Study on the Heat-Resistant EB Curing Composites

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Abstract: There are many advantages in the EB-curing process of composites. Heat-resistant EB-curing composites could substitute for polyimide composites used in aeronautical engine. 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 thermal analysis (DMTA). The experiment result shows that the mechanical property of the composites cured by EB could meet the needs of the aeronautical engine in 250℃.

Key words: electron beam curing composites Epoxy heat-resistance

INTRODUCTION

Many aeronautical engine parts were manufactured with polymer matrix composites to improve its performance [1]. Generally, the lowest in-service temperature of engine parts is 250 ℃, so the epoxy and BMI matrix composites could not meet the need. At present, the composites used in aeronautical engine is polyimide(PI) matrix composites. But the PI composites is fabricated under the condition of high temperature and high pressure, and some small molecule was generated during the curing of PI resin, so those will effect the process and the property of the composites. In addition, the hazardous raw material was used in the most of the PI resin. In order to avoid these disadvantages of PI composites, we hope to replace the PI composites by EB curing heat-resistant composites.

EXPERIMENTAL

1.Manufacturing and curing of resin: The initiator was added to the phenolic epoxy resin (F46) that has been heated to 80~100℃. The resin was cured by EB, and the cured resin was used to evaluate the curing degree and other physical properties. Beijing Normal University supplied the EB accelerator. Energy: 5KeV, current: 200 μ A, Power: 0.7kW.

2.Manufacturing of its composites: The prepreg was fabricated by solvent method. F46 epoxy resin and initiator was dissolved in acetone. The stacking sequence is $[0]_{16}$. the panel was treated under vacuum bag pressure at 70~80℃ for 1.5hr. The treated panel was cured by electron beam. The EB-curing dose was 200kGy.

3.Property Characteristics

FTIR spectra: It were taken in KBr pellets using Necolet 750 FTIR spectrophotometer
Glass translation temperature: MKIII DATA(England Science Rheological Corporation), ramp rate: 5℃/min, frequency: 1Hz
Heat decomposing temperature: Du Pont TGA 2100 was used, ramp rate: 10℃/min, atmosphere: N_2, flow rate: 25ml/min **Flexural mechanical property**: GB3356-82.

RESULT AND DISCUSSION

1.The Thermal Properties of the Cured Resin and Its Effective Factor

The EB curing cationic epoxy matrix composites possesses advantages of low moisture content, heat resistance and low curing shrinkage, and so on. In order to improve the heat resistance of the EB curing resin matrix and its composites, the cured resin must has high degree of crosslinking, and the molecular structure between the crosslinking point must be rigid. The high degree crosslinking sources from the high epoxy value of the uncured resin, The F46 possesses the character of heat resistant structure.

Table 1 shows the effect of different initiator and radiation dose on the property of the EB curing F46 resin. Initiator 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 epoxide group opening ring to polymerize (conforming to the cationic mechanism).[2, 3] The counteranion of diaryliodonium or triarylsulfonium seriously influences their effectiveness. The effect of counteranion has been described in literature[2]:

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

The experimental result has 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 the HPF_6 generated by D11, the conversion of epoxide group 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 decompose of diaryliodonium initiator is easier than triarylsulfonium, so its effectiveness is higher than that of diarylsulfonium initiator.

The radiation dose also effects the properties of the cured resin. For F46 epoxy system (initiated by D12), the Tg of the cured resin which radiation dose is 150kGy is highest. There are no obvious increases for the curing degree and the heat resistance of the resin if we continue to increase the radiation dose.

Table 1 the effects of initiator and radiation dose on the property

	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
Tg（℃）	227.2	144.7	238.1	208.3	238.1	234.4	236.7

Fig.1 is the DMTA curve of cured F46 epoxy (initiated by D12). The DMTA curve shows, though the Tg of the resin is 238℃, the decrease of its dynamic modulus (DM) at 238℃ is only 0.3 order of magnitude. The DM of the normal thermosetting resin would be decreased 0.8~1.0 order of magnitude at glass translation temperature, but there is still no such large decrease at 350℃ for the F46 resin cured by EB. From the DMTA curve of the F46 resin. The mechanical properties at high temperature can show its heat-resistance.

EB curing F46 epoxy resin not only has excellent heat-resistance, but also shows good thermal stability (shown in fig.2) the start thermal decomposing temperature (TDT) of the resin cured by EB is about 390℃, and the percentage of the residue carbon is more than 45%. The result shown that the concentration of the initiator in resin would effect the TDT (shown in table 2). When the concentration is low, the curing degree is low, so its TDT is low. When the concentration is higher, though the curing degree is higher, its TDT is also lower. While the concentration being high, though the conversion of epoxide group was increased, the linking density of the cured resin was decreased, so its decomposing temperature was decreased.

Table 2 the effect of initiator concentration on thermal decomposing temperature

concentration, wt%		1.0	2.5	3.0	4.0
conversion, %		64.5	81.17	84.42	89.60
Decomposing	1	388.9	390.8	387.8	382.8
Temperature, ℃	2	423.5	425.5	423.1	418.9

* 1 is the extrapolating start decomposing temperature, 2 is the temperature when the weightlessness rate is fastest.

2.The mechanical properties of its 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 in 250℃ is toward 70%, and that of the flexural modulus is more than 85%. It was shown that the F46 matrix cured by EB possesses good heat resistance, and its retention of mechanical property in high temperature is higher.

Table 3 the flexural properties of AS4/F46 composites

flexural strength（MPa）			flexural modulus（GPa）		
RT	250℃	Retention（%）	RT	250℃	Retention（%）
1470	1024	69.7	115	98	85.2

CONCLUSION

the initiating effectiveness of D12 in penolic epoxy resin(F46) is highest among the initiators，and the resin 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 are 2%~3%. The AS4/F46 composites in 250℃ is toward 70%.

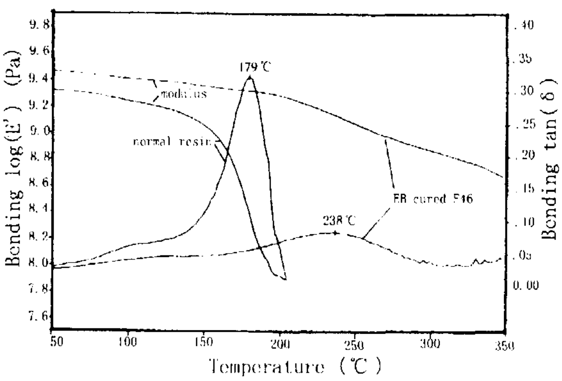

Fig.1 the DMA curve comparison of cured resin

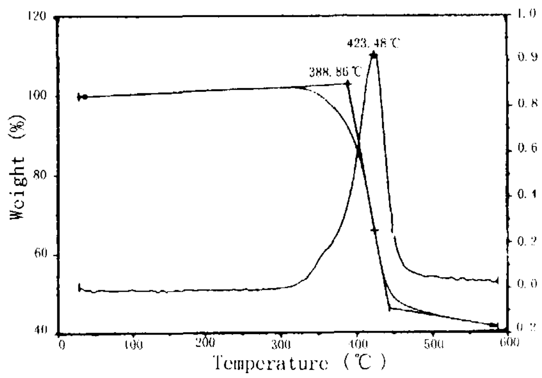

Fig.2 the TGA curve of cured F46 resin

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