Synthesis and Properties of Novel Asymmetric Addition-type Imide Oligomers with High Solubility

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Introduction

Recently, much attention has been focused on the synthesis and the properties of high heat-resistance polymer applicable for the aerospace composites. Polyimides are attractive for aerospace applications because of their excellent thermo-oxidative stability and mechanical properties. However, the processability of polyimides is inferior as compared with epoxies and bismaleimides. Previously, Yokota *et al.* developed an epoch-making addition type polyimide from the reaction of asymmetric type 2,3,3',4'-biphenyltetracarboxylic dianhydride (2,3,3'4,'-BPDA, a-BPDA), 4,4'-oxidianiline (4,4'-ODA) and 4-phenylethynylphthalic acid anhydride (PEPA)(TriA-PI 1)[1)]. The imide oligomer and cured resin have significantly irregular and asymmetric structure derived from asymmetric BPDA, resulting in low melt temperature, low melt viscosities and high glass transition temperature (Tg>300°C). Even though the molecular weight of the imide oligomer is relatively low as relative to LaRC[TM] PETI-5, the cured resin exhibits excellent mechanical properties because of chain extension caused by the phenylethynyl group reaction. Furthermore, the imide oligomers with 3,4,3',4'-BPDA(s-BPDA), 4,4'-ODA, 9,9-bis((4-aminophenoxy)phenyl) fluorine(BAOFL) and PEPA (TriA-PI 2 oligmer)also synthesized.[2)] The solubility of the imide oligomer in N-methyl pyrroridone is high(>33 wt%) because of the bulky fluorenyl groups of BAOFL structure. The cured polymer (Tri-A PI 2) of the imide oligomer maintained its thermal and excellent mechanical properties.

Now, we synthesized the novel additive-type imide oligomers with s-BPDA, 2-phenyl-(4,4'-oxydianiline)(PODA), 9,9-bis(4-aminophenoxy)fluorene(BAFL), and PEPA(TriA-PI 3 oligomer, figure 1). These solubility of imide oligomers and thermal and mechanical properties of the cured resin TriA-PI 3 were studied by various thermal analysis and tensile tests.

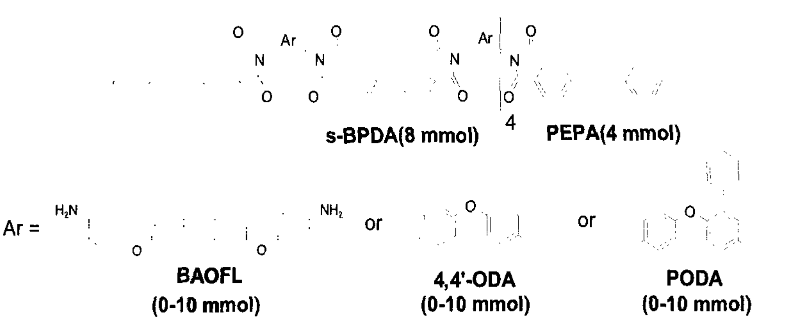

Figure 1. Structure of Tri-A imide oligomer 2 (s-BPDA/BAOFL; 4,4'-ODA/PEPA) and Tri-A imide oligomer 3 (s-BPDA/BAOFL;PODA /PEPA).

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Experimental

Synthesis of Tri-A PI 3 oligomer

4,4'-ODA was initially dissolved in NMP at room temperature under N_2, and a-ODPA was added. They were stirred at room temperature for 3h. PEPA was added in the amide acid/NMP solution, and reactions were allowed stir for 15h at room temperature. The end capped amide acid/NMP solutions were stirred at 195°C for 5h under N_2. After being cooled to room temperature, the solution was slowly poured into H_2O. The yellow precipitate was collected by filtration and washed with methanol.

Preparation of cured polymer

On the PI film (10x15cm, 75um), the PI film was cutted out the size 5 x 8 cm were stacked, and the imide oligomer was putted. The PI film was covered on the imide oligomer. The stacked imide oligomer/ PI films were pressed at 310-370 °C for 60 minutes and at under the pressure (1-2M Pa).

Results and Discussions

The solubility in NMP and the minimum melt viscosity of the imide oligomer were shown in Table 1. When only the ratio of the diamine BAOFL for 4,4'-ODA was more than 50 wt%, the solubility of the imide oligomer showed >33wt%. However, in the case of PODA/BAOFL system, each imide oligomer showed the high solubility. These data indicates that the asymmetric structure of PODA cause the disarrangement of the intermolecular aggregation of the imide oligomer to cause to be high solubility in NMP. In the processability, it was found that the each oligomer of the PODA/BAOFL system showed the lower min. melt viscosities. The each cured resin of the PODA/BAOFL system showed the high Tg and excellent mechanical properties (ε_b>10%).

Table 1. Properties of the imide oligomers and cured resins

	PODA/ BAOFL ratio(%)	4,4'-ODA/ BAOFL ratio(%)	Imide oligomers		Cured resins [b)]	
			Solubility[a)]	Min. melt viscosity(Pa.sec)	Tg(°C)[c)]	ε_b [d)]
PODA-100	100/0		Good	104	309	14.1
4,4'-ODA-100		100/0	Poor	-	-	-
PODA-75	75/25		Good	251	317	9.6
4,4'-ODA-75		75/25	Poor	-	-	-
PODA-50	50/50		Good	398	317	18.4
4,4'-ODA-50		50/50	Good	1084	330	11.9
PODA-0 or 4,4'-ODA-0	100/0	100/0	Good	2473	321	10.2

a) Measured in NMP at r.t. b) Cured at 370℃ for 1h. c) Determined by DSC at a heating rate of 10 ℃/min under nitrogen. d) ε_b; elongation at break

References

1) R. Yokota et al.: *High Perform. Polym.*, 13 (2001), S61-S72

2) T. Ogasawara et al.; Adv. Composite Mater. Vol. 11 (2003), 277-286.