Development of "TriA-X" Polyimide Composites Prepared from Imide Solution Prepregs

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1. Introduction

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. 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 thermosetting polyimide [1-3]. In this work, phenylethynyl-terminated imide oligomers based on 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA) as an asymmetric diamine, 9,9-bis(4-aminophenyl)fluorene (BAFL) and pyromellitic dianhydride (PMDA) were synthesized. Solubility, processability of the imide oligomer, and the thermal and mechanical properties of the cured resin were evaluated. An imide-solution prepregs were 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

2.1 Synthesis of the imide oligomers

p-ODA (4.5 mmol), BAFL (0.5 mmol) and N-methyl-2-pyrrolidone (NMP, 15 ml) were placed in a three-necked flask, equipped with a magnetic stirrer and nitrogen inlets. PMDA (4 mmol) was added to the solution. The reaction was allowed to stir for 2 h at room temperature under nitrogen flow. Subsequently, 4-phenylethynylphthalic anhydride (PEPA, 2 mmol) was added to the solution; the solution was stirred for 18 h at room temperature and then for 5 h at 190 °C. The total solids concentration of reaction solution was 33 wt.%. The solution was then poured into water. The product was washed with methanol, filtered, then dried for 4 h at 220-260 °C *in vacuo*.

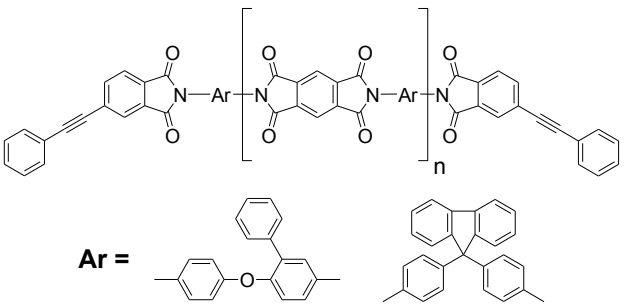

Fig. 1. Chemical structure of the PMDA/ p-ODA;BAFL/PEPA (TriA-X) imide oligomer (n = 4).

2.2 Preparation of the cured resin films

Cured resin films were prepared in a polyimide film frame (60 mm × 60 mm × 75 μm) using a hot press. The imide oligomer was heated at 310 °C for 10 min on a hot plate. It was then cured at 370°C for 1 h under 1.4 MPa.

2.3 Preparation of the imide solution prepregs

IM600 carbon fiber plain fabrics washed in acetone (6K/bundle, 300 mm × 300 mm, carbon cloth areal weight of 195 g/m^2; Toho Tenax Co., Ltd.) were dipped into the TriA-X imide oligomer solution. The plain fabrics were dried at 100 °C for 10 min. These procedures were repeated once again. Respective resin and volatile contents of the resulting prepreg were 37.8 wt.% and 17 wt.%.

2.4 Fabrication of the polyimide / carbon fiber composites

Plain fabric composites (300 mm × 300 mm, 12 ply) were fabricated using an autoclave. The lay-upped and vacuum-bagged prepregs were heated to 370 °C. The samples were held at 370°C for 1 h under pressure of 1.4 MPa.

3. Results and Discussion

TriA-X imide oligomers were synthesized from the reaction of PMDA, p-ODA, BAFL and PEPA through thermal imidization in NMP. The calculated degrees of polymerization of the imide oligomers were 4. After imidization, the reaction solutions maintained homogeneity without precipitation. The imide oligomers had excellent solubility of more than 33 wt.% in NMP. The solubility is sufficient to prepare the imide solution prepregs. The incorporation of BAFL into PMDA/PODA/PEPA imide oligomer was also found to give rise to increase the solution stability. The minimum melt viscosities were between 154 and 1323 Pa•s, measured by a

rheometer. The imide oligomers could be molded easily by using a hot press. On the other hand, PMDA/4,4'-ODA/PEPA imide oligomer was insoluble in NMP and unproccesable to cured resin. Thermal and mechanical properties of the cured resin films are shown in Table 1. The glass transition temperatures (T_gs) of the cured resins exhibited more than 346 °C, judged by DMA. T_gs of cured resins increase with an increase in the ratio of BAFL. Particularly, it is found that the cured resins have good ε_bs (>11 %) with high T_gs (> 350 °C) in addition of 5-10 wt.% of BAFL.

Table 1 Thremal and mechanical properties of (PMDA/p-ODA;BAFL/PEPA) cured resins

mol. ratio of p-ODA/BAFL	T_g (°C, DMA)	Elongation at break (%)	
		Ave.	Max.
100/0	346	15.7	17.4
95/5	350	11.7	15.2
90/10	356	11.3	13.2
75/25	369	7.4	8.2
50/50	n.d.	4.7	6.2

Imide solution prepregs were prepared from the imide oligomer solution in NMP (p-ODA/BAFL = 90/10) and carbon fiber plain woven fabric cloths. Polyimide / carbon fiber composites were fabricated from the imide solution prepregs by one-step. Imide solution prepregs were lay-upped and vacuum-bagged, and then cured at 370 °C for 1 hour under pressure of 1.4 MPa in an autoclave. The resulting composites were good quality as determined by C-scan. The optical micrographs of the composites showed no voids and cracks (Fig.2).

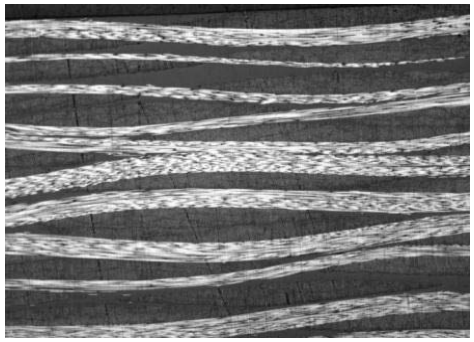

Fig. 2. Optical micrograph of the polyimide composite.

The thermal and mechanical properties of the TriA-X polyimide composite were evaluated. The composite exhibited T_g of 341 °C by DMA. Short beam shear (SBS) strengths were 65 MPa at R.T. and 34 MPa at 300 °C. Non-hole and open-hole compressive strengths of TriA-X composites are shown in Fig. 3 and 4. The NHC and OHC strengths at 300 °C were about 40-50 % of the strengths at room temperature. Polyimide composites with high quality and high heat-resistance were able to obtain easily from the imide solution prepregs.

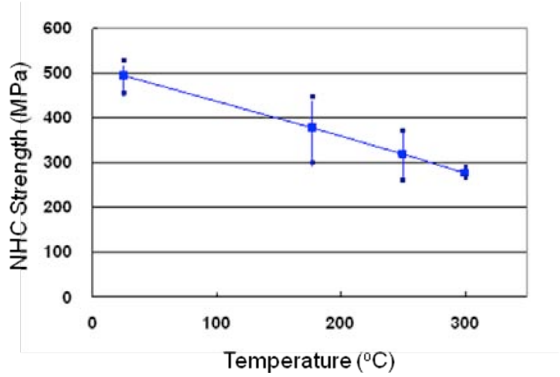

Fig. 3. NHC strength of the polyimide composite.

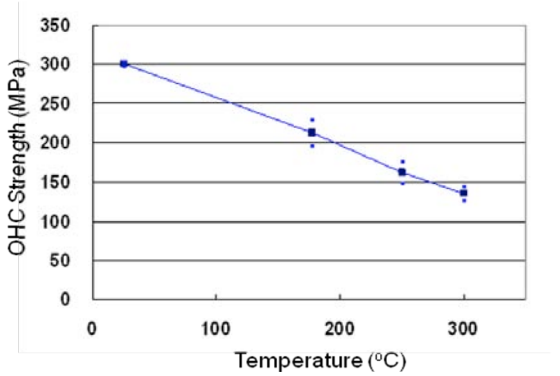

Fig. 4. OHC strength of the polyimide composite.

4. Conclusions

Novel phenylethynyl-terminated imide oligomers (n=4) derived from PMDA, p-ODA and BAFL were found to have high solubility and good processability. The imide oligomers were successfully converted to cured resins with high T_g and excellent mechanical properties. Particularly even the addition of 5-10 wt.% of BAFL was found that the obtained cured resins showed higher T_gs (> 350 °C) and good ε_bs (>11%). Imide solution prepregs were prepared directly from the imide oligomer solution and carbon fibers. Polyimide / carbon fiber composites without voids and cracks were obtained from the imide solution prepregs.

References

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