A Novel Polyimide Adhesive With Low Cure Temperature

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Introduction

Aromatic polyimides are very attractive thermal resistance materials with various superior characteristics. Because polyimide adhesives exhibit good adhesive properties and mechanical properties , along with high thermal and thermooxidative stability in wide temperature range , they have been widely used as structure adhesives for aircraft and other space industries. However , aromatic polyimides are heterocyclic polymers that have bulk and rigid backbone structures , usually have high glass transition temperatures . they are difficult to process because they are insoluble in conventional organic solvents . The thermoplastic polyimide adhesives generally must be processed in the form of their polyamic acid precursors that more soluble in solvents , and then converted to the polyimide by heating at the temperature higher than the glass transition temperature (Tg) of the polyimide . they are usually used at lower than 300°C because there are no crosslinking structures in the chain structures . The thermosetting polyimide adhesives offer the advantage of improving processability without reducing their thermal properties , but the mechanical properties are not very good at room temperature . These adhesive systems are processed in oligomeric forms that have latent crossliking end groups , which form crosslinking structures at high temperature .

In the present study , a new polyimide adhesive has been prepared in network form (semi - 2 - IPN) . The linear polymer is first in polyamic acid or polyisoimide form that is soluble in organic solvents , and then can be converted to polyimide by heating , the other component is bismaleimide that can be crosslinked in the present of the linear polymers at about 200°C . This network system exhibits excellent adhesive strengths after curing at 200°C under press . It have two advantages compared with previously available polyimide adhesives . First , these two polymers should be miscibility , the resulting network exhibits good mechanical properties both at room temperature and at high temperature . Second , because the glass transition temperature of the linear polymer and the cure temprature of the oligomer are below 250°C , the adhesive systems offer advantage in processability . This semi - 2 - INP system was characterized and adhesive properties were examined .

Experimental

The preparation of the linear polyamic acid and polyisoimide were carried out in conventional methods. The Bismaleimide was made from maleacid anhydride and aromatic diamine, of which the structure is similar to that of the monomer of the linear polyimide. Two components were mixed in DMAc or diglyme at designated ratio. An adhesive scrim cloth was prepared by coating the resin onto the cloth, and the cloth was heated in oven to remove solvent after each coating. Treated alumirium adherends were then primed with resin and heated to 120°C for one hour for several times. The scrim cloth was cut and sandwiched between the two primed adherends. The adherends were bonded by heating from 120°C to 200°C under 1MPa pressure with 1°C /min heating rate. They were held at 200°C for 2.5 hours, then allowed to room temperature under pressure. All lap shear and peel test were performed with a Shimadzu Autograph AG-50KNE by GB standard.

Results and Discussion

Linear Thermoplastic polyimide adhesive exhibits excellent lap shear strength (LSS) at room temperature up to the Tg of the polyimide, and rather low LSS at high temperature range. It is possible that the adhesive system can be used at elevated temperature by adding the thermosetting oligomer. As shown in table 1, the semi-2-IPN adhesives not only offer excellent LSS at ambient temperature but also exhibit a surprisingly high strength retention at high temperature of up to 380°C. The properties of the adhesive system depend on the structure of the linear polyimide. There is an increase in the room temperature LSS from 12MPa to 20 MPa as the content of BTDA in A component is being increased. On the other hand, the No.2 adhesive exhibits the highest mechanical properties at elevated temperature. This may indicate that the semi-2-IPN show better miscibility between B component and A component in this structure after cured at 200°C .

The relationship between adhesive strength and the ratio of A and B components were shown in Table 2. It is necessary to use bismaleimide as crosslinking component to increase the adhesive strength at elevated temperature. However, if the content of B component was excessive over 30 percent, the room temperature adhesive strength would become lower because the toughness of the adhesive system is reduced. It is very important for this semi-2-IPN adhesive system to select a suitable chemical structure of B component and control its content.

Conclusion

The new adhesive system (Semi-2-IPN) exhibits good adhesive strength at high temperature (300°C) and fine curing processability at low temperature (200°C). It can be used as structure adhesive in aircraft and other advanced industries.

Table 1. Effect of Chemical Structure on the Properties of the polyimide adhesives

Series	1	2	3	4
A components (molar ratio)				
2.2-bis[4-(3-aminophenoxy)phenyl]propane	1.00	1.00	1.00	1.00
BTDA	1.00	0.80	0.65	0.50
PMDA	0	0.20	0.35	0.50
Lap Shear strength (MPa)				
Room temperature	20	19	11	12
300 C	7.8	9.0	/	/
380 C	1.9	5.4	2.1	2.0

B component : Bismaleimide oligomer A/B = 10/3 (w/w) in scrim cloth
A/B = 10/2 (w/w) in prime resin

Table 2. Effect of Ratio of A and B Component on properties of the polyimide adhesives

Series		1	2	3	4
A component (molar ratio)					
2.2-bis[4-(3-aminophenoxy)phenyl]propane		1.00	1.00	0.65	0.65
4.4 - ODA		0	0	0.35	0.35
BTDA		0.80	0.20	0.65	0.65
PMDA		0.20	0.20	0.35	0.35
A/B (w/w)	in scrim cloth prepreg	10/3	10/2	10/3	10/3
	in prime resin	10/3	10/2	10/2	10/3
Lap shear strength (MPa)					
Room temperature		10	20	/	/
300 C		/	7.9	4.1	4.7
350 C		5.1	4.6	/	/

B Component : Bismaleimide oligomer