



DEVELOPMENT OF HIGHLY SOLUBLE ADDITION-TYPE IMIDE OLIGOMER AND POLYIMIDE / CARBON FIBER COMPOSITE PREPARED BY IMIDE SOLUTION PREPREG

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Abstract

Novel highly soluble addition-type imide oligomer was synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA), 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene (BAOFL), and 4-phenylethynylphthalic anhydride (PEPA) to fabricate carbon fiber reinforced plastics (CFRP) by routing imide-solution prepreg. The imide oligomer was soluble in *N*-methyl-2-pyrrolidone (NMP) of more than 33 wt.%. Imide oligomer had good processability when using a hot press. The glass transition temperature (T_g) and 5% weight loss temperature (T_{d5}) of the cured resin were 321°C and 551°C, respectively. The elongations-at-break of the cured resin film was 10.2 %. An imide-solution prepreg was prepared from the imide oligomer solution and carbon fibers. Because the imide-solution prepreg generates no water during curing process, volatiles of the prepreg (i.e. solvents) were removable easily below 200°C. Polyimide / carbon fiber composite without voids was fabricated from the imide-solution prepreg.

1 Introduction

Aromatic polyimides are well known as high performance polymers. They have excellent thermal stability, mechanical properties, and electronic properties. Usually, aromatic polyimides have no solubility and a high melting temperature. Consequently, polyimide films were produced by imidization from poly(amide acid) solutions as precursors. The processability of polyimides is inferior compared to that of epoxies and bismaleimides. Therefore, polyimides prepared through a polycondensation reaction require

extremely severe processing conditions for molding. For moldable materials and matrices of carbon fiber composites, many addition-type polyimides (i.e. imide oligomers terminated with reactive groups) have been developed [1, 2]. One of them, PMR-15, which is prepared from 3,3',4,4'-benzophenonetetracarboxylic acid dimethyl ester (BTDE), 4,4'-methylene dianiline (MDA), and 5-norbornene-2,3-dicarboxylic acid monomethyl ester, had a high glass transition temperature (T_g) of 340°C [3]. However, PMR-15 is very brittle because of its high crosslink density. Furthermore, it has low thermo-oxidative stability because of its aliphatic bonds. Another addition-type polyimide, PETI-5, was developed by NASA Langley Research Center. It was prepared from the reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA), 3,4'-diaminodiphenyl ether (3,4'-ODA), 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB), and 4-phenylethynylphthalic anhydride (PEPA) [4–8]. The cured PETI-5 has high fracture toughness (elongation at break > 30%), high thermo-oxidative stability, and good processability. However, the cured resin has a relatively low T_g of 270°C because flexible diamines were introduced for the purpose of high melt fluidity.

Recently, Yokota et al. developed an amorphous, asymmetric, and addition-type polyimide "TriA-PI". TriA-PI was prepared from asymmetric monomer, 2,3,3',4'-biphenyltetracarboxylic dianhydride (*a*-BPDA), 4,4'-diaminodiphenyl ether (4,4'-ODA), and PEPA [9–11]. Both the imide oligomer and cured polymer have irregular and asymmetric structures that are derived from *a*-BPDA, resulting in a low melting temperature and a low melt viscosity for the imide oligomer, and a high T_g value of 343°C for the

cured polymer. Along with good processability, TriA-PI has high heat resistance, high thermo-oxidative stability, and good fracture toughness.

Usually, composites of carbon fibers and thermosetting polyimides are fabricated by routing an amide acid solution prepreg, because an uncured imide oligomer's solubility of more than 30 wt.% is required to produce a prepreg [6-8, 11]. In this route, water generated as a by-product of imidization in the curing process may cause the generation of voids in the composites. In previous works, in order to improve the solubility of the imide oligomer while maintaining high thermal resistance, fluorenylidene groups were introduced to an asymmetric thermosetting polyimide "TriA-PI" [12, 13]. In this work, an imide oligomer based on symmetric 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and a diamine containing fluorenylidene diphenyl ether group (9,9-bis[4-(4-aminophenoxy)phenyl]fluorene, BAOFL) was synthesized. Solubility, processability of the imide oligomer, and the thermal and mechanical properties of the cured resin were evaluated. An imide-solution prepreg was prepared from a highly concentrated solution of the imide oligomer and carbon fibers. Furthermore, a polyimide / carbon fiber composite was made from the imide solution prepreg.

2 Experimental Section

2.1 Synthesis of the imide oligomer

BAOFL (2.663 g, 5 mmol) and N-methyl-2-pyrrolidone (NMP, 8.8 ml) were placed in a three-necked flask, equipped with a magnetic stirrer and nitrogen inlets. s-BPDA (1.177 g, 4 mmol) was added to the solution. The reaction was allowed to stir for 2.5 h at room temperature, for 1.5 h at 60°C, and then for 1 h at room temperature under nitrogen flow. Subsequently, 4-phenylethynylphthalic anhydride (PEPA, 0.497 g, 2 mmol) was added to the solution; the solution was stirred for 18 h at room temperature and then for 5 h at 175°C. The solution was then poured into water (150 ml). The product was washed with methanol (60 ml), filtered, then dried at 60°C *in vacuo*.

2.2 Preparation of the cured resin film

Cured resin film was prepared in a polyimide film frame (80 mm × 50 mm × 75 μm) using a hot press. The imide oligomer (*ca.* 0.5 g) was heated at 310°C for 20 min on a hot plate. It was then cured at 370°C for 1 h under 2 MPa.

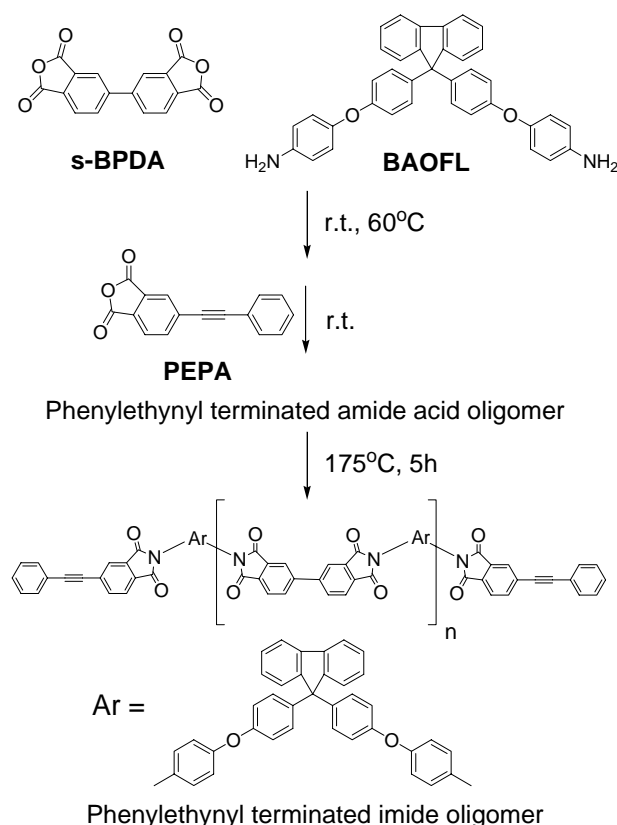


Fig. 1. Chemical structure of the imide oligomer containing fluorenylidene groups ($n = 4$).

2.3 Preparation of the imide-solution prepreg

IM600 carbon fiber plain fabrics washed in acetone (6K/bundle, 300 mm × 300 mm, carbon cloth areal weight of 194 g/m²; Toho Tenax Co., Ltd.) were dipped into the imide oligomer solution. The plain fabrics were dried at 100°C for 10 min. These procedures were repeated once again. The respective resin and volatile contents of the resulting prepreg were 36.4~38.8 wt.% and 13.5 wt.%, respectively.

2.4 Fabrication of the polyimide / carbon fiber composite

Plain fabric composites (150 mm × 150 mm, 12 and 24 ply) were cured using an autoclave. The lay-upped and vacuum-bagged prepreg was heated to 370°C. The sample was held at 370°C for 1 h under pressure of 14 kg/cm². After the curing, the pressure was released and the sample cooled to room temperature.

2.5 Characterization

Rheological measurement was conducted on an AR2000 (TA Instruments) at a heating rate of

4°C/min. Specimen disk (2.5 cm diameter) was prepared by compression-molding imide powder at room temperature. The test was run from 230–450°C at a heating rate of 4°C/min with a cycling frequency of 1 Hz and strain of 0.1%. Differential scanning calorimetry (DSC) was carried out using a DSC 6200 (Seiko Instruments Inc.) at a heating rate of 10°C/min under an atmosphere of flowing argon. Thermogravimetric analysis (TGA) was carried out using a TGA 6300 (Seiko Instruments Inc.) at a heating rate of 10°C/min under an atmosphere of flowing argon. Tensile test of film was performed at a tensile speed of 5 mm/min on specimens of 20 mm length, 3 mm width, and 120 μm thickness. A dynamic mechanical thermal analysis (DMA) was carried out in a TA Instruments ARES in the torsion test mode with 50 mm length, 12 mm width, and 2 mm thickness. Test was run at 25–450°C at a heating rate of 5°C/min with a 6.2832 rad/s cycling rate and strain of 0.01%. Short beam shear (SBS) strength was determined on a 24-ply specimen (25.4 mm length, 8.4 mm width, 4 mm thickness, and 16.7 mm span length) at 24°C. The SBS test was conducted on a mechanical testing machine under a constant displacement of 1 mm/min.

3 Results and Discussion

3.1 Properties of the imide oligomer and cured resin

The imide oligomer was synthesized from the reaction of s-BPDA, BAOFL, and PEPA through thermal imidization in NMP, as shown in Fig. 1. The calculated degrees of polymerization of the imide oligomer were 4. After imidization, the reaction solution maintained homogeneity without precipitation. Table 1 shows the properties of the imide oligomer. The imide oligomer had excellent solubility of more than 33 wt.% in NMP. The solubility is sufficient to prepare the imide-solution prepreg. The minimum melt viscosity was 326 Pa·s, measured by a rheometer. The imide oligomer could be molded easily by using a hot press. Thermal and mechanical properties of the cured resin are shown in Table 2. The glass transition temperature (T_g) of the cured resin exhibited 321 °C, judged by DSC. The 5% weight loss temperature (T_{d5}) was 551 °C. The tensile modulus, tensile strength, and elongations-at-break of the cured resin film were 2.78 GPa, 110 MPa, and 10.2 %, respectively. The cured resin exhibited excellent heat resistance and good mechanical properties.

Table 1. Properties of the imide oligomer

Solubility in NMP (wt.%)	Minimum melt viscosity ^{a)} (Pa·s)	Processability
33	326	good

a) Measured by a rheometer.

Table 2. Properties of the cured resin^{a)}

T_g ^{b)} (°C)	T_{d5} ^{c)} (°C)	E ^{d)} (GPa)	σ_b ^{e)} (MPa)	ϵ_b ^{f)} (%)
321	551	2.79	110	10.2

a) Cured at 370 °C for 1h. b) Determined by DSC at a heating rate of 10 °C/min under argon. c) Determined by TGA at a heating rate of 10 °C/min under argon. d) E; tensile modulus e) σ_b ; tensile strength f) ϵ_b ; elongation at break

3.2 Fabrication of polyimide / carbon fiber composite from imide solution prepreg

An imide solution prepreg was prepared from the imide oligomer solution in NMP. Properties of the imide prepreg are summarized in Table 3. Volatile components were more easily removable below 200 °C, measured by TGA.

Table 3. Properties of the imide-solution prepregs

Matrix resin	Imide-solution prepreg
	s-BPDA/BAOFL/PEPA = 4 / 5 / 2
Solvent	N-methyl-2- pyrrolidone
Carbon fiber	Toho Tenax IM600-6K
Weaving construction	Plain woven fabric
Carbon fiber areal weight (g/m ²)	194
Resin contents (wt %)	36.4~38.8
Volatiles (wt %)	13.5 (200°C 30min.)

A polyimide / carbon fiber composites (150 mm × 150 mm, 12 and 24 ply) were fabricated from the imide-solution prepreg by one-step. Imide-solution prepreg was lay-upped and vacuum-bagged, and then cured at 370°C for 1 hour under pressure of 14 kg/cm² in an autoclave. The resulting composite was good quality as determined by C-scan. The optical micrograph of the composite showed no voids nor matrix cracks (Fig. 2). The composite exhibited a T_g value of 308°C, determined by the onset temperature of decrease in the storage modulus E' of DMA curve. The short beam shear (SBS) strength was 76 MPa, which was almost the same value as that of the TriA-PI composite (77 MPa). A composite with high quality and high heat-resistance was obtained easily from the imide-solution prepreg.



Fig. 2. Optical micrograph of the polyimide composite (24 ply).

4 Conclusions

A novel soluble addition-type imide oligomer and its cured resin were developed. The introduction of BAOFL resulted in an increase in solubility of the imide oligomers prepared from not only asymmetric BPDA but also s-BPDA. An imide-solution prepreg was prepared directly from the imide oligomer solution and carbon fibers. Volatiles of the imide prepreg were more removable at lower temperatures than those of the amide acid prepreg. A polyimide / carbon fiber composite without voids and cracks was obtained from the imide solution prepreg.

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References

- [1] Connell J.W., Smith J.G.Jr. and Hergenrother P.M., "Oligomers and Polymers Containing Phenylethynyl Groups" *J. Macromol. Sci., Part C: Polymer Reviews*, vol. 40, No. 2&3, pp 207-230, 2000
- [2] Hergenrother P.M., "The Use, Design, Synthesis, and Properties of High Performance/High Temperature Polymers: An Overview" *High Perform. Polym.*, vol. 15, No. 1, pp 3-45, 2002
- [3] Selafini T.T., "Polyimides: Synthesis, Characterization, and Applications" vol. 2, Mittal K.L., eds., New York: Plenum, p157, 1984
- [4] Hergenrother P.M. and Smith J.G.Jr., "Chemistry and Properties of Imide Oligomers End-capped with Phenylethynylphthalic Anhydride" *Polymer*, vol. 35, No. 122, pp 4857-4864, 1994
- [5] Hergenrother P.M., Connell J.W. and Smith J.G.Jr., "Phenylethynyl Containing Imide Oligomers" *Polymer*, vol. 41, No. 13, pp 5073-5081, 2000
- [6] Hou T.H, Jensen B.J. and Hergenrother P.M., "Processing and Properties of IM7/PETI Composites" *J. Comp. Mater.*, vol. 30, No. 1, pp 109-122, 1996
- [7] Hergenrother P.M., "Developments of Composites, Adhesives and Sealants for High-speed Commercial Airplanes" *SAMPE J.*, vol. 36, No. 1, pp 30-41, 2000
- [8] Smith J.G.Jr., Connell J.W. and Hergenrother P.M., "The Effect of Phenylethynyl Terminated Imide Oligomer Molecular Weights on the Properties of Composites" *J. Comp. Mater.*, vol. 34, No. 7, pp 614-628, 2000
- [9] Yokota R., Yamamoto S., Yano S., Sawaguchi T., Hasegawa M., Ozawa H. and Sato R., "Molecular Design of Heat Resistant Polyimides Having Excellent Processability and High Glass Transition Temperature" *High Perform. Polym.*, vol. 13, pp S61-S72, 2001
- [10] Yokota R., Yamamoto S., Yano S., Sawaguchi T., Hasegawa M., Ozawa H. and Sato R., "Novel Phenylethynyl-terminated Asymmetric BPDA Based Polyimides Having Excellent Processability and Thermo-oxidative Stability" *Polyimides and Other High Temp. Polym.*, vol. 1, No. 1, pp 101-111, 2001
- [11] Ogasawara T., Ishikawa T., Yokota R., Ozawa H., Taguchi M., Sato R., Shigenari Y. and Miyagawa K., "Processing and Properties of Carbon Fiber Reinforced Triple-A Polyimide (Tri-A PI) Matrix Composites" *Adv. Composites Mater.*, vol. 11, No. 3, pp 277-286, 2003
- [12] Ishida Y., Ogasawara T. and Yokota R., "Development of Highly Soluble Imide Oligomers for Matrix of Carbon Fiber Composite (I): Imide Oligomers Based on Asymmetric Biphenyltetracarboxylic Dianhydride and 9,9-Bis(4-aminophenyl)fluorene" *High Perform. Polym.*, vol. 18, No. 5, pp 727-737, 2006
- [13] Ishida Y., Ogasawara T. and Yokota R., "Development of Highly Soluble Addition-type Imide Oligomers, Imide Wet Prepregs and Polyimide / CF Composites" *Proceedings of the 37th SAMPE Fall Technical Conference (37th ISTC)*, Seattle, CD-ROM, 2005