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Synthesis and Properties of Highly Soluble Addition-Type Imide Oligomers for Matrices of High Temperature Carbon Fiber Composites

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Asymmetric, additive, and amorphous polyimide "TriA-PI"[1] based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), 4,4'-diaminodiphenyl ether (4,4'-ODA), and 4-phenylethynylphthalic anhydride (PEPA) has good processability, high thermal stability, and is very tough. 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. In this work, in order to improve solubility of imide oligomer 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.

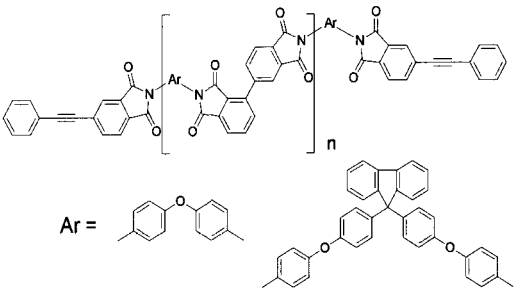

Fig.1 Chemical structure of the imide oligomer containing fluorenylidene groups (n = 4).

The imide oligomers were synthesized from the reaction of a-BPDA, 9,9-bis(4-(4-aminophenoxy) phenyl)fluorene (BAOFL), 4,4'-ODA, and PEPA through thermal imidization in NMP. The imide oligomers had excellent solubility of more than 40 wt% in aprotic polar solvents. Moreover, solutions of the imide oligomers were stable at room temperature for over 1 month. Melting temperatures and minimum melt viscosities were almost the same as those of TriA-PI. The imide oligomers could be molded easily by using a hot press.

Thermal and mechanical properties of the cured resins are summarized in Table 1. The glass transition temperatures (T_gs) of the cured resins exhibited above 315 °C, judged by DSC. T_gs decreased slightly with increasing components of BAOFL. The 5% weight loss temperatures (T_{d5}) were higher than 550 °C. Elongations-at-break of the BAOFL copolymers were higher than 9.5 %.

Imide solution prepreg was prepared from the o-BAOFL-50 imide oligomer solution and carbon fibers. Polyimide / carbon fiber composite without voids and matrix cracks was fabricated successfully from the imide oligomer prepreg.

Table 1 Properties of the imide oligomers and cured resins

	BAOFL:ODA[a)]	Imide oligomers		Cured resins (film)[d)]				
		Solubility[b)] (wt%)	Solution stability[c)]	T_g[e)](°C) (DSC)	T_{d5}[f)](°C) (Argon)	E[g)] (GPa)	σ_b[g)] (MPa)	ε_b[g)] (%)
o-BAOFL-0	0 : 100	20	g	337	553	2.55	118	15.5
o-BAOFL-25	25 : 75	40	h	332	560	2.64	112	11.6
o-BAOFL-33	33 : 67	40	h	329	557	2.64	111	10.7
o-BAOFL-50	50 : 50	40	h	325	557	2.47	105	10.6
o-BAOFL-100	100 : 0	40	h	317	551	2.65	107	9.5

a)BAOFL: 9,9-bis(4-(4-aminophenoxy)phenyl)fluorene, ODA: 4,4'-diaminodiphenyl ether b)Measured in NMP at r.t. c)Stored at r.t. for 1 month. g: gelation, h: homogeneous solution d)Cured at 370°C for 1h under 2 MPa using hot press. e)Determined by DSC at a heating rate of 10°C/min under argon. f)Determined by TGA at a heating rate of 10°C/min under argon. g)Obtained by tensile test.

Reference

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