

## FOCUS REVIEW

# Highly soluble phenylethynyl-terminated imide oligomers based on KAPTON-type backbone structures for carbon fiber-reinforced composites with high heat resistance

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Novel addition-type phenylethynyl-containing imide oligomers (degree of polymerization:  $n = 1-10$ ) derived from 1,2,4,5-benzenetetracarboxylic dianhydride or pyromellitic dianhydride (PMDA), 2-phenyl-(4,4'-diaminodiphenyl ether) (p-ODA) and 4-phenylethynylphthalic anhydride (PEPA) were prepared and evaluated as a matrix resin for high heat-resistant carbon fiber-reinforced composites. The uncured imide oligomers showed good solubility ( $> 30$  wt%) in *N*-methyl-2-pyrrolidone and very low melt viscosities. These imide oligomers were successfully converted to crosslinked structures after curing at 370 °C. The glass transition temperature ( $T_g$ ) and the elongation at break ( $\epsilon_b$ ) of the cured imide resin were found to be excellent (almost 340 °C and  $> 15\%$ , respectively). The carbon fiber prepreg was prepared from the imide oligomer solution and used to fabricate void-free laminates with high  $T_g$ . The thermal and mechanical properties of the laminates were determined at ambient temperature.

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## INTRODUCTION

Aromatic polyimides (PIs), such as Kapton (DuPont, Wilmington, DE, USA) and Apical (Kaneka Corporation, Osaka, Japan), derived from 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA) and 4,4'-oxydianiline (4,4'-ODA), and Upilex-R (Ube Industries, Tokyo, Japan), derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride (symmetric-BPDA (s-BPDA)) and 4,4'-ODA, are well known to have high dimensional stability, low thermal expansion, and outstanding thermal and mechanical properties, as well as environmental stability.<sup>1–3</sup> These properties are attributed not only to their rigid structures (planar and symmetric pyromellitimide or biphenylimide) but also to the formation of high-ordered structures due to chain-to-chain interactions. Accordingly, these aromatic PIs did not exhibit high molecular mobility at temperatures higher than their glass transition temperature ( $T_g$ ), indicating that the processing conditions for molding were extremely severe. Significant effort has been devoted to the development of aromatic imide oligomers with good processability and high  $T_g$  by disrupting chain-to-chain interactions.

One well-known, high-performance, thermosetting PI is PMR-15, developed by NASA in the early 1970s for aerospace applications. High-temperature composites from low-molecular-weight resins that

are end capped with reactive groups, such as PMR-15, are generally fabricated by autoclave processing. The PMR-15 cured resin exhibited a cured  $T_g$  of  $> 300$  °C, but the resin lacked toughness because of its high crosslink density.<sup>4</sup> Consequently, the PMR-15 composites exhibited low impact resistance or compressive strength after impact and displayed microcracking upon thermal cycling.

The second-generation development of high-temperature matrix resins at NASA focused on phenylethynyl-containing imide oligomers. The resins were designed for use in high-temperature structural composites with applications in advanced aerospace vehicles, such as the once-proposed high-speed civil transport. The materials for this vehicle were required to have stable mechanical properties for 60 000 h at 177 °C. PETI-5 was the material selected for the matrix resin of high-speed civil transport vehicles and was prepared from the reaction of s-BPDA and two aromatic diamines, with 4-phenylethynylphthalic anhydride (PEPA) as the reactive end cap at a calculated molecular weight of 5000 g mol<sup>-1</sup>.<sup>5–8</sup> The cured PI film exhibited a moderate  $T_g$  of 270 °C and more than 30% elongation at break ( $\epsilon_b$ ). The moldings and composite laminates exhibited high toughness, indicating that upon thermal curing, the chain extension of the imide oligomers is significant and occurs by the thermal

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reaction of PEPA.<sup>9,10</sup> The phenylethynyl end cap offered important benefits, such as a large processing window and good thermo-oxidative stability. The PETI-5 imide exhibited excellent processability during the fabrication of neat resin molding, bonded panels and composites by autoclave processing under pressures of 1.4 MPa or less for approximately 1 h at 350–370 °C. PETI-5 was extensively evaluated and selected as a candidate for use as the adhesive and composite matrix for high-speed civil transport vehicles.<sup>11–13</sup>

Yokota *et al.*<sup>14–17</sup> recently found that a PI based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (asymmetric-BPDA or a-BPDA) and 4,4'-ODA exhibited a  $T_g$  higher than that of a similar s-BPDA-based PI, and the a-BPDA-based PI also showed a large drop in the storage modulus,  $E'$ , at temperatures higher than the  $T_g$ .

These observations are attributed to the decrease in the intermolecular interactions of the PIs that are derived from a-BPDA, which have asymmetric and nonplanar structures. On the basis of the thermal and rheological behavior of a-BPDA-based PIs, Yokota *et al.*<sup>18,19</sup> designed an a-BPDA-based phenylethynyl-terminated oligomer (TriA-PI) with excellent processability, high temperature resistance and more than 20%  $\epsilon_b$  after curing at 370 °C for 1 h.

Because TriA-PI is insufficiently soluble in the imide form, the prepreps were manufactured by impregnating the carbon fibers with a TriA-PI amide acid oligomer solution at high concentrations. However, the evolution of water caused by the imidization of the amide acid oligomers during molding has a tendency to create voids in the composites. The preparation of void-less, high heat-resistant composites can be achieved using prepreps prepared by impregnating the fibers with a high concentration solution of imide oligomers if imide oligomers can be synthesized with both high solubility and good processability.

We describe in this paper the design and preparation of a phenylethynyl-terminated imide oligomer derived from pyromellitic dianhydride (PMDA) and an asymmetric diamine, 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA). PMDA has symmetric and planar structures, and p-ODA is an extremely simple diamine with asymmetric and nonplanar structures. The effects of the asymmetry and the resulting nonplanar structure on the solubility and processability of addition-type aromatic imide oligomers were investigated.

On the basis of the thermal and rheological behavior of the PI(PMDA/p-ODA) film, we found by using dynamic mechanical analysis (DMA) measurements that the asymmetric and nonplanar structures of p-ODA were able to prevent the intramolecular–intermolecular interactions of the PMDA-based PI chains. Moreover, the PEPA-terminated aromatic imide oligomers were found to have high solubility in *N*-methyl-2-pyrrolidone (NMP) (> 33 wt%) and good processability. In addition, upon thermal curing at 370 °C for 1 h, the crosslinked polymers exhibited excellent thermal ( $T_g$  > 340 °C) and mechanical properties (elongation at break,  $\epsilon_b$  > 10%).

## MATERIALS AND METHODS

### Materials

The following chemicals were purchased from the indicated sources and used without further purification: PMDA (Tokyo Kasei, Tokyo, Japan; melting point 286 °C), NMP (Kanto Kagaku, Tokyo, Japan) and PEPA (Manac, Tokyo, Japan; melting point 152–153 °C). 4,4'-ODA (melting point 189–190 °C) and p-ODA (melting point 115–116 °C) were kindly supplied by Seika (Wakayama, Japan).

### Measurements

Differential scanning calorimetry (DSC) was performed using a TA instruments DSC-2010 thermal analyzer at a heating rate of 20 °C min<sup>-1</sup>, with the  $T_g$  taken at the inflection point of the differential heat flow ( $\Delta H$ ) versus temperature

curve in a nitrogen atmosphere. The samples were measured in a sealed aluminum pan. DMA were performed on thin film specimens (23.7 mm long, 5.0 mm wide and 0.05–0.15 mm thick) using a rheometric solids analyzer (RSA II instrument) at a heating rate of 10 °C min<sup>-1</sup> and load frequency of 1 Hz in air. Dynamic thermogravimetric analyses were conducted using a TA instruments SDT-2960 thermal analyzer at a heating rate of 5 °C min<sup>-1</sup>. Melt viscosity measurements were performed on a AR-2000 dynamic rheometer (TA Instruments, New Castle, DE, USA) at a heating rate of 5 °C min<sup>-1</sup>. Specimen disks (25.4 mm diameter and 1.0–1.5 mm thick) were prepared by compression molding of the imide oligomer powder at room temperature.

### PI films

PMDA/p-ODA and PMDA/4,4'-ODA PIs were prepared using a conventional two-step procedure from poly(amic acid)s with the corresponding diamine and dianhydride, as described in an earlier report.<sup>20</sup>

### PMDA/p-ODA/PEPA imide oligomers

Phenylethynyl-containing imide oligomers were prepared from the reaction of PMDA and PEPA with the appropriate quantity of p-ODA.<sup>21</sup> Initially, the aromatic diamine(s) were dissolved in NMP at room temperature under nitrogen, and the appropriate quantities of PMDA were added and stirred into one portion. 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 allowed to stir for 2 h at room temperature. The imide oligomers were prepared directly from the amide acid solutions by imidization at 195 °C for 5 h in an oil bath. The p-ODA-based imide oligomers ( $n=1-4$ ) remained soluble during the imidization process. By contrast, the 4,4'-ODA-based imide oligomer ( $n=4$ ) precipitated during the imidization process. The imide oligomers were isolated by adding the reaction mixtures to water and washing with methanol. The yellow powders were dried at ~240 °C for 4 h under vacuum to a constant weight, with yields > 95%.

### Preparation of cured resins

The obtained imide oligomers were molded using a MP-WNL MINI TEST PRESS machine (Toyo Seiki Seisaku-Sho, Tokyo, Japan). A 6 cm × 6 cm × 0.05 mm PI film frame was put onto a 20 cm × 20 cm stainless-steel plate with UPILEX-S separator films. The imide oligomers were initially heated at 310 °C for 10 min and subsequently heated to 370 °C and held for 1 h at a pressure of 1.4 MPa. Brown-colored, film-like specimens of 6 cm × 6 cm × 0.05 mm were obtained.

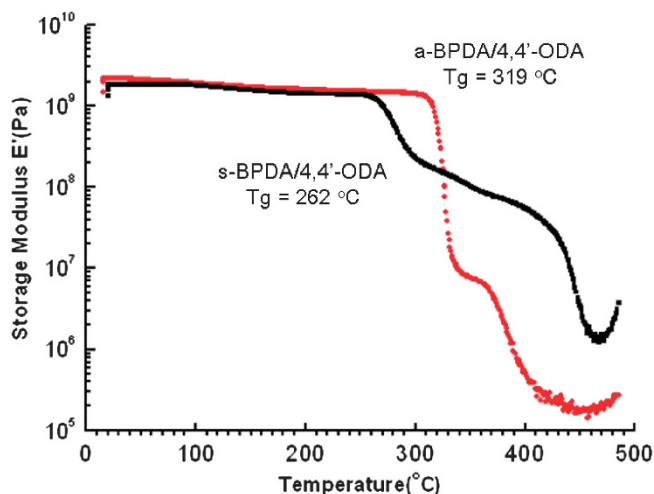
### Processing of PI/carbon fiber composites

An NMP solution of imide oligomers (35 wt%) was impregnated into a 30 cm<sup>2</sup> of plain woven carbon fiber (Toho Tenax IM600-6K, desized by washing with acetone and then drying). The imide oligomer solution prepreg was dried at 100 °C for 10 min. The average areal weight of the prepreps was almost 380 g m<sup>-2</sup>. The average solid, volatile and carbon fiber contents were 35, 17 and 48 wt%, respectively. The plain fabric composites (12 Ply) were cured in a vacuum hot press machine (Kitagawa Seiki, Hiroshima, Japan, KVHCII-Press). The solvent (NMP) was initially removed at 260 °C for 2 h without applying any pressure. The temperature was subsequently increased to 370 °C and held for 1 h at a pressure of 1.4 MPa. DMA was performed on a rectangular specimen (17.5 mm span length, 5.0 mm width and 2.1 mm thick), using a TA Instruments DMA Q-800 in the single cantilever beam test mode at a heating rate of 10 °C min<sup>-1</sup> with a 1 Hz cycling rate and strain of 0.1% in air. The laminates were ultrasonically scanned (C-scanned, Pulse echo), cut into specimens and tested for mechanical properties. The panel was examined for microcracks and voids using a microscope at up to × 400 magnification. The short beam shear strength, based on a three-point bending test, was determined for the specimens (approximately 80 mm long, 60 mm width and 20 mm thick). Five specimens were tested at room temperature.

## RESULTS AND DISCUSSION

### Thermal and rheological properties of PMDA/p-ODA PIs

Recently, Yokota *et al.* found that the thermoplastic PI a-BPDA/4,4'-ODA exhibited a high  $T_g$  of 319 °C and a remarkably large drop

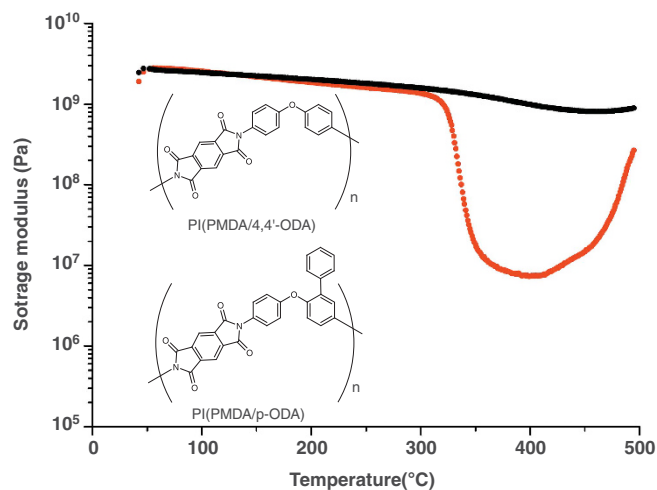


**Figure 1** Dynamic mechanical analysis (DMA) curve of PI(s-BPDA/4,4'-ODA) (black line) and PI(a-BPDA/4,4'-ODA) (red line). PI(a-BPDA/4,4'-ODA) showed both a higher glass transition temperature ( $T_g$ ) and a remarkably large drop above the  $T_g$ . Asymmetric-BPDA, 2,3,3',4'-biphenyltetracarboxylic dianhydride; 4,4'-ODA, 4,4'-oxydianiline; PI, polyimide; 3,3',4',4'-biphenyltetracarboxylic dianhydride, symmetric-BPDA.

in the  $E'$  above the  $T_g$  (Figure 1). The difference in the temperature dependence of the DMA curves between PI(a-BPDA/4,4'-ODA) and PI(s-BPDA/4,4'-ODA) was attributed to the geometric structures of the PI chains. The a-BPDA-based PIs not only have an amorphous morphology but also have a higher  $T_g$  because of the restriction of free rotation as a result of internal steric hindrance.

Figure 2 shows the temperature dependence of the  $E'$  curves of PI(PMDA/p-ODA) and the PI(PMDA/4,4'-ODA) films observed by the DMA measurement in air. The  $T_g$  was determined from the  $E'$  as the tangent taken at the curve before and after the drop-off in the modulus. The PI(PMDA/4,4'-ODA) film did not show an obvious  $T_g$  based on the high-ordered molecular interaction of the polymer chains with a symmetric and rigid structure.<sup>22,23</sup> In contrast, PI(PMDA/p-ODA) clearly showed not only a high  $T_g$  at 325 °C but also a remarkably large drop of  $E'$  from  $10^9$  to  $10^7$  Pa (the rubbery plateau region) above the  $T_g$ . The observed high  $T_g$  and the remarkably large drop in  $E'$  are attributed to the pendant phenyl group of p-ODA, which restricted rotation. Moreover, the intra/intermolecular interactions of the PI(PMDA/p-ODA) chains were also prevented by the steric hindrance of the pendant phenyl group substituted onto the PI(PMDA/4,4'-ODA) chain. In Figure 2, the increasing behavior of  $E'$  observed at temperatures above 420 °C is attributed to the thermo-oxidative crosslinking of cured resin caused by the DMA measurement in air. The wide-angle X-ray diffraction patterns of PI(PMDA/p-ODA) showed only a broadened peak without a dependency on the annealing temperature, indicating that PI(PMDA/p-ODA) did not form a high-ordered structure.<sup>20</sup>

The thermal and mechanical properties of the aromatic PI(PMDA/p-ODA) film, determined by DSC and tensile measurements, are summarized in Table 1. The PI(PMDA/p-ODA) showed a high  $T_g$  up to 330 °C in a nitrogen atmosphere and high  $T_{d5}$  values were recorded as 549 °C on the thermal gravimetry analysis curve. Moreover, the PI(PMDA/p-ODA) was also found to be very tough on the basis of the high elongation of the thin film tensile specimens.



**Figure 2** Dynamic mechanical analysis (DMA) curve of PI(PMDA/4,4'-ODA) (black line) and PI(PMDA/p-ODA) (red line).  $E'$  of PI(PMDA/p-ODA) showed a remarkably large drop above the glass transition temperature ( $T_g$ ). 4,4'-ODA, 4,4'-oxydianiline; PI, polyimide; PMDA, 1,2,4,5-benzenetetracarboxylic dianhydride or pyromellitic dianhydride; p-ODA, 2-phenyl-(4,4'-diaminodiphenyl ether).

**Table 1** Thermal and mechanical properties of PI(PMDA/p-ODA) film

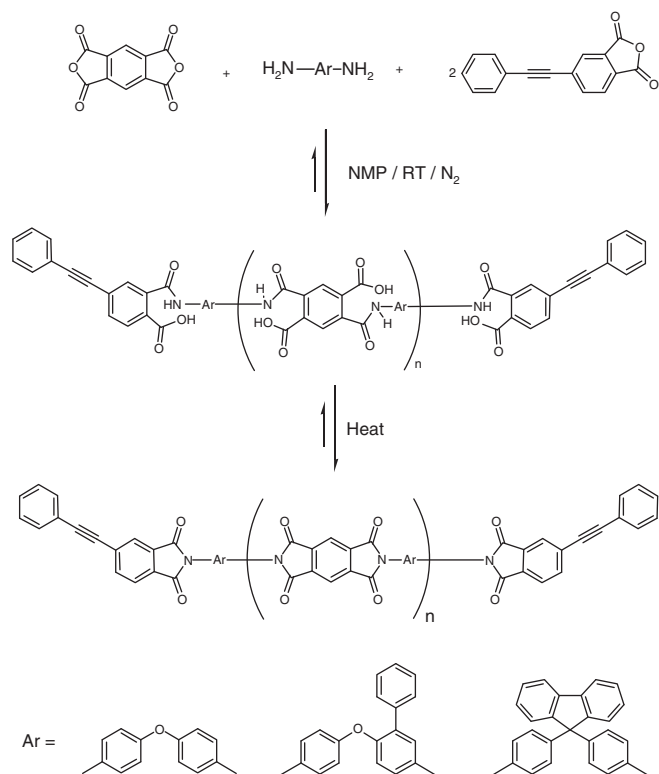
	$[\eta]_{\text{NMP}, 30^\circ\text{C}}$ ( $\text{dL g}^{-1}$ ) <sup>a</sup>	$T_g$ ( $^\circ\text{C}$ )		$T_{d5}$ ( $^\circ\text{C}$ ) <sup>b</sup>	$E_{ave}$ ( $\text{GPa}$ ) <sup>c</sup>	$\sigma_{b,ave}$ ( $\text{MPa}$ ) <sup>d</sup>	$\epsilon_{b,ave}$ (%) <sup>e</sup>
		DSC	DMA				
PI(PMDA/p-ODA)	2.0	333	325	549	3.3	158	38.5

Abbreviations: DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry;  $\epsilon_b$ , elongation at break; NMP, *N*-methyl-2-pyrrolidone; PAA, poly(amic acid)s; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride or 1,2,4,5-benzenetetracarboxylic dianhydride;  $T_g$ , glass transition temperature. PI(PMDA/p-ODA) has a high  $T_g$  and excellent mechanical properties. <sup>a</sup>Inherent viscosity of PAA(PMDA/p-ODA) measured in NMP at 30 °C. <sup>b</sup>Five percent of weight loss measured in  $\text{N}_2$ . <sup>c</sup>Average values of modulus. <sup>d</sup>Average values of tensile strength. <sup>e</sup>Average values of elongation at break.

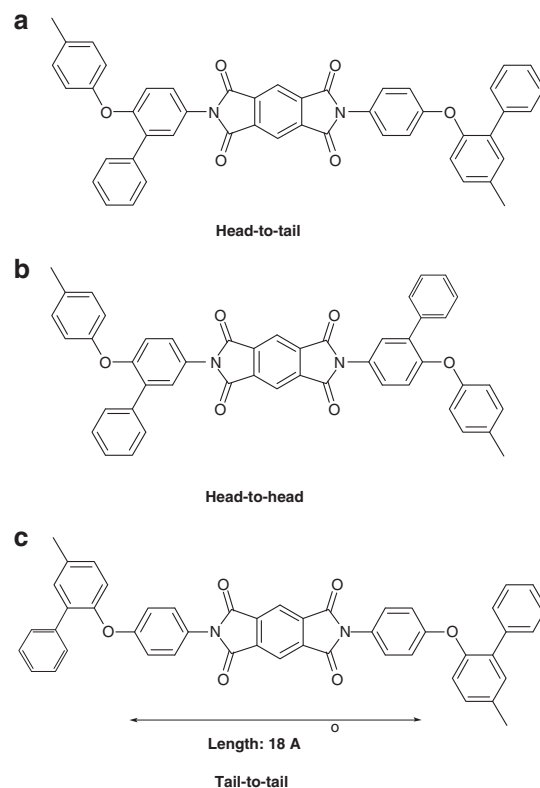
### Solubility, processability and thermal properties of imide oligomers

The PMDA-based imide oligomers derived from 4,4'-ODA and p-ODA were obtained from the imidization of the solution of the corresponding amide acid oligomers (Figure 3). The PMDA/4,4'-ODA/PEPA imide oligomer ( $n=4$ ) was insoluble in NMP and could not be compression molded because of the lack of melt flow. In contrast, the PMDA/p-ODA/PEPA imide oligomers ( $n=1-4$ ) were completely soluble in the NMP solution at high concentrations, even at room temperature (> 30 wt%).

Table 2 summarizes the solubility and thermal and mechanical properties of the PMDA/p-ODA/PEPA imide oligomer and cured resin ( $n=1-10$ ). The minimum melt viscosity of the imide oligomers also increased with the degree of polymerization (Supplementary Figure S1). However, all of these materials exhibited their respective minimum melt viscosities at temperatures at which the phenylethynyl groups react. Thus, all of these imide oligomers are not



**Figure 3** Synthesis of phenylethynyl-terminated imide oligomers. The phenylethynyl-terminated imide oligomers were prepared via amide acid oligomers by the solution imidization process.



**Figure 4** The three possible types of repeated units in a (PMDA/p-ODA) polymer chain. Three possible types ((a) head-to-tail, (b) head-to-head and (c) tail-to-tail) of repeat units exist because of the asymmetric structure of p-ODA. PMDA, 1,2,4,5-benzenetetracarboxylic dianhydride or pyromellitic dianhydride; p-ODA, 2-phenyl-(4,4'-diaminodiphenyl ether).

**Table 2** Solubility and thermal and mechanical properties of (PMDA/p-ODA/PEPA) imide oligomers ( $n=1-10$ ) and their cured resin

n	Imide oligomer				Cured resin <sup>a</sup>		
	Calculated number-average molecular weight ( $M_n \times 10^3$ )	Solubility in NMP (wt%)	$T_g$ (°C) <sup>b</sup>	Min. melt viscosity ( $\text{Pa} \cdot \text{s}$ ) (°C) <sup>c</sup>	$T_g$ (°C) <sup>d</sup>	$T_{d5}$ (°C) <sup>e</sup>	$\varepsilon_b$ (%) <sup>f</sup>
1	1.19	> 33 <sup>g</sup>	152	1 (336)	356	528	9.6
2	1.65	> 33 <sup>g</sup>	178	30 (338)	348	530	10.2
3	2.11	> 33 <sup>g</sup>	202	144 (337)	348	536	11.4
4	2.57	> 33 <sup>h</sup>	226	208 (340)	346	539	15.7
6	3.48	Partially	226	2239 (341)	342	543	16.9
10	4.86	Insoluble	252	11 100 (330)	336	543	11.9

Abbreviations: DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry;  $\varepsilon_b$ , elongation at break; NMP, *N*-methyl-2-pyrrolidone; PEPA, 4-phenylethynylphthalic anhydride; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride or 1,2,4,5-benzenetetracarboxylic dianhydride; TGA, thermogravimetric analyses;  $T_g$ , glass transition temperature.

The (PMDA/p-ODA/PEPA) imide oligomers have good solubility and excellent processability for molding composites. Each cured resin was also found to have high  $T_g$  values and good  $\varepsilon_b$ .

<sup>a</sup>Cured at 370 °C for 1 h under the pressure of 1.4 MPa.

<sup>b</sup>Determined on powdered samples by DSC at a heating rate of 20 °C min<sup>-1</sup> in N<sub>2</sub>.

<sup>c</sup>Determined by rheometer at a heating rate of 5 °C min<sup>-1</sup>.

<sup>d</sup>Determined by DMA at a heating rate of 10 °C min<sup>-1</sup> in air.

<sup>e</sup>Determined by TGA at a heating rate of 5 °C min<sup>-1</sup> in air.

<sup>f</sup>Average values of elongation at break.

<sup>g</sup>Solution stable for up to a few months.

<sup>h</sup>Gelation occurred after a few days.

stable at the temperatures of their minimum melt viscosities.<sup>8</sup> These results indicate that the PMDA/p-ODA/PEPA imide oligomer has significantly better processability for molding fiber-reinforced, heat-resistant composites compared with conventional PMDA-based PIs. The low melt viscosities of the imide oligomer ( $n=1-4$ ) are thought to be due to the formation of randomized repeating units of three types, shown in Figure 4: (a) head-to-tail, (b) head-to-head and (c) tail-to-tail.

### Thermal and mechanical properties of the cured resins

In Table 2, the thermal and mechanical properties of the cured resin (PMDA/p-ODA/PEPA) were obtained from 100 to 150 mm homogeneous brown films. The  $T_g$  values of each cured resin, measured by DMA, were found to be very high. The  $E'$  of the cured resin also exhibited a large drop at temperatures above  $T_g$ , as the pendant phenyl group of p-ODA in the polymer chain disrupts intermolecular interactions. The pattern of increase of  $E'$  was observed at temperatures up to 420 °C because of the thermo-oxidative crosslinking caused by performing the measurements in air. All of the cured resins exhibited high  $T_{d5}$  values (>525 °C). Surprisingly, the  $\varepsilon_b$  values of the cured polymers were very high (>9.5%), indicating that the reaction mechanism of the PEPA was mainly chain extension rather than cyclization or crosslinking, as reported by Meyer *et al.*,<sup>9,10</sup> Nakamura *et al.*<sup>24</sup>



**Table 3 Thermal and mechanical properties of (PMDA/p-ODA(90);BAFL(10)/PEPA) imide oligomer ( $n = 4$ )**

Imide oligomer		Cured resin <sup>a</sup>				
Calculated number-average molecular weight ( $M_n \times 10^3$ )	Solubility in NMP (wt%)	$T_g$ (°C) <sup>b</sup>	Min. melt viscosity		$T_{d5}$ (°C) <sup>e</sup>	$\epsilon_b$ (%) <sup>f</sup>
			(Pa·s) <sup>c</sup>	(Pa·s) <sup>d</sup>		
2.60	> 33 <sup>g</sup>	220	154	356	548	11.3

Abbreviations: BAFL, 9,9-bis(4-aminophenyl)fluorene; DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry;  $\epsilon_b$ , elongation at break; NMP, *N*-methyl-2-pyrrolidone; PEPA, 4-phenylethynylphthalic anhydride; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PMDA, pyromellitic dianhydride or 1,2,4,5-benzenetetracarboxylic dianhydride;  $T_g$ , glass transition temperature.

The imide oligomer exhibited good solution stability and very low melt viscosity. The cured resin was also found to have a high  $T_g$  and a good  $\epsilon_b$ .

<sup>a</sup>Cured at 370 °C for 1 h under the pressure of 1.4 MPa.

<sup>b</sup>Determined on powdered samples by DSC at a heating rate of 20 °C min<sup>-1</sup> in N<sub>2</sub>.

<sup>c</sup>Determined by rheometer at a heating rate of 5 °C min<sup>-1</sup>.

<sup>d</sup>Determined by DMA at a heating rate of 10 °C min<sup>-1</sup> in air.

<sup>e</sup>Determined by TGA at a heating rate of 5 °C min<sup>-1</sup> in air.

<sup>f</sup>Average values of elongation at break.

<sup>g</sup>Solution was stable for up to a few months.

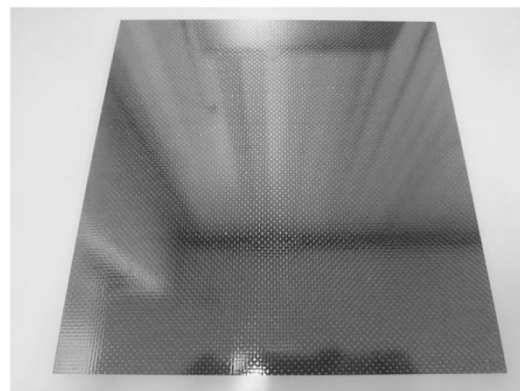
### Incorporation of the BAFL diamine monomer into the PMDA/p-ODA/PEPA imide oligomers

After preparing a highly concentrated NMP solution of the PMDA/p-ODA/PEPA imide oligomer (33 wt%,  $n = 4$ –10) at 150 °C, the solution formed a gel after storage for several days at room temperature. When the gel was heated to 150 °C for 1 h, it gradually changed to a solution without any precipitation of solids. This behavior is possibly due to the intermolecular interactions of the tail-to-tail units (Figure 4c) in the oligomer chains in the NMP solution, resulting in some molecular order that leads to the formation of a reversible gel.

In general, the preparation of the prepreg from solution requires an approximately 30 wt% solid solution to obtain sufficient resin content in a single dip process. The above gelation behavior is undesirable; therefore, it was proposed to investigate the use of a second diamine that would provide more steric hindrance and prevent gelation from occurring. The addition of a bulky substituent on the polymer side chain is well known to improve solubility; therefore, we selected 9,9-bis(4-aminophenyl)fluorene (BAFL), which contains a bulky fluorenyl side group, as a diamine monomer to copolymerize with the PMDA/p-ODA imide oligomer.

Table 3 shows the solubility and thermal and mechanical properties of the PI imide oligomer containing 10 mol% of BAFL. An addition of a small amount of BAFL allowed the imide oligomer solution to remain stable for over a few months with no sacrifice in the melt viscosity or the  $T_g$  of the cured resin. Only a decrease in the  $\epsilon_b$  of the cured resin was observed, indicating that the molecular mobility and flexibility derived from the ether linkage of the p-ODA in the polymer chains was decreased concomitantly with the increase in the rigid units of PMDA-BAFL-PMDA. Increasing the amount of BAFL in the oligomers produces improved solubility, a higher  $T_g$  and increasing melt viscosity (Supplementary Table S1).

On the basis of these results, the PI PMDA/p-ODA(90);BAFL(10) imide oligomer was found to have high solubility (> 33 wt%), storage stability in an NMP solution and low melt viscosity (< 1500 Pa·s). Upon thermal curing, the imide oligomer exhibited both a high  $T_g$  (> 350 °C) and good mechanical properties ( $\epsilon_b$  > 13%).



**Figure 5** The polyimide/carbon fiber composite (30 cm × 30 cm). A polyimide/carbon fiber composite without voids was fabricated from the imide solution prepreg.

### Carbon fiber-reinforced PI composites

The prepreg of the phenylethynyl-terminated PMDA/p-ODA(90);-BAFL(10) imide oligomers was prepared by impregnating a carbon fiber plain woven cloth with the NMP solution of the imide oligomer.<sup>25–27</sup> A PI/carbon fiber composite was fabricated from the prepreg in two steps. First, the laid-up prepreps (12 ply) were heated at 260 °C for 2 h on a hot plate under vacuum to remove the solvent. The laminate was subsequently cured at 370 °C for 1 h under 1.4 MPa of pressure. The resultant composite was of good quality as determined by an ultrasonic inspection (Figure 5). No void or cracks were observed in the composites by optical microscopy or a c-scan. The fibers in the composite appeared to be well wet-out by the resin.

The  $T_g$  of PI/carbon fiber composite was 356 °C, the same as that of the neat cured resin (Table 3). The short beam shear strength of the composite was found to be high (63 MPa), presumably due to the excellent quality of the laminate. In the fabrication of the 12 ply laminates, no problems were encountered with the removal of volatiles. It is unknown whether the removal of the volatiles will be more difficult with thicker laminates.

The detailed thermal and mechanical property measurements of the composites prepared from the phenylethynyl-terminated (PMDA/p-ODA; BAFL) imide oligomers are now in progress. We believe that this PMDA/p-ODA-type imide resin possesses a variety of excellent properties that will greatly enhance the possibilities for developing new heat resistance composite materials.

### CONCLUSIONS

A novel phenylethynyl-terminated, addition-type imide oligomer ( $n = 1$ –4) with a Kapton-type backbone structure was found to have high solubility and good processability. The imide oligomers were successfully converted to a cured resin with a  $T_g$  > 345 °C and excellent preliminary mechanical properties. Preliminary studies were conducted for processing and determining the thermal and mechanical properties of the carbon fiber-reinforced PMDA/p-ODA(90);-BAFL(10) composite. The IM600 plain woven composite exhibited excellent processability, high  $T_g$  and good mechanical properties at high temperatures.

We believe that these excellent properties of the PMDA/p-ODA-based addition-type aromatic PIs suggest promising possibilities for the application to highly heat-resistant composites prepared by imide solution prepreg techniques.

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