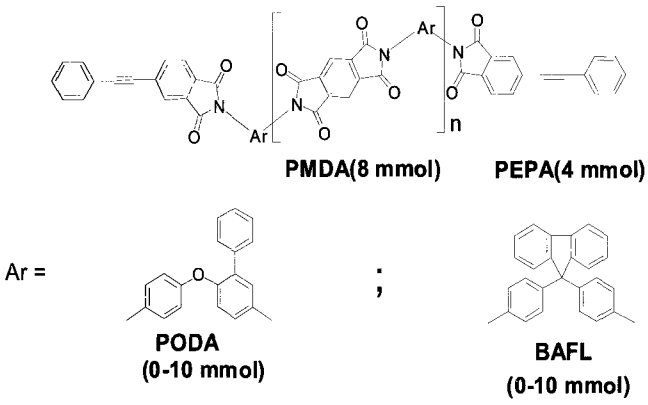
Structures and Properties of Novel Addition-type Polyimides Derived from PMDA and Asymmetric Diamine p-ODA

Ken-ichi Kazama (風間健一)[1]*, Masahiko Miyauchi (宮内雅彦)[2], Yuichi Ishida (石田雄一)[3], Toshio Ogasawara (小笠原俊夫)[3], Takashi Sawaguchi (澤口孝志)[1], and Rikio Yokota (横田力男)[4]

[1]Graduate School of Science and Technology, Nihon University (1-8-14, Kandasurugadai, Chiyoda-ku Tokyo 101-8308) [2]Frontier Material Development Laboratories, Kaneka Corporation (5-1-1, Torikai-nishi, Settu OSAKA 566-0072) [3]Aerospace Research and Development Directorate, Japan Aerospace Exploration Agency(JAXA) (6-13-1 Ohsawa, Mitaka city, Tokyo 181-0015) [4]Institute of Space and Astronautical Science, JAXA (3-1-1 Yoshinodai, Sagamihara city, Kanagawa 229-8510, Tel: +81-50-3362-5710, Fax: +81-42-759-4251, E-mail: yokota.rikio@jaxa.jp)

1. Introduction

Polyimide (PI) / carbon fiber composites have been expected to apply for aerospace components as light weight and high heat resistant materials. We have studied asymmetric aromatic addition-type imide oligomers for the matrix resins with high thermal stabilities, good processabilities and excellent elongation-at-breaks (ε_bs) [1].



Scheme 1. Structures of novel imide oligomers(n=4)

Recently, we found that 4-phenylethynyl phthalic anhydride (PEPA) terminated aromatic imide oligomers derived from 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA) and 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA) (repeating units n=4) had various unique properties. In spite of this imide oligomer had typical planar and symmetric structures of PMDA, nonplanar and asymmetric structures of p-ODA were found to give rise to restrict the aggregation themselves, resulting in good solubility and low melt viscosity. In addition, the cured resin was found to exhibit high glass transition temperature (T_g) of 347°C and more than 17% ε_b [2].

In this paper, we report thermal and mechanical properties of the PMDA/p-ODA/PEPA imide oligomers with various number of repeating units (n=1-10) and these cured resins. Moreover, 9,9-Bis(4-aminophenyl)fluorene (BAFL) which has a bulky fluorenyl group was copolymerized to improve the solubility and the storage stability of PMDA/p-ODA/PEPA imide oligomers (n=4). The effect of the incorporation of BAFL on thermal stability of the cured resins was also investigated.

2. Experimental

The amide acid oligomer solution was prepared by the conventional method at a concentration of 33% (w/w) solid content in N-methyl pyrrolidone (NMP). The amide acid oligomer in NMP solution was imidized at 195 °C/5 hours under N_2 flow. The obtained homogeneous solution was pored into water, filtrated and washed with methanol. The residue was dried in vacuum oven at 200-250 °C to obtain the imide oligomer powder. The film-like cured resins (50-120 μm) were molded with hot-press machine at 370 °C/1 h under 2 MPa [2].

Table 1. Solubility and thermal properties of PMDA/p-ODA/PEPA imide oligomers and cured resins

n	non cure			cured		
	Solubility in NMP (wt%)	T_g[b] (°C)	Min.melt viscosity (Pa·s)	T_g[c] (°C)	T_{d5}[d] (°C)	Residual $Wt_{800°C}$[d] (%)
1	>33	152	1 (300-350°C)	356	528	63.7
2	>33	178	30 (308 °C)	349	530	63.5
4	>33[a]	226	208 (343°C)	347	539	63.6
6	>33[a]	226	2239 (341 °C)	343	543	64.1
10	>33[a]	252	11100 (330 °C)	337	543	64.3

a)gel after 1day. b) Determined by DSC at a heating rate of 20°C/min under nitrogen. c) Determined by DMA at a heating rate of 5°C/min under air. d) Determined by TGA at a heating rate of 5°C/min under nitrogen.

3. Results and Discussions

Table 1 shows solubility and thermal properties of PMDA/p-ODA/PEPA imide oligomers (n=1-10) and these cured resins. All imide oligomers were found to soluble in NMP at a high concentration (> 33 wt%). Especially, the oligomers (n=1 and 2) were showed higher solubility and the NMP solutions of these imide oligomers (33 wt%) were observed no gelation in the storage for a few month at room temperature. In addition, melt viscosity of these oligomers (n=1-6) were particularly low, even though the oligomer (n=10) was found to be able to be molded by hot press.

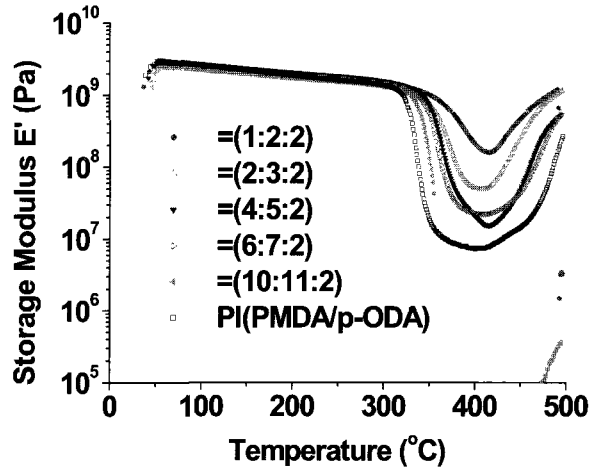


Fig.1. DMA curves of cured resins (PMDA/p-ODA/PEPA)

These data indicates that these high solubility and low melt viscosity of imide oligomers were attributed to asymmetric and nonplanar structure of p-ODA. Moreover, the steric hindrance of phenyl substitute of p-ODA was thought to inhibit to form intermolecular ordered structure.

Table 2. Thermal and thermo-mechanical properties of PIs(PMDA/p-ODA;BAFL)

BAFL content	Annealing temp. (°C)	Tg[a] (°C)	ΔE'[a] at Tg	T_{d5}[b] (°C)	Residual $Wt_{800°C}$[b] (%)
0	400	325	Large	542	59.8
10	400	364	Large	550	61.6
25	450	400	Large	550	61.1
50	450	424	Small	552	62.0
75	450	418	Small	557	65.7
100	450	n.d.	Small	560	69.1

a) Determined by DMA at a heating rate of 5 °C/min under air. b) Determined by TGA at a heating rate of 5 °C/min under nitrogen.

All cured resins exhibited higher T_g compared with PI(PMDA/p-ODA). The T_gs of these cured resins were also found to increase with decreasing the repeating units, namely according to increase the concentration of PEPA. Fig.1 shows the DMA curves of these resins. These data showed that ΔE' above T_g decreased with reducing the number of repeating units, indicating that the increase of the crosslink densities of cured resins resulted in the restriction of the molecular mobility.

We also found that T_{d5} of cured resins increased with an increasing the number of repeating units. Particularly, T_{d5} of cured resin (n=6 and 10) was almost equal to that of PI(PMDA/p-ODA).

Table 2 shows thermal and thermo-mechanical properties of PIs(PMDA/p-ODA;BAFL). Fig. 2 also shows DMA curves of PIs(PMDA/p-ODA:BAFL). T_g was found to increase exponentially with increasing the content of BAFL, even though small amount of BAFL was copolymerized. Furthermore, the observed large drops of E' above T_g was attributed to maintain the high molecular mobility of cured resin. However, when BAFL content for total diamine was more than 50 mol%, ΔE' above T_g is very small. It was thought that all PIs (PMDA/p-ODA;BAFL) showed large drops of E' above T_g due to amorphous structures formed by steric hindrance of bulky fluorenyl group. [Next see p116]

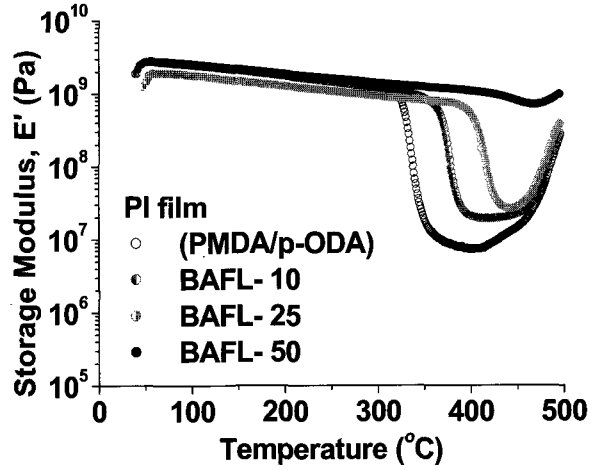


Fig.2. DMA curves of PIs(PMDA/p-ODA;BAFL)

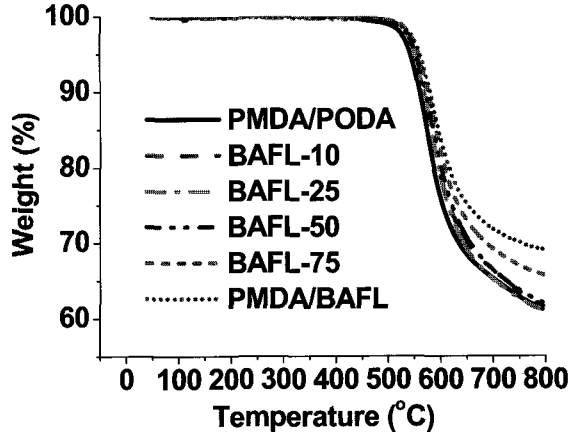


Fig.3. TGA curves of PIs(PMDA/p-ODA;BAFL)