Epoxy-Polyimide Heat Resistance Adhesive

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Abstract

In order to increase the heat resistance of the epoxy, a polyimide precursor was used as the cure agent. The precursor is soluble in THF and can be imidized into polyimide by heating. So the epoxy (four functional groups) is mixed with the precursor easily. The curing of the epoxy and form of the polyimide take place at the same time. The epoxy-polyimide adhesive exhibited good bonding property and heat resistance. The adhesive strength can be increased by adding fluorine rubber. The adhesive shear strength (Al/Al) reached 20MPa and 4MPa at room temperature and 250℃ respectively.

Keyword: Epoxy, Polyimide, Precursor, Fluorine Rubber, Tetraglycidyldiaminodiphenylmethane, Adhesive

Introduction

Epoxy resins are widely used as adhesives and matrix resins of composite materials. But their heat resistance are not high, and can not exceeded 180℃ in long-life performance . It has been known that polyimide exhibits good mechanical properties and high heat resistance. It can reach 250℃ and 300℃ for long time and short time usage, respectively. It has been reported that epoxy and polyamic acid blending was used as adhesives[1-4]. Because the hydrolysis of polyamic acid takes place easily its storage stability is poor. We synthesized the polyimide precursor that is a polyester ammonium. It is soluble in THF and formed into polyimide by heating. Therefore it can be mixed with epoxy resin easily. In order to increase the heat resistance of the epoxy resin, we used a epoxy with four functional groups (tetraglycidyldiaminodiphenylmethane, AG-80). Its heat resistance can reach 180℃ the same as the matrix resin of the composite material[5]. It exhibits both the specialties of the epoxy and the polyimide, that is a good adhesive of epoxy and high heat resistance of polyimide. It can be used as an heat-resistant adhesive for aerospace industry.

Experimental

Materials:

3,4,3',4'-benzophenonetetracarboxylic dianhydride (BTDA) was obtained from Daicel Chemicals in Japan. Epoxy with four functional groups AG-80 and 3,4,3'4'-oxydiphthalic anhydride (ODPA) were made in Shanghai Research Institute of Synthetic Resins. Fluorine rubber FB-1 and FB-2 were obtained from Shanghai 3F Company. Mixed diaminodiphenylmethane (MMDA) was purchased from Shandong Yantai Chemical Company. Others were used from purchase without purification. .

Synthesis of polyimide precursor[6]

165g of ODPA, mixed with 100.38g of diaminodiphenylmethane (MMDA) and 300ml of methanol were added into 1000ml flask equipped with stirring, thermometer and condenser. then the mixture was heated until reflux and kept for 3hours. A yellow solution was obtained. and methanol was distilled away. The viscous product was poured into plate and dried under vacuum at room temperature for 24 hours. The polyimide precursor of polyester ammonium (PIP) was thus obtained

Adhesives

At first, PIP was dissolved in THF then mixed with AG-80 and fluorine rubber. It was coated on the surface of Al piece and stick to each other under some pressure. It was cured at 200℃ for 2 hours. Shear strength were determined at different temperatures with Shimadzu Autograph Ag-50KNE by GB Standard.

Results and Discussion

We investigated the effects of the ratio of PIP to AG-80; adding fluorine rubber; curing temperature and time. Here, PIP has two functions, the first is a curing agent and the second is to form polyimide. We found shear strength reached maximum when the ratio of PIP and AG-80 was 20:80 (Fig.1). If PIP was more than 20%, the adhesive strength decreased. When PIP is less than 20%, the heat resistance of the adhesive decreased. The higher shear strength was obtained at a curing temperature of 200℃ for 2-3 hours (Fig.2). The adhesive can be cured at room temperature, but polyimide cannot be formed. PIP can form polyimide when curing temperature was rose up to 150℃[3]. In order to increase the extent of imidization and the strength, it was suitable to cure and imidize at 200℃ for 2-3 hours. We investigated the methods of surface treatment for metal because it is very important for metal adhesive. Four methods were used for surface treatment. They were rubbing, acid washing, using surface active agent (KH 560) and no treatment. The results were listed in Table 1. We found that the best method was rubbing, acid washing and using KH 560 together. It was because surface area was increased by rubbing and acid washing, then the strength of the interface between the metal and the adhesive was increased by using KH 560. Thus we used this method for surface treatment in our next tests The shear strength was increased by adding fluorine rubber (Fig.3). The effects of adding various amounts and grades of fluorine rubbers were discussed. It found that the maximum shear strength at 200℃ were achieved by adding 9 wt.% and 12wt.% for FB-1 and FB-2 grades respectively. Because of FB-2 molecular weight is higher than that of FB-1, this could affect on their compatibility and toughness. Two kinds of tetracarboxylic dianhydride were used for preparation of PIP. At room temperature adhesion of BTDA system is higher than that of ODPA system. But the shear strength of ODPA system was higher than that of BTDA system at 250℃ (Table 2). It is because ether bond of ODPA could be better than carbonyl group in heat stability. Therefore the latter is stronger than the former for metal adhesive at room temperature.

Conclusion

The new heat-resistant adhesive was obtained by mixing AG-80 and PIP and curing at 200℃ for 2-3 hours. It exhibits good heat resistance and bonding strength. The shear strength reached 20MPa and 4MPa at room temperature and 250℃, respectively. It can be used as structural adhesive in aerospace field.

Reference

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Table 1 The Effect of Surface Treatment for metal

Shear Strength (MPa)	Rubbing, Acid washing, KH 560	Acid washing, KH 560	Rubbing, KH 560	No treatment
ODPA	9.37	6.67	8.76	8.26

Table 2 The Effect of PIPs from ODPA and BTDA

Shear Strength (MPa)	R. T	200℃	250℃	270℃
ODPA	16.17	12.32	4.87	3.93
BTDA	22.6	4.78	3.84	2.35

R.T: Room temperature, Epoxy/PIP=80/20, Adhesive/Rubber=100/12.
Curing condition: 200℃ for 2 hours.

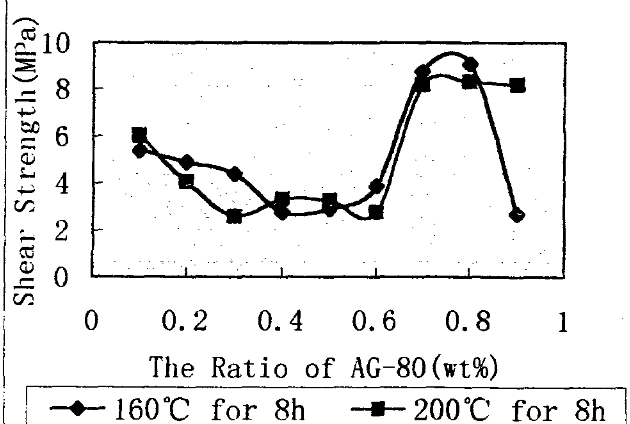


Fig1 The Effect of Ratio of AG-80

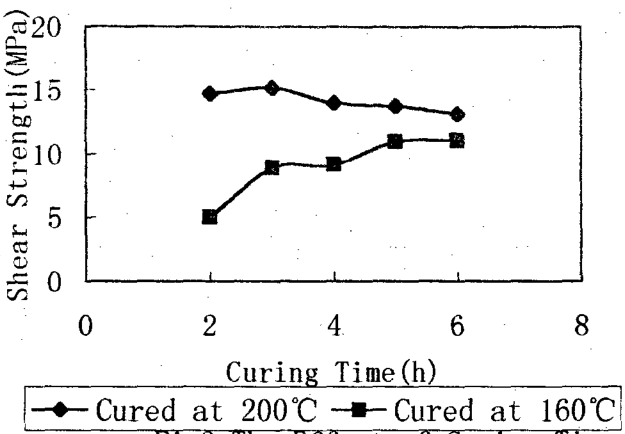


Fig2 The Effect of Curing Time

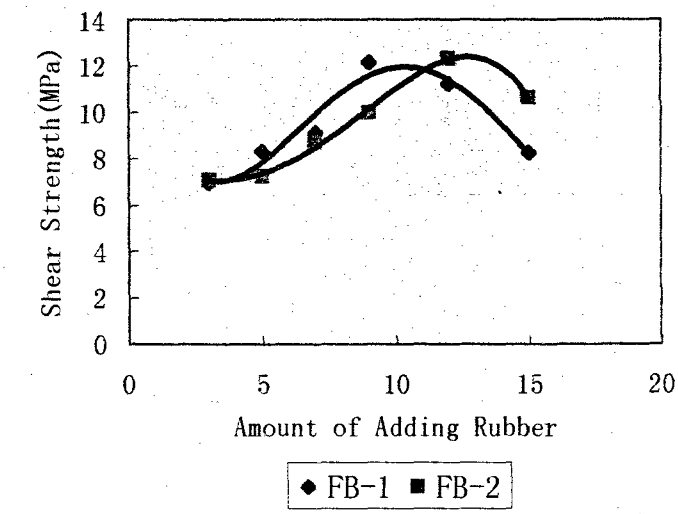
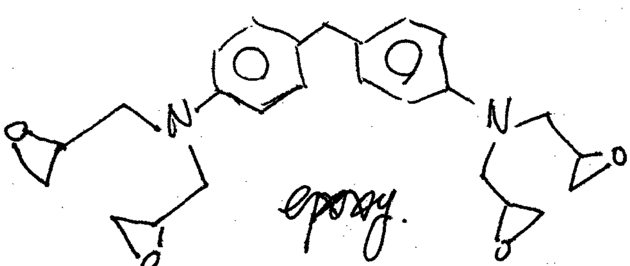


Fig3 The Effect of Adding Rubber



epoxy.

AG-80