Novel Asymmetric and Addition-type Imide Resins for High Temperature Composite Materials

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Introduction

Polyimide/carbon fiber composites have been used successfully as lightweight materials in place of alloys of aluminum, steel and titanium in aerospace components used for high temperature applications[1-3]. Now we prepared novel phenylethynyl terminated imide oligomers (degree of polymerization: n = 1-10) derived from 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), 2-phenyl-(4,4'-diaminodiphenyl ether)(p-ODA) which has asymmetric and non-planar structure for the matrix resin of high heat resistant carbon fiber-reinforced composites[4-5]. The uncured imide oligomers (degree of polymerization: n = 1-4) showed good solubility (more than 30 wt%) in aprotic solvents) (Figure 1, Table 1). The minimum melt viscosity of the imide oligomer was also found to be very low at > 300 ^{o}C (Figure 2).

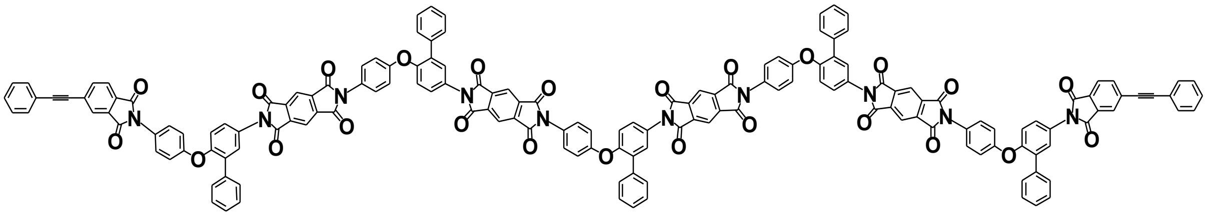

Figure 1. Structures of PMDA/p-ODA/PEPA imide oligomers (n=4)

Results and Discussion

The imide oligomers were successfully converted to cross-linked structures after curing at 370 ^{o}C for one hour. Thermal and mechanical properties of the cured resins (PMDA/p-ODA/PEPA) are summarized in Table 2. All data were obtained from 100-150 μm homogeneous brown-colored films. The Tg values measured by DMA were found to be very high, respectively. All cured resins showed high Td5s (>525 ^{o}C). Surprisingly, the ε_{bs} value of cured polymers were very high (> 9.5 %), indicating that the reaction mechanism of the PEPA was mainly chain extension rather than cyclization or crosslinking [6-7].

Preliminary studies for processing, thermal and mechanical properties of carbon fiber reinforced polyimide composites were conducted. The CF composites derived from IM600/cured imide oligomer (n=4) coporimerized 10% of 9,9'-bis(aminophenylfluorene) in order to increase its solubility and solution stability in NMP were prepared via imide wet prepregs using single-dipping method. The CF composite exhibited excellent processability and very high Tg at 370 ^{o}C. Figure 3 shows the cross-sectional optical micrograph pictures of the CF composite. No voids and no cracks were observed in the composite. Imide resin was sufficiently found to be impregnated into filaments of IM600 plain fabric of the composite.

We believe that these excellent properties of PMDA/p-ODA based addition-type aromatic polyimides suggest promising possibilities for application to highly heat-resistant composites in aerospace field.

References

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Table 1. Thermal and mechanical properties of (PMDA/p-ODA/PEPA) imide oligomers (n = 1-10).

n	Calculated Number-average Molecular Weight (Mn x 10^3)	Solubility in NMP (wt%)	Tg (^{o}C) b)	Min. melt viscosity (Pa.sec)
1	1.19	>33	152	1
2	1.65	>33	178	30
3	2.11	>33	202	144
4	2.57	>33	226	208
6	3.48	Partially	226	2239
10	4.86	Insoluble	252	11100

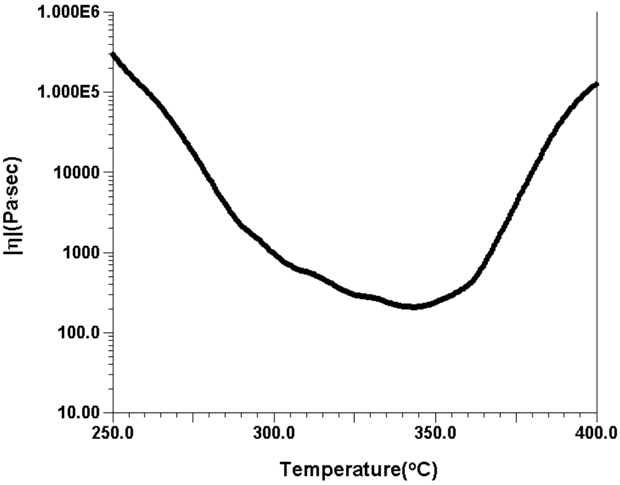

Figure 2. Rheology data of (PMDA/p-ODA/PEPA) imide oligomers (n = 4, Ramp rate: 5^{o}C/min in Air).

Table 2. Thermal and mechanical properties of (PMDA/p-ODA/PEPA) cured resins (n=1-10).

n	T_g a) (^{o}C)	T_{d5} b) (^{o}C)	$\varepsilon_{bAve.}$ (%)
1	356	528	9.6
2	348	530	10.2
3	348	536	11.4
4	346	539	15.7
6	342	543	16.9
10	336	543	11.9

a) Determined by DMA at a heating rate of 10 ^{o}C/min under air. b) Determined by TGA at a heating rate of 5^{o}C/min under nitrogen.

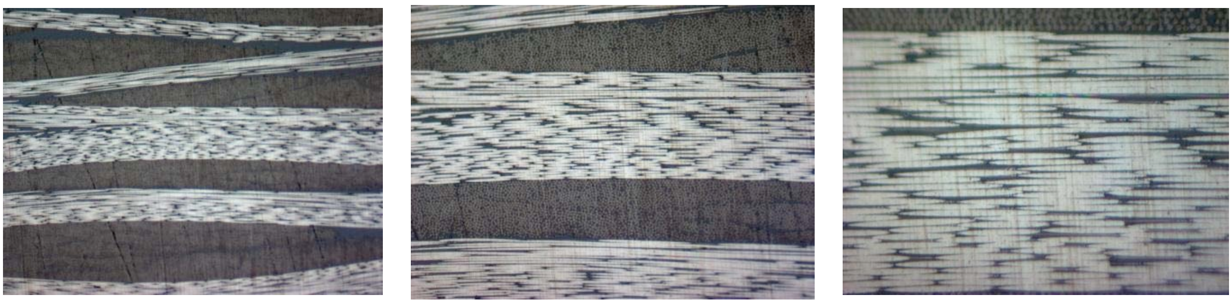

Figure 3. Optical micrographs captured from cross-sectional area of TriA-X CFRP.