

Thermal and Mechanical Properties of NewTriA-X: Copolymerization with 1,3-Diamino-4-Phenoxybenzene

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Abstract: We have recently developed novel phenylethynyl-terminated addition type imideoligomer (IO) “TriA-X” which showed excellent heat resistance and melt fluidity due to an asymmetric structure of diamine: 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA). The purpose of this research is to evaluate the effect of copolymerization of p-ODA and a new diamine on thermal and mechanical properties of TriA-X. We tried to introduce 1,3-diaminobenzene having a pendent phenoxy group (1,3-diamino-4-phenoxybenzene: DAPOB) as a new diamine into TriA-X. The minimum melt viscosities of IOs (DAPOB = 25, 50, 75 mol%) were sufficiently low, and the *N*-methyl-2-pyrrolidone (NMP) solutions of IOs (DAPOB = 25, 50 mol%) maintained solution state over a month. T_g of the cured resins was significantly improved as the copolymerization ratio of DAPOB increased to 50 mol%. DAPOB was found to be a promising guest diamine.

Keywords: phenylethynyl-terminated addition type imideoligomer / TriA-X / asymmetric structure / solution storage stability

1. Introduction

Thermosetting imide oligomer (IO) using an end-capping agent “4-phenylethynylphthalic anhydride (PEPA)” has been developed as one of the promising matrix resin of high heat-resistant carbon fiber reinforced plastic (CFRP). Yokota et al. developed TriA-PI¹⁾ and TriA-X²⁾, which showed high T_g and good melt fluidity because of a rigid and asymmetric structure in the backbone of IOs. Owing to the non-planar molecular structure caused by steric hindrance, the formation of the ordered structure was suppressed.

Prepreg process has been studied as one of the molding methods of the polyimide CFRP. Typical prepreg method, a semi-dried sheet-like prepreg is prepared by impregnating fibers with the resin solution, then CFRP is fabricated by heat curing the laminated prepreg in an autoclave.

We have already prepared addition-type imide oligomers derived from pyromellitic dianhydride (PMDA), 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA), and PEPA. The uncured imide oligomer (degree of polymerization: $n = 4$) showed good melt fluidity, and T_g of the cured resin film was observed at 346°C. However, gelation of the NMP solution of the IO occurred in a few days after preparing the solution. In order to solve this problem, we have recently developed novel addition-type imide oligomer TriA-X derived from PMDA, p-ODA, 9,9-bis(4-aminophenyl)fluorene (BAFL)

(p-ODA;BAFL=90:10 molar ratio), and PEPA. The storage stability of the NMP solution was significantly improved (stable over a month), and T_g of the cured resin film was increased (356 °C). This result indicated that copolymerization with a bulky monomer such as BAFL was effective in improvement of solution stability.

In this paper, we report an effect of copolymerization of 1,3-diaminobenzene having a pendent phenoxy group (1,3-diamino-4-phenoxybenzene: DAPOB³) into TriA-X instead of BAFL. The storage stability of the IO solution and thermal and mechanical properties of the cured resin films were investigated.

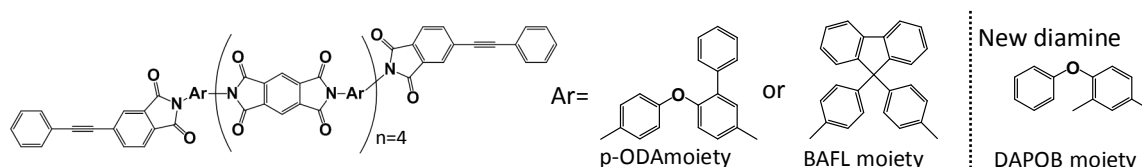


Figure 1. Chemical Structures of TriA-X

2. Results and Discussion

2.1. Solution stability of IOs

IOs were prepared by imidization of amic acid solutions (solvent : NMP) of PMDA / p-ODA / DAPOB / PEPA at 180 °C / 5h. After imidization, IO powders were obtained by reprecipitation of the IO solutions into pure water. The cured resin films were molded by hot-press at 370°C / 1h. Postcure of the films was performed at 400 °C / 10 min.

The NMP solution of IO (DABOB 0 mol%) gelled in a day after preparation (Table 1), which indicated that the aggregation between IO molecular chains was occurred because of the rod-like planar structure of PMDA. The solutions of IO (DAPOB 25 mol%) and IO (DAPOB 50 mol%) were stable over a month. IO molecular chains were randomized by copolymerization with DAPOB. The solutions of IO (DAPOB 75 mol%) and IO (DAPOB 100 mol%) gelled immediately after preparation. It was that IO molecules aggregated due to containing many rigid structure of *m*-PDA. Thus, the solution stability was strongly affected by the ratio of random structure and bulky substituents of the IO molecular chain.

2.1. Thermal and mechanical properties of the cured resin films

T_g was increased as the copolymerization ratio of DAPOB increased (Table 1). Drop of Storage modulus after T_g of the cured resin films became gradual in DMA measurement with increasing DAPOB content (Figure 2). It suggested that the rigidity of the IO molecular chain was increasing. In spite of increasing the rigid structure, elongation at break (ϵ_b) was > 10%. ϵ_b of IO (DAPOB 100%) was slightly lower due to high rigidity of IO molecular chain.

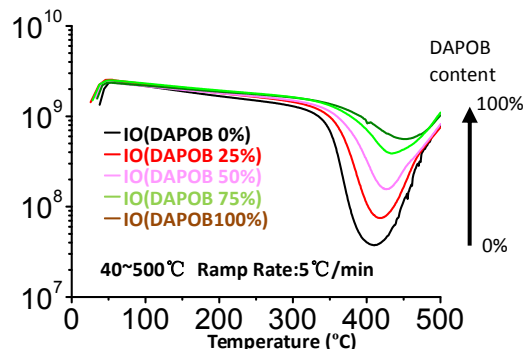


Figure 2. DMA curves of cured resins of IO (DAPOB 0~100%) cured at 370°C

Table 1. Thermal and mechanical properties of TriA-X copolymerized with DOPBA

IO(content of DAPOB%)	T_g (°C)		Min melt viscosity η^* (Pa·sec)	Modulus E (GPa)	Stress at break σ_b^b (MPa)	Elongation at break ϵ_b^b (%)	Solution storage stability ^{c)}
	Imide oligomer	Cured resin ^{b)}					
	DSC ^{a)}	DMA					
DAPOB 0%	221	346	63	3.02	119	11.2	△
DAPOB 25%	223	363	105	2.91	127	13.0	○
DAPOB 50%	227	368	77	2.84	113	12.9	○
DAPOB 75%	230	375	86	2.80	111	10.8	×
DAPOB 100%	235	383	86	2.82	110	8.9	×

a)40-460°C Ramp Rate :20°C/min

b)postcured at 400°C/10 min.DAPOB 0%: not postcured

c)○ :solution for a few months, △ :gelation after a few days, × : insoluble

3. Conclusions

As a result of introduction DAPOB into TriA-X, it was found to be greatly improved storage stability of NMP solutions and thermal stability of cured resins thanks to the rigid structure of *m*-PDA and bulky phenoxy group. Therefore, it was found to be a very useful diamine.

References

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