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High Temperature Polyimide Matrix Resins and Carbon Fiber-reinforced Polymer Composites

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Introduction

Carbon fiber-reinforced PMR (*in situ* Polymerization of Monomeric Reactants) polyimide composites have been developed for the applications in aerospace and aviation industry as structural or sub-structural components in supersonic aircraft and missile airframes. Extensive research has been reported in recent years to improve the composite manufacturing processability as well as the composite performance at elevated temperature [1-3]. The micro-cracks of the composite parts initiated and advanced inward at elevated temperatures in the thermal servicing have been a big concern because the micro-cracks were found to deteriorate the material mechanical properties. It was recognized that improvement in impact toughness might reduce the possibility of the microcrack development. However, dramatic increase in impact toughness without sacrificing the servicing temperature as well as other mechanical properties has been a great technical challenge.

Thus, a series of novel PMR polyimide matrix resin were designed and synthesized, which was then employed to produce carbon fiber-reinforced polyimide composites for high temperature application. The chemistry of the matrix resin as well as the mechanical properties of the carbon fiber-reinforced polyimide composites were investigated.

Results and Discussion

The polyimide matrix resin was prepared by incorporating flexible ether-bridged aromatic segments into PMR polyimide backbone, which was produced from anhydrous alcohol solution of diethyl ester of 3,3',4,4'-oxydiphthalic acid, monoethyl ester of cis-5-norbornene-endo- 2,3-dicarboxylic acid, p-phenylenediamine (p-PDA), and 4,4'-methylenedianiline. The mole ratio of reactants endcap: dianhydride:diamines was 2: n: (n+1), in which *p*-PDA content in the diamine mixture was designed as 1:1. The homogeneous matrix resin solution containing 42 wt.% of solid content with absolute viscosity 60-75 m Pa.s at 25 °C, was stable for storing of more than 3 weeks at room temperature (25 °C) and longer than 3 months in refrigerator (4 °C). After storing for 21 days at room temperature, there isn't apparent changes observed i tt -IR absorption and in ^{1}H NMR spectrum.

Carbon fiber-reinforced polyimide composites were developed by thermally cured of B-staged prepregs prepared by impregnating of carbon fibers with the polyimide matrix resin solution in ethyl alcohol, followed by evaporating the solvent at room temperature. The carbon fiber prepregs, with the matrix re sin covered uniformly on carbon fiber, exhibited good processing characteristics for composite preparation, and the adhesion of matrix resin on carbon fiber is good enough to ensure the prepreg being layuped in mold. The unidirectional composite laminates showed great mechanical properties at 20 °C: flexural strength: 1730 M Pa; flexural modulus: 99.1 G Pa, and interlayer shear strength (ILSS): 98.3 M Pa. At 320 °C, flexural strength: 729 M Pa; flexural modulus: 81.6 G Pa; and interlayer shear strength (ILSS):

41.2 M Pa.

The mechanical strength, especially the flexural strength and interlayer shear strength (ISSL) was, to some extent, deteriorated upon the thermal aging time. For instance, the flexural strength at 20 °C and 320 °C reduced 16% and 33%, respectively, after thermal aged for 500 hrs in air. However, the flexural modulus and interlayer shear strength did not changed obviously after the 500 hrs thermal aging, implying that the composite exhibited excellent thermal stabilities.

The glass transition temperatures of the composites were changed slightly with the thermal aging. For instance, the Tg determined by DMA decreased 8 °C after thermal aging for 500 hrs at 320 °C in air. Experimental results indicated that the composite exhibited great hygrothermal resistance. After hygrothermally exposed at 120 °C and 2 atmosphere for 100 hrs, no apparent changes were observed in DMA curves.

Conclusions

A series of novel PMR polyimide matrix resin were designed and synthesized, which was then employed to produce carbon fiber-reinforced polyimide composites for high temperature application. The continuous carbon fiber-reinforced polyimide composites exhibited outstanding thermal and thermo-oxidative stability, hygrothermal resistance as well as great mechanical properties.

References

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耐高温聚酰亚胺基体树脂及其碳纤维增树脂基复合材料

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