

# Synthesis and Properties of Novel Asymmetric Addition-type Imide Resins derived from Kapton<sup>®</sup>-type structure

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## Abstract

*Novel addition-type imide oligomer derived from 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), 2-phenyl-(4,4'-diaminodiphenyl ether)(p-ODA) which has asymmetric and non-planar structure, 9,9-bis(4-aminophenoxy)fluorene, and 4-phenylethynyl phthalic anhydride was synthesized for the matrix of high heat resistant fiber-reinforced composites. The uncured imide oligomers (degree of polymerization:  $n=4$ ) showed good solubility (more than 30 wt%) in aprotic solvents such as N-methyl-2-pyrrolidone (NMP). The minimum melt viscosity of the imide oligomer was also found to be very low (almost 200 Pa sec) at 340 °C. These high solubility and low melt viscosity of imide oligomers were accomplished by preventing the aggregation of imide oligomers which caused by the phenyl group of p-ODA as a side substituent unit in solution or melting state. The imide oligomers were successfully converted to cross-linked structures after curing at 370 °C for one hour. The thermal and rheological properties of the imide oligomers were characterized by differential scanning calorimetry, thermogravimetric analysis, and dynamic rheometry. The glass transition temperature and elongation at break ( $\epsilon_b$ ) of the cured resin were found to be almost 360 °C and >15%. These excellent properties of p-ODA based addition-type aromatic polyimides demonstrate a promising possibility for application of high heat resistant composites.*

## 1. 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. Over past 30 years many addition-type polyimides also have been developed for advanced composites in aerospace applications. PMR-15 prepared from the reacting of 3,3'-4,4'-benzophenonetetracarboxylic dianhydride and 4,4'-methylene dianiline with a nadic acid derivative for the reactive end cap is well known as a composite resin for use at 300 °C. However, the cured resin is brittle due to the high cross-link density [1]. As a result, composites exhibit poor impact resistance or compressive strength after impact. PETI-5 was prepared from the reaction of s-BPDA and two aromatic diamines with PEPA for the reactive end cap at a calculated molecular weight of 5,000 g/mol [2,3]. The cured polyimide exhibits a moderate T<sub>g</sub> of 270 °C and more than 30% elongation-at-break ( $\epsilon_b$ ) for a film at room temperature, indicating that the formation of the converted cured resin was mainly attributed to the chain extension of imide oligomers caused by the thermo-additional polymerization of PEPA [4,5,6,7]. The properties of cured PETI-5 are very similar to those of a thermoplastic and not a thermoset. Furthermore, it was noted that phenylethynyl end cap offered distinct advantages such as a large processing window and when cured, good thermo-oxidative stability compared with other reactive end caps such as nadic acid derivative and maleic acid. In general, to obtain good processability and high fracture toughness, heat resistant resins must have properties similar to PETI-5. This means that if these resins are to achieve processability, the oligomer must possess a low melt viscosity. The imide oligomer between the end caps has to maintain thermoplasticity though a flexible structure and relatively low T<sub>g</sub>. The cured resin must exhibit a high T<sub>g</sub> which may appear to be in consideration with processability for the heat resistant polymeric matrix resins [8,9].

Recently, Yokota et al. found that a polyimide based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (asymmetric-BPDA, a-BPDA) and 4,4'-oxydianiline(4,4'-ODA) exhibited a higher  $T_g$  than that of 3,3',4',4'-biphenyltetracarboxylic dianhydride(symmetric-BPDA, s-BPDA)/4,4'-ODA and also showed a large drop in the storage modulus,  $E'$  above the  $T_g$  [10,11,12].

These data are attributed to the decrease in the intermolecular interactions of the polyimides derived from a-BPDA which have asymmetric and non-planar structures. Based on the thermal and rheological behavior of a-BPDA based polyimides, Yokota et al. have also successfully designed a-BPDA based phenylethynyl-terminated, addition-type a-BPDA imide oligomers (TriA-PI) with excellent processability to give rise to cross-linked polyimides with high temperature resistance and more than 20% of  $\epsilon_b$  after curing at 370 °C/1h [13,14].

Since TriA-PI exhibits insufficient solubility, the prepregs were manufactured by impregnating carbon fibers with TriA-PI amide acid solution at high concentrations. However, the water evolution caused by imidation of amide acid oligomers has a tendency of remaining as voids in the composites. If the imide oligomers with both high solubility and good processability can be synthesized, the preparation of void-less high heat resistant composites can be achieved by using prepregs prepared by impregnating fibers with high concentration solution of imide oligomers.

The excellent properties of aromatic polyimides such as KAPTON<sup>®</sup> and APICAL<sup>®</sup> from PMDA and 4,4'-ODA (DuPont Co. and Kaneka Co., respectively) and UPILEX-R<sup>®</sup> from s-BPDA and 4,4'-ODA (Ube Industry Co.) are well-known as high dimensional stability, low thermal expansion and outstanding thermal and environmental stability. These properties are attributed not only to their rigid (planar and symmetric pyromellitimide or biphenylimide) structures, but also to the formation of high-ordered structures beyond the  $T_g$ . Accordingly, these aromatic polyimides do not display high molecular mobility above  $T_g$ , indicating that processing conditions for molding were extremely severe. Therefore on the basis of above concept the aromatic imide oligomers with good processability and high solubility have not been reported for application of the composites with high temperature resistance as matrixes ( $T_g > 300$  °C).

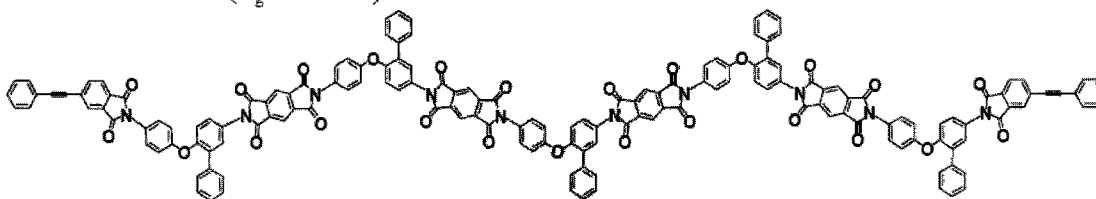


Figure 1. Structures of PMDA/p-ODA/PEPA imide oligomers (n=4)

In this paper, we describes molecular design, the preparation of phenylethynyl-terminated, addition-type polyimides derived from pyromellitic dianhydride(PMDA) with symmetric and planar structures as diacids and 2-phenyl-4,4'-diaminodiphenyl ether(p-ODA) which is thought to be a most simple asymmetric and nonplanar structures as a diamine(Figure 1). The effect of asymmetricity, nonplanar structures and restriction of free rotation of ether linkage of p-ODA (Figure 2) on the solubility and processability of addition-type aromatic imide oligomers were investigated.

We found that the asymmetric and nonplanar structures of p-ODA molecules were drastically able to prevent aromatic PMDA based PI chains from the intra/intermolecular aggregation by DMA measurements (Kazama et al. report in this conference). Moreover based on the thermal and rheological behavior of PI(PMDA/p-ODA), the synthesized PEPA-terminated aromatic imide oligomers (n=4) was also found to have high solubility in NMP (>33 wt%) and good procesabilities (Minimum melt viscosity: almost 200 Pa·sec) to convert the cross-linked polymers with excellent thermal stabilities( $T_g > 350$  °C) and mechanical properties (elongation-at-break,  $\epsilon_b > 14\%$ ) with curing at 370 °C/1h.

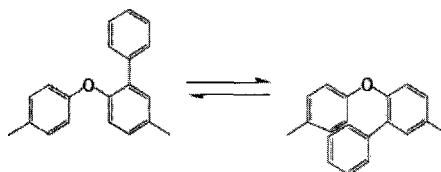


Figure 2. Steric hindrance of p-ODA

## 2. Experimental Sections

### 2.1 Materials

3,3',4,4'-Tetracarboxylic dianhydride (PMDA), and 9,9-bis(4-aminophenoxy)fluorene (BAFL) were purchased from Tokyo Kasei Co.. N-Methyl-2-pyrrolidone (NMP) was purchased from Kanto Kagaku

Co.. 4-Phenylethynylphthalic anhydride (PEPA) was purchased from Manac Co.. 2-phenyl-4,4'-oxydianiline (p-ODA) was kindly supplied by Wakayama Seika Co. These materials were used as received.

## 2.2 Measurements

Differential scanning calorimetry (DSC) was performed on a TA instruments DSC-2010 thermal analyzer with the sample sealed in an aluminum pan. Glass transition temperatures ( $T_g$ s) were determined with DSC at a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed on thin film specimens (23.7 mm long, 5mm width, 0.05 - 0.15mm thick) on a Rheometric Solids Analyzer RSA II instrument at a heating rate of  $5\text{ }^\circ\text{C min}^{-1}$  and load frequency of 1 Hz in an air atmosphere. Melt viscosity measurements were performed on a TA Instruments Co. AR-2000 dynamic rheometer at heating rate of  $5\text{ }^\circ\text{C min}^{-1}$ . The compact resin disks with 25 mm diameter and almost 2 mm thickness were prepared by press molding of the powder-like imide oligomers at r.t..

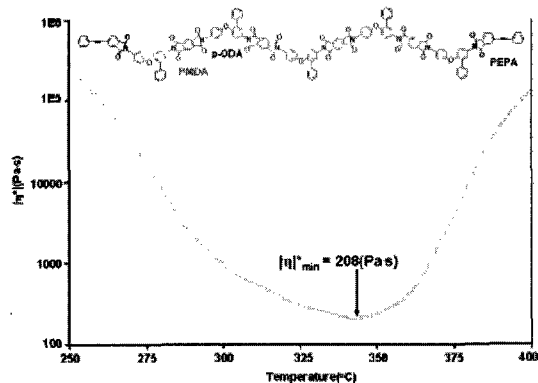


Figure 3. Dynamic rheological properties of uncured PMDA/p-ODA/PEPA imide oligomer.

## 2.3 Synthesis of PMDA/p-ODA/PEPA Imide Oligomers(n=4)

The terminated PEPA imide oligomers derived from PMDA and p-ODA were synthesized according to a previous literatures [13,14]. 5.0 mmol of p-ODA and NMP were added in a dried 100ml three necked round-bottom flask which was equipped with nitrogen inlet and magnetic stirrer. After the diamine was dissolved completely, 4.0 mmol of PMDA was added and the reaction mixture was stirred for almost 2 hours at room temperature under  $\text{N}_2$  flow. After the complete dissolution of PMDA, 2.0 mmol of PEPA was added with extra NMP to adjust the concentration of total solids to 33 wt% (w/w). The solution was stirred for another 2 hours at room temperature to obtain the PEPA end-capped amide acid oligomer (n=4).

After the attachment of a reflux condenser to the flask, the amide acid oligomers in NMP solutions were imidized at  $195\text{ }^\circ\text{C}$  in oil bath for 5 hours. After cooling the flask until room temperature, the obtained solution was completely clear without precipitations. The solutions were pored into water to reprecipitate the imidized oligomer. The precipitation were filtrated, washed with methanol and dried at  $220\text{-}260\text{ }^\circ\text{C}$  in vacuum oven for up to 4 hours.

## 2.4 Preparation of Cured Resins

The obtained imide oligomers were molded by using a 6 cm x 6cm x 0.05 mm polyimide film frame on a 20 cm x 20cm stainless steel plate with UPILEX-S separator films under 1.4 MPa by heating initially to  $310\text{ }^\circ\text{C}$  for 10 min and subsequently to  $370\text{ }^\circ\text{C}$  for one hour. The dark red film-like specimens of 6 cm x 6cm x 0.05 mm were obtained

## 3. Results and Discussions.

### 3.1. Solubility, Processability and Thermal Properties of Phenylethynyl-terminated PMDA/p-ODA Imide Oligomers

PMDA based imide oligomers (n=4) derived from 4,4'-ODA or p-ODA were obtained from the imidiation of the solution of corresponding amide acid oligomers at  $195\text{ }^\circ\text{C}$  for 5h. PMDA/4,4'-ODA/PEPA imide oligomer was insoluble in NMP and unprocessable to cured resin because  $T_g$  was not observed at  $<370\text{ }^\circ\text{C}$ . On the other hand, surprisingly, the latter PMDA/p-ODA/PEPA imide oligomer

Table 1. Thermal and mechanical properties of (PMDA/4,4'-ODA/PEPA) and (PMDA/p-ODA/PEPA) imide oligomers (n=4) and these cured resins ( $370\text{ }^\circ\text{C}/1\text{h}$ ).

diamine	Imide oligomer		Cured resin	
	solubility (NMP, wt%(w/w))	Min. melt viscosity (Pa sec)	$T_g$ ( $^\circ\text{C}$ , DMA)	Elongation at break (Maximum. %)
4,4'-ODA	insoluble	no melt	unprocessable	
p-ODA	> 33 (gel after 1 day)	208	346	17.4

was completely soluble in NMP solution with high concentration even at room temperature (> 30 wt%). Figure 3 shows the dynamic rheological properties of the PMDA/p-ODA/PEPA (n=4) imide oligomer. The minimum melt viscosity of the imide oligomer was only 200 Pa·sec at around 340 °C, resulting in significant improvements of PMDA-based polyimide resin in processability for molding the fiber-reinforced heat resistant composites with high quality.

### 3.2. Thermal and Mechanical Properties of Cured Resins

Thermal and mechanical properties of the cured (PMDA/p-ODA/PEPA) are summarized in Table 1. All data were obtained from 100-150 mm homogeneous brown-colored films. The T<sub>g</sub> values measured by DSC and DMA were also found to be very high, respectively. As can be seen in Figure 4, E' of cured resin also shows a large drop above T<sub>g</sub>, indicating that the pendant phenyl group of p-ODA in polymer chain which was obtained by curing corresponding the imide oligomer also decrease in the intensity of the intermolecular interaction. Surprisingly, the ε<sub>s</sub> value of cured polymers were very high (> 14 %), indicating that the reaction mechanism of the PEPA was mainly chain extension rather than cyclization or crosslinking as reported by McGrath et al.[5,6]. These data might be supported by the large drops of E' on DMA curves

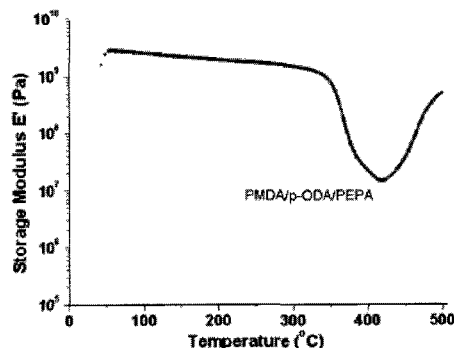


Figure 4. DMA data of (PMDA/p-ODA/PEPA) cured resin.

### 3.3. Incorporation of BAFL diamine into PMDA/p-ODA/PEPA imide oligomers

After preparing NMP solution of the imide oligomer (33 wt%) at 150 °C, unfortunately the imide oligomer solution was allowed to turn into a gel during the cooling until room temperature. When the gel was heated at 150 °C for 1h again, it gradually changed a solution without precipitation repeatedly, indicating that intermolecular aggregation of imide oligomer is thought to be easily formed between the intermolecular tail-to-tail units with planar structure (Figure 5).

In general, it is required that the concentration of the matrix resin is needed more than 30 wt% in the solution for manufacturing the prepregs without gel or precipitations. These data suggest that it is necessary to randomize the continuous monomer units with an addition of third components for this imide oligomer [15-16].

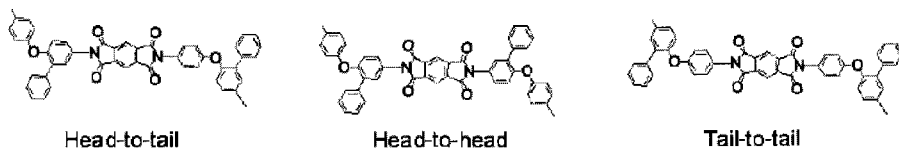


Figure 5. Possible structures of repeated units in PMDA/p-ODA oligomers

It is well-known that the introduction of bulky substituent to polymer side chain is able to improve the solubility of original polymer with an increase of the solvation. We selected BAFL diamine which has the bulky fluorenyl substituent as a candidate for copolymerization to PMDA/p-ODA imide oligomer (Figure 6).

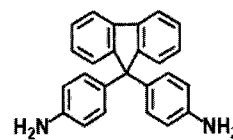


Figure 6. Structure of BAFL diamine

Table 2 shows the solubility and minimum melt viscosities of PMDA/p-ODA:BAFL/PEPA imide oligomers with different diamine ratio of (p-ODA/BAFL). Even the addition of a small amount (5 wt%-10 wt% for the total weight of diamine) of BAFL was allowed the imide oligomers to be able to remain dissolved in NMP for a few months without affecting the processability. These data were attributed to randomize the regularity of continuous monomer units (PMDA/p-ODA units, n=4) with an addition of small amount of BAFL. In other words, the addition of 10 wt% of BAFL as a diamine in imide oligomer (n=4) theoretically exhibits that a half of total obtained imide oligomer molecules is PMDA/p-ODA/PEPA (= 4/5/2 ratio) and the other half is PMDA/p-ODA:BAFL/PEPA (= 4/4;1/2 ratio). The replacement of the latter for the half of original PMDA/ p-ODA/PEPA imide oligomers was found to prevent the formation of intermolecular aggregation.

Table 3 shows the thermal and mechanical properties of (PMDA/p-ODA:BAFL/PEPA) cured resins. These T<sub>g</sub>s of cured resins increase with an increase in the ratio of BAFL, indicating that not only the

decrease of number of flexible ether linkage of p-ODA, but also the formation of continuous zigzag structure of the rigid repeated units of PMDA-p-phenyl group (BAFL) give rise to the increase of T<sub>g</sub>. Particularly, in addition of 5-10wt% of BAFL, it is found that the cured resins have good ε<sub>b</sub>s (>13 %) with high T<sub>g</sub>s (> 350 °C).

#### 4. Conclusion

Novel phenylethynyl-terminated, addition-type imide oligomers (n=4) derived from PMDA and p-ODA was found to have high solubility and good processability. The imide oligomers were successfully converted to cured resins with high T<sub>g</sub> and excellent mechanical properties at 370 °C. The incorporation of BAFL into (PMDA/p-ODA/PEPA) imide oligomer was also found to give rise to increase the solubility. Particularly even the addition of 5-10 wt% of BAFL was found that the obtained cured resins showed higher T<sub>g</sub>s (> 350 °C) and good ε<sub>b</sub>s (>13%).

We believe these excellent properties of p-ODA based addition-type aromatic polyimides possess a promising possibility for application of high heat resistant composites.

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**Table 2. Solubility and minimum melt viscosities of (PMDA/p-ODA;BAFL/PEPA) imide oligomers**

mol. ratio of p-ODA/BAFL	Solubility (wt-% in NMP)	Min. melt viscosity (Pa.sec)
95/5	>33 <sup>1)</sup>	226
90/10	>33 <sup>1)</sup>	154
75/25	>33 <sup>1)</sup>	1323
50/50	>33	731
25/75	insoluble	No-melt

1) Imide oligomers remain dissolved in NMP for a few months.

**Table 3. Thermal and mechanical properties of (PMDA/p-ODA;BAFL/PEPA) cured resins**

mol. ratio of p-ODA/BAFL	T <sub>g</sub> (°C, DMA)	Elongation at break(%)	
		Ave.	Max.
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
25/75	unprocessable		