Adhesive of Benzoxazine Resin and Adhesion Property

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Key words: Benzoxazine; high temperature resistance; film adhesive

ABSTRACT

In this paper, a benzoxazine resin-based (BZ) adhesive with high temperature resistant was developed with BA-a benzoxazine resin. The fabricated benzoxazine-based film adhesive has high adhesion reliability, with single-lap shear strength of 23.20 MPa, 28.36 MPa and 20.04 MPa at room temperature, 140°C and 175°C respectively. The curing process of the film adhesive matches well with that of carbon fiber reinforced BZ prepreg and the film adhesive has stable adhesion properties. Its biggest advantage is that, during storage and transportation, there is no need of refrigeration. After storage for 60 days at room temperature, its process performance and adhesion properties remain unchanged. It is expected to be used in aerospace, high-speed rail and other applications.

1. INTRODUCTION

In recent years, benzoxazine resin has attracted wide attention from scientific researchers due to its excellent property.A lot of research on the synthesis[1-4], reaction mechanism of benzoxazine resin[5], intermolecular hydrogen bonds in benzoxazine resin[6], thermal weight loss during curing process[7], modified blending[8,9], RTM molding benzoxazine resin[10] At present, there are few research reports about benzoxazine resin adhesive and its adhesion properties [11-13].

Compared with epoxy-based film adhesive, the benzoxazine-based film adhesive shows better heat resistance and flame retardancy. Comparison with phenolic-based film adhesive, the fabricated film adhesive has better durability while doesn't release small molecules or form microcracks or bubbles during curing process. Compared with bismaleimide-based film adhesive, the fabricated film adhesive has significant advantages in cost and curing temperature, i.e. the curing process could be completed in just 3 h at only 190 °C. It is expected to be used in aerospace, high-speed rail and other applications.

2. Experimental

2.1 Materials

BA-a benzoxazine resin was obtained from Sichuan University, carbon fiber reinforced benzoxazine prepreg was purchased from Sichuan Xinwanxing Carbon Fiber Composites Co., Ltd.

2.2 Characterization

Single-lap shear strength was tested according to ASTM D1002-05 and drum peel strength was tested according to ASTM D1781 using Instron 4505 electronic materials testing machine. Aluminum alloy (model LY12CZ) was anodized before bonding. Glass transition temperature was tested by DMA method on DMS 6100 dynamic thermal mechanical analyzer, with sample size of 18 mm×5 mm×1.5 mm, frequency of 1 Hz, and heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was carried out on TGA4000 thermal gravimetric analyzer in air and N_2 atmosphere, with heating rate of 10°C/min, and test temperature range of 25~800°C.

3. RESULTS AND DISCUSSION

3.1 Heat resistance of benzoxazine resin film adhesive

Figure 1 shows the dynamic mechanical analysis (DMA) curves of cured benzoxazine resin film adhesive. As can be seen from the figure 1, the glass transition temperature of the cured adhesive was 224.7°C, indicating that it has good high temperature resistance. So the cured adhesive could be used at about 180°C for a long time. Figure 2 shows the thermal gravimetric analysis (TGA) curves of the cured benzoxazine resin film adhesive. As can be seen from the figure 2, 5% weight loss temperature of the cured adhesive in air atmosphere was 400.4°C and there is almost no weight loss below 350°C, indicating that the cured adhesive has good heat resistance. The char yield at 800°C in nitrogen atmosphere remains at 48%, indicating that the cured adhesive has good ablation resistance. High char yield is a typical feature of flame retardant materials, because the carbon generated during material decomposition will cover the surface of the material, which could reduce the decomposition rate and gas diffusion rate of the material which results in flame retarding. The char yield of most organic adhesives at 800°C in nitrogen is relatively low. For example, the char yield of epoxy adhesive is generally only 5%~15%, while the char yield of phenolic resin adhesive at 800°C generally remains at 40%~60%.

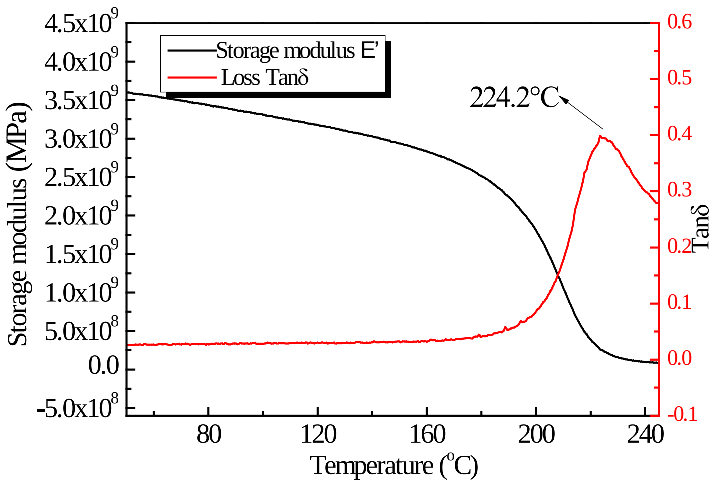

Figure 1. DMA curves of the cured adhesive.

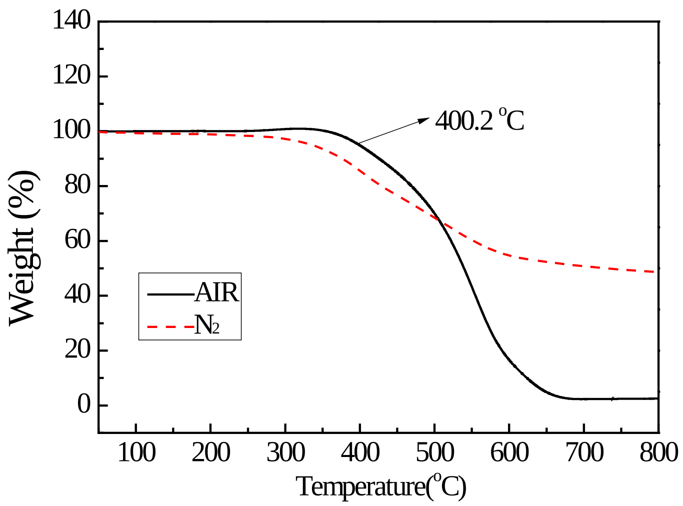

Figure 2. TGA curves of the cured adhesive.

3.2 Assessment of adhesion, hygrothermal aging and thermal aging properties of benzoxazine resin film adhesive

Tab. 1 shows the tensile shear strength of the cured benzoxazine resin film adhesive. As can be seen from the table 1, the adhesive has good adhesion mechanical properties. The shear strength was 23.20 MPa, 28.36 MPa and 20.04 MPa at room temperature, 140 °C and 175°C respectively. As can be seen from the standard deviation, the tensile shear strength data of the adhesive are concentrated, with low degree of dispersion, indicating stable adhesion properties. The shear strength at different test temperatures after hygrothermal aging declines unobviously, and the shear strength at different test temperatures after hygrothermal aging for 500h remains above 90 %. This is because cured benzoxazine resin adhesive has large amounts of intra-molecular and inter-molecular hydrogen bonds, which shield the interaction between water molecules and polymer, leading to excellent hygrothermal aging properties. As can be seen from the thermal aging properties in Tab. 1, the shear strength of the adhesive at 180°C after thermal aging for 200 h remains unchanged, showing good heat resistance.

Tab. 1 The shear strength of BZ film adhesive

	Test Temperature (°C)	Dry	σ	500 hrs. at 71 ℃ & 95% R.H.	σ	200 hrs. at 180℃	σ
Single lap shear strength (MPa)	-55	22.10	0.52	21.50	0.54	22.54	0.62
	25	23.20	0.48	21.50	0.51	23.42	0.61
	140	28.36	0.56	26.16	0.58	27.61	0.47

	175	20.04	0.59	18.52	0.62	19.45	0.82

3.3 Shear strength of benzoxazine film adhesive-bonded composites

Tab. 2 shows the shear strength of benzoxazine film adhesive-bonded carbon fiber reinforced benzoxazine composites. As can be seen from the table 2, when carbon fiber composites are used as base material, the shear strength was lower and more dispersion than that of aluminium alloy as base material. This is because the tensile failure forms of sheared sample with composites as base material are usually interlayer failure and mixed failure patterns of composites, which affects the characterization of the strength of the film adhesive. Aluminium alloy base material could better reflect the intrinsic strength of the film adhesive material.

Tab. 2 Shear properties of BZ film adhesive-bonded BZ composites

	Test Temperature (°C)	Dry	σ	Failure form
Shear strength (MPa)	-55	14.10	1.74	Composite failure
	25	16.30	1.63	Mixed failure dominated by composite failure
	140	24.12	0.95	Mixed failure dominated by cohesive failure
	175	18.04	0.82	Cohesive failure

The micrographs of failure sections of sheared sample of benzoxazine film adhesive-bonded carbon fiber reinforced benzoxazine composites are shown in Figure 3. Figure 3a, 3b, 3c and 3d correspond to failure sections of the sheared sample at test temperatures of -55°C, 25°C, 140°C and 175°C respectively. What is particularly noteworthy is that the tensile shear failure form of the film adhesive-bonded composites at low temperature are dominated by composite failure. The failure sections are mostly carbon fiber bundle tear and rupture with greater dispersion. As the temperature increases, the failure direction moves to film adhesive interlayer, shear strength gradually get concentrated, and the failure form transforms to film adhesive interlayer failure at 175°C. This is because the interlayer toughness of the composites at low temperature is poor, so in the case of force different from the direction of the fibers, the force couldn’t be conducted away timely, which directly damage the fiber layer. At high temperature, the interlayer toughness of the composites becomes excellent, and force different from the direction of the fibers could be conducted away, so the failure occurs between layers of composites.

As can be seen from Figure 3, there are clear adhesive interface layers, so the adhesive maintains its good shape during the curing process, indicating that there is no permeation between the adhesive and the composite matrix resin, and both the adhesive and the composites maintain their own material properties. Benzoxazine film adhesive shows good interfacial adhesion properties with benzoxazine composites.

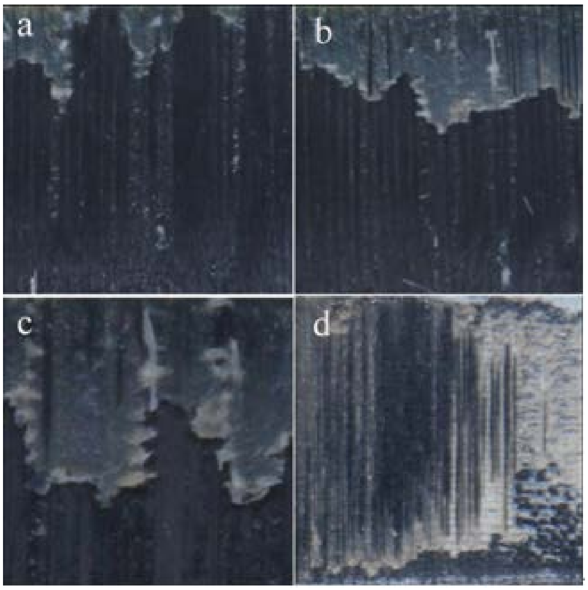

Figure 3. Micrographs of shear sections of BZ film adhesive-bonded composites

3.4 Storage period of benzoxazine resin film adhesive

Compared with other resin film adhesives, benzoxazine resin film adhesive could be stored at room temperature for a long time. In this study, epoxy and DDS were added to benzoxazine resin film adhesive, but the amount of DDS was less and DDS was not pre-polymerized with the resin during the adding process, so the storage period was not affected. The film adhesive was stored at room temperature (20~25°C) in a dark and dry environment. The performance during the storage period is shown in Tab. 3. As can be seen from the table 3, the adhesion strength of high-temperature benzoxazine resin film adhesive almost unchanged within 60 days. In addition, the film adhesive remained soft within 60 days, showing outstanding paving process performance.

Tab. 3 BZ film adhesive out of freezer life

Property	Test Temperature, °C	Fresh	30 days out time	60 days out time
Shear strength (MPa)	-55	22.4	22.7	22.8
	23	23.5	23.9	23.1
	140	28.8	28.7	28.2
	175	20.5	20.7	20.3
Flatwise tensile (MPa)	23	4.5	4.4	4.6
	140	5.5	5.4	5.6
Drum peel strength (N·mm/mm)	23	32.1	31.8	31.7

4. CONCLUSIONS

In summary, the high glass transition temperature of benzoxazine resin film adhesive was 224 °C，and the 5% weight loss temperature in air of was 400 °C. The cured film adhesive has good ablation resistance with char yield of 48 % in nitrogen at 800°C. The film adhesive has high adhesion reliability, with shear strength of 23.20 MPa, 28.36 MPa and 20.04 MPa at room temperature, 140°C and 175°C respectively. The aluminum honeycomb drum peel strength was 32.1N·mm/mm. The film adhesive has no need of refrigeration. After storage for 60 days at room temperature, its process performance and adhesion properties remain almost unchanged. It is expected to be used in aerospace, high-speed rail and other applications.

ACKNOWLEDGEMENTS

The authors would like to thank Qichao Ran from Sichuan University for him help and useful suggestions.

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