

Novel Asymmetric Addition-type Imide Resins for High Temperature Composites

A. Masahiko Miyauchi¹, Nobuaki Oshiro¹, Yuichi Ishida², Toshio Ogasawara²,
Rikio Yokota^{3*}

¹*Frontier Material Development Laboratories, Kaneka Corporation*

²*Institute of Aerospace Technology, Japan Aerospace Exploration Agency(JAXA)*

³*Institute of Space and Astronautical Science, JAXA*

*e-mail address: yokota.rikio@jaxa.jp

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Abstract

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 were synthesized for the matrix resin of high heat resistant carbon fiber-reinforced composites. The uncured imide oligomers (degree of polymerization: $n = 1-4$) showed good solubility (more than 30 wt%) in aprotic solvents). The minimum melt viscosity of the imide oligomer was also found to be very low at > 300 °C. The imide oligomers were successfully converted to cross-linked structures after curing at 370 °C for one hour. The glass transition temperature and elongation at break (ϵ_b) of the cured imide resin were found to be almost 360 °C and >15 %. Carbon fiber plain woven and PMDA/p-ODA-based polyimide resin composite prepared with excellent processability also exhibited a high Tg and good short beam shear strengths at high temperature.

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 Tg of 270 °C and more than 30% elongation-at-break (ϵ_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 thermo-plasticity though a flexible structure and relatively low T_g . The cured resin must exhibit a high T_g 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].

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 ϵ_b after curing at 370 °C/1h [12].

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 imidization 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.

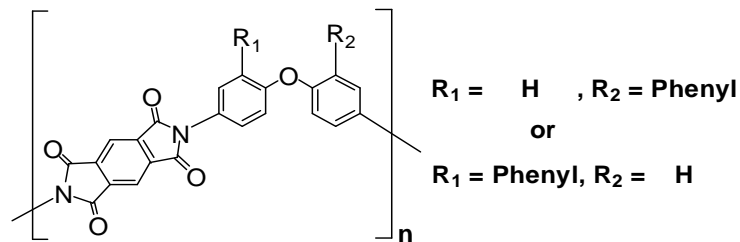


Figure 1. Structures of PI(PMDA/p-ODA)

The excellent properties of aromatic polyimides such as KAPTON[®] and APICAL[®] from PMDA and 4,4'-ODA (DuPont Co. and Kaneka Co., respectively) and UPILEX-R[®] 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).

In addition, previously we reported the 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)[13]. We also 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.

In this paper, based on the above thermal and rheological behavior of PI(PMDA/p-ODA), the synthesized PEPA-terminated aromatic imide oligomers ($n=1-10$) was also found to have high solubility in NMP (>33 wt%) and good processability to convert the cross-linked polymers with excellent thermal stabilities ($T_g > 340$ °C) and mechanical properties (elongation-at-break, $\epsilon_b > 14\%$) with curing at 370 °C/1h (Figure 2).

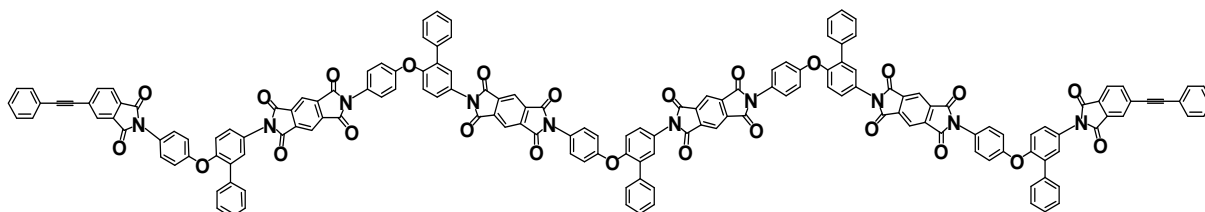


Figure 2. Structures of PMDA/p-ODA/PEPA imide oligomers ($n=4$)

2. Experimentation

2.1. Materials

PMDA was 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.. p-ODA was kindly supplied by Wakayama Seika Co. These materials were used as received. CF plain woven fabric (Besfight, IM600-6K, areal weight:194g/m²) were purchased by Tohotenax Co.

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_{gs}) were determined with DSC at a heating rate of 20 °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 °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 °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 room temperature.

2.4. Preparation of PMDA/p-ODA/PEPA Imide Oligomers

PEPA terminated imide oligomers derived from PMDA and p-ODA were synthesized according to a previous literatures [14-15]. 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, PMDA was added and the reaction mixture was stirred for almost 2 hours at room temperature under N₂ flow. After the complete dissolution of PMDA, 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.

After the attachment of a reflux condenser to the flask, the amide acid oligomers in NMP solutions were imidized at 195 °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 in vacuum oven for up to 4 hours.

2.5. 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 °C for 10 min and subsequently to 370 °C for one hour. The dark red film-like specimens of 6 cm x 6cm x 0.05 mm were obtained.

2.6. Processing of Plain Woven Composites.

An imide oligomer/NMP solution was impregnated into 30 cm square of plain woven fabrics (Toho Tenax IM600-6K). The imide wet prepregs were dried at 100°C for 10 min. The average areal weight of prepregs was almost 380 g/m². The average solid and volatile contents were almost 35 and 17 vol%. Plain fabric composites (12 Ply) were cured in a vacuum hot press. The solvent (NMP) was removed 260 °C for 2 hours without pressure. The temperature was subsequently increased to 370 °C and held for 1 hour, and pressure (1.4 MPa) was applied.

3. Results

3.1. Solubility, Processability and Thermal Properties of Phenylethynyl-terminated Imide Oligomers

PMDA based imide oligomers (n=1-10) derived from 4,4'-ODA or p-ODA were obtained from the imidization of the solution of corresponding amide acid oligomers at 195 °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 °C. On the other hand, surprisingly, the latter PMDA/p-ODA/PEPA imide oligomer was completely soluble in NMP solution with high concentration even at room temperature(> 30 wt%).

Figure 3 shows the DSC curves of PMDA/p-ODA uncured imide oligomer(n=1-4) . The DSC curve of uncured PMDA/p-ODA imide oligomer showed an endothermic shift (T_g) at the range from 150 - 226 °C and a large exothermic peak around 410 °C. The increase behavior of T_g was observed over a wide temperature range from 150 to 250 °C because of an increase of the degree of polymerization(Table 1)

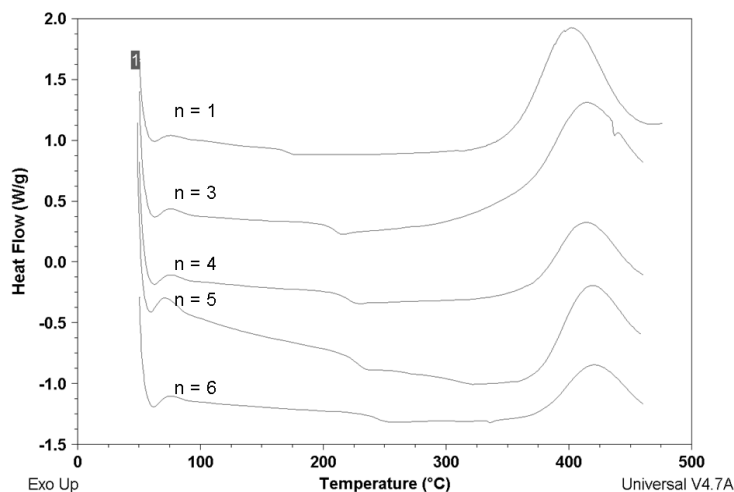


Figure 3. DSC curves of (PMDA/p-ODA/PEPA) imide oligomer (n=4).

Figure 4 shows the dynamic rheological properties of the PMDA/p-ODA/PEPA imide oligomer. (n=1-10) The minimum melt viscosity of the imide oligomers also increased with increase of the degree of polymerization. These data shows significant improvements of PMDA-based polyimide resin in processability for molding the fiber-reinforced heat resistant composites. These excellent low melt viscosities is thought to be accomplished by the formation of randomized repeating units of three types (head-to-tail (a), head-to-head (b), and tail-to-tail (c)) in a PMDA/p-ODA oligomer chain in order to restrict the intermolecular interaction of the 18 Å length of the planar and rigid phenyl-pyromellitimide-phenyl structures (Figure 5).

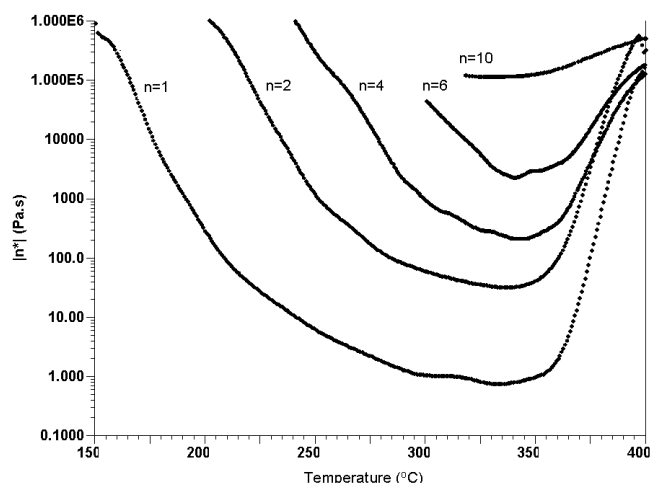


Figure 4. Dynamic rheological behavior of uncured (PMDA/p-ODA/PEPA) imide oligomer (n=1-6).

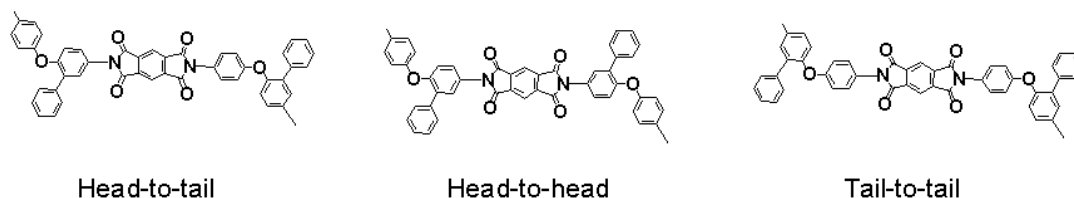


Figure 5. Possible structures of repeated units in PMDA/p-ODA oligomers.

3.2. Thermal and Mechanical Properties of Cured Resins

Thermal and mechanical properties of the cured rein(PMDA/p-ODA/PEPA) are summarized in Table 2. All data were obtained from 100-150 mm homogeneous brown-colored films. The T_g values measured by DMA were also found to be very high, respectively. As can be seen in Figure 6, E' of cured resin also shows a large drop above T_g, indicating that the pendant phenyl group of

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 °C/1h).

n	Calculated Number-average Molecular Weight (M _n x 10 ³)	Solubility in NMP(wt%)	T _g (°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 soluble	226	2239
10	4.86	Insoluble	252	11100

p- ODA in polymer chain which was obtained by curing corresponding the imide oligomer also decrease in the intensity of the intermolecular interaction. Increase behavior of E' was observed at temperature regions up to 420 °C because of thermo-oxidative crosslinking caused by the measurement in air. All cured resins showed high T_{d5s} (>525 °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.[5, 18]

Figure 8 shows the DMA curves of TriA-X composite. The storage modulus (E'), loss modulus and tangent delta were plotted as a function of temperature. The estimated T_g determined from E' by setting up tangents to the linear portion of the curve before and after the modulus drop off was approximately 370 °C. The TriA-X composite exhibited higher T_g due to Kapton-type rigid backbone structure in comparison with the TriA-PI(a-BPDA/4,4'-ODA) composite ($T_g = 340$ °C).

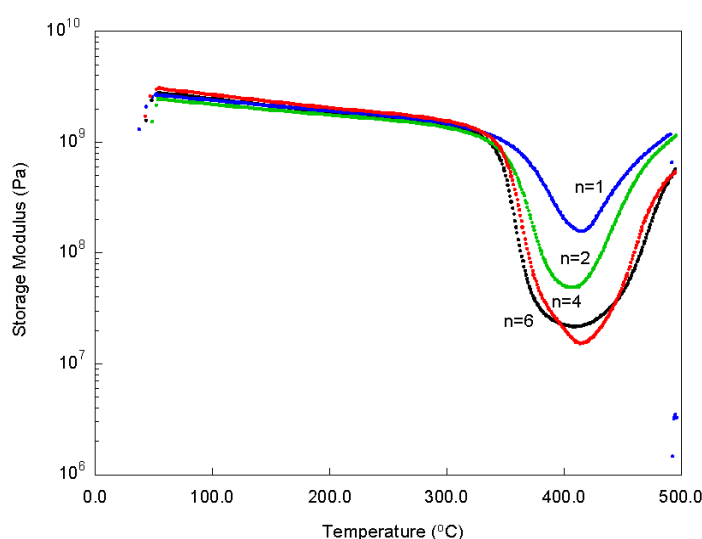


Figure 6. DMA data of (PMDA/p-ODA/PEPA) cured resins

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

n	T_g^a (°C)	T_{d5}^b (°C)	$\epsilon_{bAve.}$ (%)
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 5oC/min under air. b) Determined by TGA at a heating rate of 5oC/min under nitrogen.

3.3. Plain Woven Fabric Composites

Figure 7 shows the cross-sectional optical micrograph pictures of a composite derived from IM600/Cured imide oligomer (n=4) copolymerized 10% of 9,9'-bis(aminophenyl fluorene) in order to increase its solubility in NMP and T_g of cured resin ($T_g=370$ °C) (TriA-X composite) [17-19]. No void and crack were observed in the composites. TriA-X resin was sufficiently found to be impregnated into filaments of IM600 plain fabric of the composite.

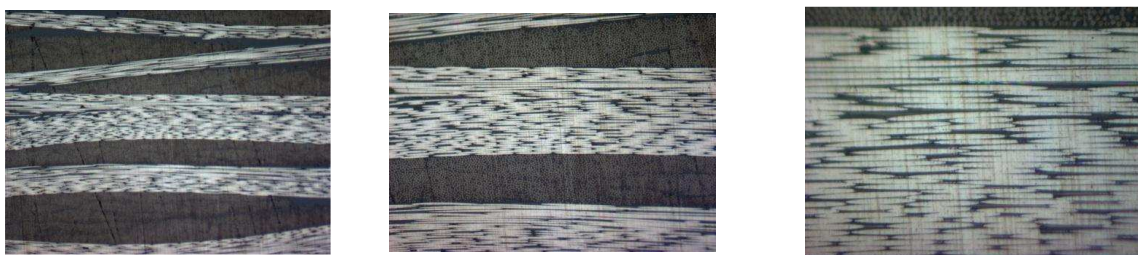


Figure 7. Optical micrograph captured from cross-sectional area of TriA-X CFRP.

Figure 8 shows the DMA curves of TriA-X composite. The storage modulus (E'), loss modulus and tangent delta were plotted as a function of temperature. The estimated T_g determined from E' by setting up tangents to the linear portion of the curve before and after the modulus drop off was approximately 370 °C. The TriA-X composite exhibited higher T_g due to Kapton-type rigid backbone structure in comparison with the TriA-PI(a-BPDA/4,4'-ODA) composite ($T_g = 340$ °C).

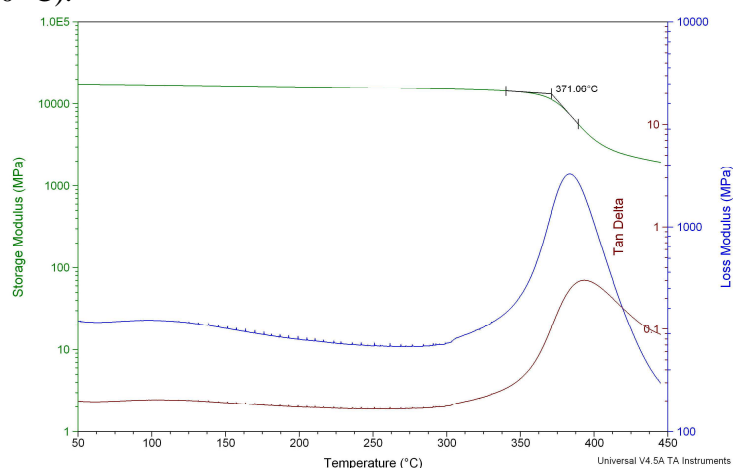


Figure 8. DMA data of TriA-X(PMDA/p-ODA;BAFL/PEPA) composite.

Conclusions

Novel phenylethynyl-terminated, addition-type imide oligomer ($n=1-4$) with Kapton-type backbone structure was found to have a high solubility and a good processability. The imide oligomer was successfully converted to cured resin with high T_g at > 345 °C and excellent mechanical properties. Preliminary studies for processing, thermal and mechanical properties of carbon fiber reinforced TriA-X composite were conducted. IM600 plain woven/TriA-X composite exhibited excellent processability, $T_g(= 370$ °C), and mechanical properties at high temperature. 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 prepared by imide wet prepreg and using a Resin Transfer Molding system.

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