Synthesis and Properties of Novel Soluble Addition-Type Imide Oligomers Containing Fluorenylidene Groups and Cured Resins

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Introduction

Asymmetric, additive, and amorphous polyimide "TriA-PI" based on 2,3,3',4'-biphenyltetracarboxylic anhydride (a-BPDA), 4,4'-oxidianiline (4,4'-ODA), and 4-phenylethynylphthalic anhydride (PEPA) has good processability, high thermal stability, and is very tough[1)]. Usually, composites of TriA-PI and carbon fiber are fabricated by routing amide acid wet prepreg. In this route, water generated as a by-product of imidization in the curing process may cause the generation of voids in the composites. Because the solubility of a TriA-PI imide oligomer is less than 20 wt% in N-methyl-2-pyrroridone (NMP) and the solution is often set to gel, the imide wet prepreg can not be prepared. In this work, in order to improve solubility and solution stability maintaining thermal resistance, fluorenylidene groups were introduced to TriA-PI. Solubility, solution stability, processability of the imide oligomers, and the thermal and mechanical properties of the cured resins were evaluated.

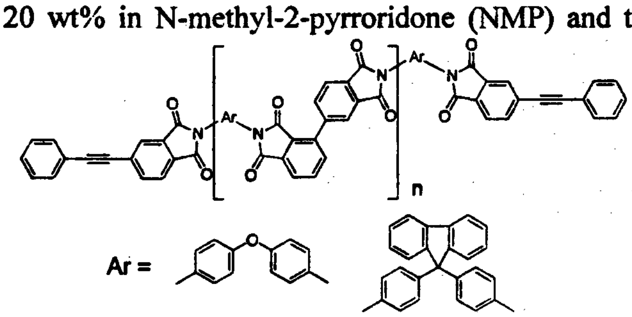

Fig.1 Chemical structure of the imide oligomer containing fluorenylidene groups (n = 4).

Experimental

Synthesis of the imide oligomer (o-BAFL-50): In a three-necked flask, equipped with a magnetic stirrer and nitrogen inlets, were placed 9,9-bis(4-aminophenyl)fluorene (BAFL) (1.742 g, 5 mmol), 4,4'-ODA (1.001 g, 5 mmol), and NMP (14 mL). a-BPDA (2.354 g, 8 mmol) was added to the solution, and the reactions were allowed to stir for 2 hours at room temperature under nitrogen flow. PEPA (0.993 g, 4 mmol) was added to the solution and then the solution was stirred for 21 hours at room temperature and then at 175°C for 5h. The solution was then poured into water (150 mL). The product was washed with methanol (60 mL), filtered, and dried at 60°C in vacuo.

Curing: The film of cured resin was prepared at 370°C for 1 hour under 2 MPa (for o-BAFL-0, -10, -25) or 5 MPa (for o-BAFL-50, -100) using a hot press.

Results and Discussion

The imide oligomers were synthesized from the reaction of a-BPDA, 9,9-bis(4-aminophenyl)fluorene (BAFL), 4,4'-ODA, and PEPA. The imide oligomers had excellent solubility of more than 35 wt% in aprotic polar solvents such as NMP and N,N'-dimethylacetamide (DMAc). Also, solutions of the imide oligomers consisted of more than 25 mol% BAFL per total diamines (o-BAFL-25, o-BAFL-50, and o-BAFL-100 in Table 1) were stable at room temperature for over 1 month, whereas gelation occurred in the case of imide oligomer solutions consisting of less than 10 mol% BAFL (o-BAFL-0, o-BAFL-10). Melting temperatures and minimum melt viscosities increased as the BAFL component increased, because BAFL is more rigid than 4,4'-ODA. The imide oligomers, except o-BAFL-100, could be molded easily by using a hot press. Because o-BAFL-100 imide oligomer displayed no melting flow, its molding could not be obtained.

Table 1 Properties of the resulting imide oligomers

	BAFL : 4,4'-ODA	Solubility in NMP at r.t (wt%)	Solution stability	Melt viscosity (Pa s)	Processability for hot press
o-BAFL-0 (TriA-PI)	0 : 100	20	×	81	O
o-BAFL-10	10 : 90	35	×	100	O
o-BAFL-25	25 : 75	40	O~Δ	338	O
o-BAFL-50	50 : 50	40	O	1810	O
o-BAFL-100	100 : 0	40	O	No flow	Δ~×

Thermal and mechanical properties of the cured resins are summarized in Table 2. The glass transition temperatures (T_gs) of the cured resins exhibited above 340 °C, judged by DSC. T_gs were increased when the BAFL component was increased. The 5% weight loss temperatures (T_{d5}) were higher than 550 °C. Fluorenylidene groups affected the tensile modulus and tensile strength slightly. On the other hand, elongations-at-break of the BAFL copolymers were less than that of o-BAFL-0.

Table 2 Thermal and mechanical properties of the cured resin

	BAFL : 4,4'-ODA	T_g (°C)[a] (cured)	T_{d5} (°C)[b] (in Ar)	E [c] (GPa)	σ_b [c] (MPa)	ε_b [c] (%)
o-BAFL-0	0 : 100	340	556	2.55	118	15.5
o-BAFL-10	10 : 90	343	553	2.57	109	7.6
o-BAFL-25	25 : 75	353	552	2.87	122	7.7
o-BAFL-50	50 : 50	362	561	2.65	112	6.9
o-BAFL-100	100 : 0	> 370	566	- [d]	- [d]	- [d]

a) Determined by DSC at a heating rate of 10°C/min under argon. b) Determined by TGA at a heating rate of 10°C/min under argon. c) Obtained by tension test. d) Film was brittle.

Conclusions

Novel soluble addition type imide oligomers and their cured resins were developed. The introduction of BAFL resulted in an increase in solubility, solution stability, and T_g of the cured resin. Highly concentrated solution of the imide oligomer has the potential of avoiding the arising of voids in composites for the routing of wet prepreg because of no water volatility in the curing process.

Reference

1) R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa and S. Sato, *High Perform. Polym.*, **13**, S61 (2001)