles evolved during composite manufacturing is reduced, and the hazardous curing agent which is harmful to the environment and the workers is eliminated.

The EB curing process could be combined with other composite manufacturing methods, such as pultrusion, winding, RTM, and so on. Generally, the EB curing process can save 25%~65% of the manufacturing cost of the composites.

In order to improve the performance of aeronautical engines, many engine parts were manufactured with polymer matrix composites^[5], such as inner duct, outer duct, and so on. Generally, the lowest in-service temperature of engine parts is 250°C, so the epoxy and BMI matrix composites could not meet this requirement.

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At present, the composites used in aeronautical engines are polyimide (PI) matrix composites. But the PI composites should be fabricated under conditions of high temperature (higher than 300°C) and high pressure (higher than 2 MPa), and moreover, some small molecules (such as water) will be generated during the curing of PI resin, so these factors will affect the process and the properties of the composites. In addition, some hazardous raw materials (such as 4,4'-methylenedianiline) were used in most of the PI resins. In order to avoid these disadvantages of PI composites, we hope to replace the PI composites by EB curing heat-resistant composites.

EXPERIMENTAL

Manufacturing and Curing of EB Curable Resin

The initiator was added to the phenolic epoxy resin (F46) that has been heated to 80~100°C, and the resin system was stirred to facilitate the dissolution of initiator the resin. The resin was cured by electron beam, and the cured resin was used to evaluate the cure degree and other physical properties. Beijing Normal University is the proprietor of the electron beam accelerator. Energy: 5 keV, current: 200 μ A, power: 0.7 kW.

Manufacturing of Its Composites

The prepreg was fabricated by the solvent method. F46 epoxy resin (30 wt%) and initiator were dissolved in acetone. The weight percentage of the resin in the prepreg was within the range of 30 wt%~35 wt%. The prepreg was dried at room temperature, then cut and laid up. The stacking sequence is [0]16. In order to consolidate the panel and exclude air between the plies, the panel was treated under vacuum bag pressure at 70~80°C for 1.5 h. The treated panel was cured by electron beam under vacuum bag pressure in Beijing Normal University. The EB-curing dose was 200 kGy.

Characterization

FTIR spectra

FTIR-spectra were recorded on a Nicolet 750 FTIR spectrometer with KBr-pelleted samples.

Glass transition temperature

MKIII DMTA (England Science Rheological Corporation) was used, temperature programming rate: 5 K/min, frequency: 1Hz.

Thermal decomposition temperature

Du Pont TGA (thermogravimetric analysis) 2100 was used, temperature programming rate: 10 K/min, atmosphere: N₂, flow rate: 25 mL/min.

Flexural mechanical property

This was tested according to GB3356-82.

RESULTS AND DISCUSSION

The Thermal Properties of the Cured Resin and Its Effective Factor

In early research work, the EB-curing composites were limited to acrylate epoxy matrix composites. Acrylate epoxy resin can be easily cured by electron beam, but its T_g is low, the curing shrinkage is serious, and its hydrothermal property is poor. Now, most of the research focuses on the cationic epoxy, which has both good processibility and excellent properties. The EB curing cationic epoxy matrix composites possess many advantages, such as low moisture content, heat resistance, low curing shrinkage, and so on. In order to further improve the heat resistance of the EB curing resin matrix and its composites, the cured resin must have a high degree of crosslinking, and the molecular structure between the crosslinking points must be rigid. The high degree of crosslinking results from the high epoxy value of the uncured resin, and the rigid molecular structure originates from the trapezium or ladder-like structure. The phenolic epoxy resin (F46) possesses such a heat resistant structure:

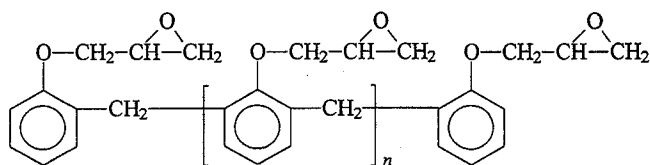


Table 1 shows the effect of different initiators and radiation doses on the properties of the EB cured F46 resin. Initiators D10, D11, and D12, are triaryl sulfonium hexafluoroantimonate, triaryl sulfonium hexafluorophosphate, and diaryl iodonium hexafluoroantimonate, respectively. During the radiation curing of the resin system, the initiator was decomposed to generate strong proton acid HX that catalyzed the opening of the ring of the epoxide and initiated the polymerization (conforming to the cationic mechanism)^[6, 7]:

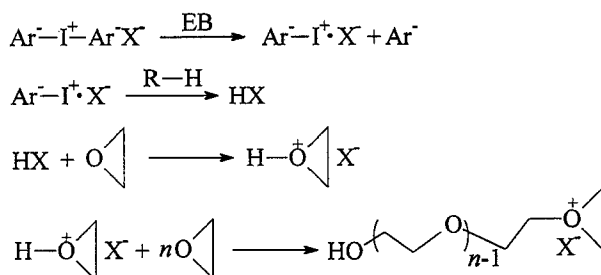
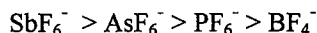


Table 1. The effects of initiator and radiation dose on the properties of cured F46 resin

	Initiator			Radiation dose (KGy) (D12)			
	D10	D11	D12	100	150	200	300
Curing degree (%)	79.45	65.35	81.15	75.02	81.15	81.3	82.1
T_g (°C)	227.2	144.7	238.1	208.3	238.1	234.4	236.7

The counter-anion of diaryliodonium or triarylsulfonium seriously influences their effectiveness. The effect of counteranion has been described in the literature^[6]:



Namely, the effectiveness of the initiator is inversely related to the nucleophilicity of the counteranion. The initiators having an anion of weaker nucleophilicity are generally efficient, because they generate a stronger acid.

Experimental results have shown that the effectiveness of D12 is higher than that of the D11. Because the acidity of HSbF_6 generated by D12 is stronger than that of HPF_6 generated by D11, the conversion of epoxide groups of the resin system initiated by D12 is higher than that of the D11 initiator, and the heat resistance of the former is better than that of the latter. The radiation decomposition of diaryliodonium initiator is easier than triarylsulfonium, so its effectiveness is higher than that of triarylsulfonium initiator.

The radiation dose also affects the properties of the cured resin. For the F46 epoxy system (initiated by D12), the T_g of the cured resin is highest at a radiation dose of 150 kGy. There is no obvious increase in the curing degree and the heat resistance of the resin if we continue to increase the radiation dose.

Figure 1 is the dynamic mechanical analysis curve of cured F46 epoxy (initiated by D12). It shows that though the T_g of the resin is 238°C, the decrease of the dynamic modulus at 238°C is only 0.3 order of magnitude. The dynamic modulus of the normal thermosetting resin would decrease by 0.8~1.0 order of magnitude at the glass transition temperature, but there is still no such large decrease at 350°C for the F46 resin cured by EB. From the DMA curve of the F46 resin, the T_g cannot be used to evaluate the heat-resistance of the resin. The mechanical properties at high temperature can signify the heat-resistance of the cured resin.

EB cured F46 epoxy resin not only has excellent heat-resistance, but also shows good thermal stability (shown in Fig. 2). The starting thermal decomposition temperature of the resin cured by EB is about 390°C, and

the percentage of the residue carbon is more than 45%. The experimental result shows that the concentration of the initiator used in the resin would affect the thermal decomposition temperature (shown in Table 2). When the initiator concentration is low, the curing degree is low, so the thermal decomposition temperature is also low. When the concentration is higher, the thermal decomposition temperature is also lower, though the curing degree is higher. At high concentration, though the conversion of epoxide group was increased, the linking density of the cured resin was decreased, so the decomposition temperature was decreased.

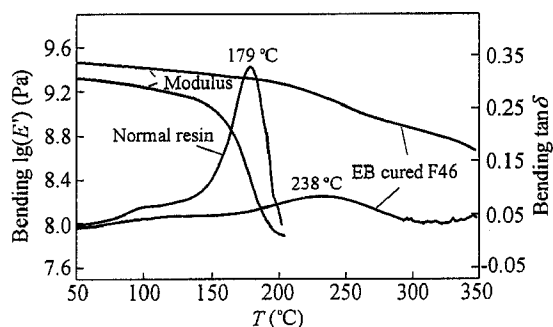


Fig. 1 The DMA curve of cured F46 resin

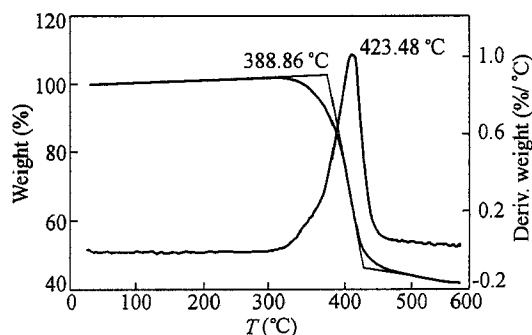


Fig. 2 The TGA curve of cured F46 resin

Table 2. The effect of initiator concentration on the thermal decomposition temperature

Concentration (wt%)	1.0	2.5	3.0	4.0
Conversion (%)	64.5	81.17	84.42	89.60
Decomposition temperature (°C)	1*	388.9	390.8	387.8
	2*	423.5	425.5	423.1
				418.9

* 1 The extrapolated starting decomposition temperature

2 The temperature at which the weightlessness rate is fastest

The Mechanical Properties of the Composites

Table 3 shows the flexural properties of F46 epoxy resin matrix composites reinforced by AS4 graphite fiber. The retention of the flexural strength of the AS4/F46 composites at 250°C is about 70%, and that of the flexural modulus is more than 85%. It is shown that the F46 matrix cured by EB possesses good heat resistance, and its retention of mechanical properties at high temperature is higher. The AS4/F46 composites might be used in some engine parts.

Table 3. The flexural properties of AS4/F46 composites

Flexural strength (MPa)			Flexural modulus (GPa)		
RT	250°C	Retention (%)	RT	250°C	Retention (%)
1470	1024	69.7	115	98	85.2

CONCLUSION

The initiating effectiveness of diaryl iodonium hexafluoroantimonate (D12) in penolic epoxy resin (F46) is the highest among the initiators, and the resin initiated by D12 possesses good heat resistance and thermal stability. At the same time, the cured resins have the most excellent heat resistance and thermal stability when the concentration of the initiators used are within the range of 2%–3%. The retention of the flexural strength of AS4/F46 composites at 250°C is about 70%. These materials may be of use in some engine parts.

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