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Processing and properties of carbon fiber reinforced triple-A polyimide (Tri-A PI) matrix composites

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Abstract—This paper presents experimental results for the processing and mechanical properties of carbon fiber reinforced composites of a newly developed amorphous, asymmetric, and addition type polyimide (Triple-A PI). The imide oligomers were synthesized from the reaction of 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA), 4,4′-oxydiaminine (ODA), and phenylethynyl phthalic anhydride (PEPA). Because of amorphous structure, the melting point and melt viscosities of the polymer are relatively lower as compared with similar polyimides such as LaRC™ PETI-5. In spite of the lower molecular weight of the imide oligomer (<2500 g/mol), the cured polymer exhibits excellent mechanical properties because of the irregular and asymmetric structure as well as flexible end-capper. Carbon fiber reinforced composites were fabricated by routing prepreg consolidation. The composites exhibit excellent mechanical properties with high glass transition temperature ($>320°$C).

Keywords: Polyimides; high temperature composite; mechanical properties.

1. INTRODUCTION

Polyimides are attractive for aerospace applications because of their excellent thermo-oxidative stability and mechanical properties. However, the processability of polyimides is inferior as compared with epoxies and bismaleimides. Phenylethynyl terminated polyimide LaRC™ PETI-5 developed by NASA Langley Research Center (LaRC) possesses good processability and excellent mechani-

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cal properties for an adhesive and composite matrix resin [1–4]. Therefore a great amount of effort has been devoted to application of PETI-5 to a future high-speed civil transport (HSCT) in NASA for several years [5]. It has been believed that PETI-5 is one of the candidate materials for HSCT.

Although PETI-5 exhibits excellent heat resistance for HSCT, the operation temperature is restricted below 200°C. In order to improve heat resistance of cured polyimide, the molecular weight of imide oligomer should be decreased. However, lower molecular weight imide oligomers increase the degree of crystallinity, melting point and melt viscosities, resulting in poor processability [4]. For PETI-5, random co-oligomer prepared from 3,3′,4,4′-BPDA (3,3′,4,4′-Bipheyl tetracarboxylic dianhydride, s-BPDA), 3,4′-ODA (oxydiamiline), 1,3-APB (bis 3-aminophenoxy benzene), and 4-PEPA (Phenylethynylphthalic anhydride) has been applied in order to decrease melting point and melt viscosities. Furthermore, the lower molecular weight oligomer had the lower fracture toughness, because of the higher crosslink density. Therefore, optimization of imide oligomer molecular weight is significantly important in order to manage both good processability and excellent mechanical properties. The molecular weight of PETI-5 was optimized to be 5000 g/mol, and it is difficult to decrease the molecular weight of PETI-5 without affecting the mechanical properties and processability [4].

Recently, Yokota *et al.* developed an epoch-making addition type polyimide from the reaction of asymmetric type BPDA (2,3,3′,4′-BPDA, a-BPDA), diaminine, and PEPA [6–8]. A new polyimide is referred to as ‘Triple A-PI (Tri-A PI)’ from the characteristics of the polymer, namely amorphous, asymmetric, and addition type. The commercial name of the polyimide is UPILEX™-AD, which is provided by Ube Industries Ltd. Both the imide oligomers and cured polymers have significantly irregular and asymmetric structure derived from asymmetric BPDA, resulting in low melt temperature, low melt viscosities and high glass transition temperature ($T_g > 300$°C). Furthermore, even though the molecular weigh of the imide oligomer is relatively low, the cured polymer exhibits excellent mechanical properties because of chain extension caused by the phenylethynyl group reaction [6–8].

Higher heat resistance will be required for a future reusable space vehicle and jet engine applications as well as HSCT. National Aerospace Laboratory of Japan, Institute of Space and Astronautical Science, Ube Industries Ltd., and IHI Aerospace Co. Ltd. have conducted a joint program to develop and evaluate the composite system since September 1999 [9]. Lower molecular weight Tri-A PI polymers were selected for higher glass transition temperature ($T_g >$ 300°C), lower apparent melting point (m.p. $<$ 300°C), and lower melt viscosities without affecting the mechanical properties (toughness and elongation). This paper presents preliminary experimental results for processing and mechanical properties of carbon fiber reinforced composites with the 1600 and 2500 g/mol version imide oligomers. The effects of imide oligomer molecular weight and cure temperature on the composite properties were also investigated.

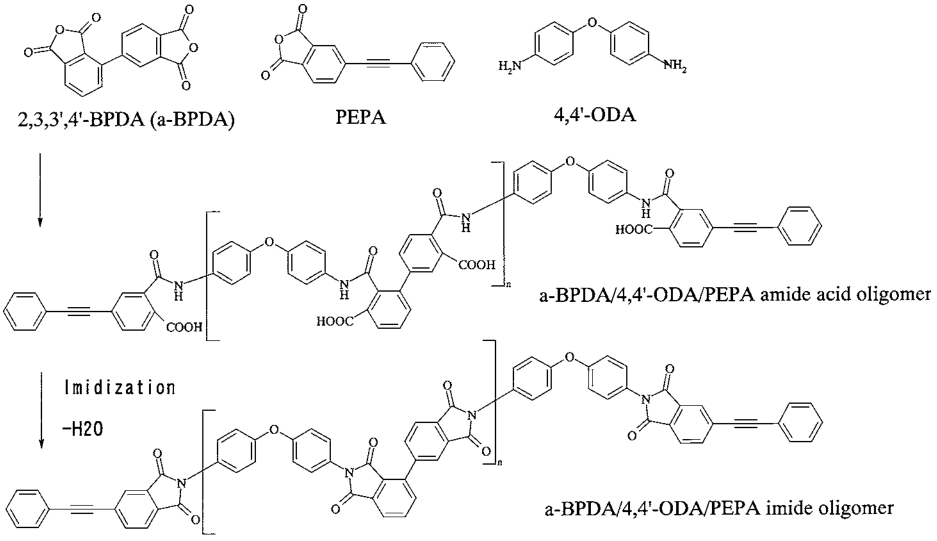


Figure 1. Synthetic scheme of the imide oligomers from the reaction of a-BPDA, 4,4′-ODA, and PEPA.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Tri-A PI

The following chemicals were used without further purification: 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA, m.p. 172°C, Ube Industries Ltd., Japan), 4,4′-oxydianiline (4,4′-ODA, m.p. 187°C, Tokyo Kasei Co., Japan), phenylethynylphthalic anhydride (PEPA, m.p. 151°C, Manac Inc., Japan), and N-methyl-2-pyrrolidinone (NMP).

The synthetic scheme for the imide oligomer is shown in Fig. 1. The diamine (4,4′-ODA) was initially dissolved in NMP at room temperature under nitrogen. The dianhydride (a-BPDA) and endcapper (PEPA) were added in the 4,4′-ODA/NMP solution, and the reactions were allowed to stir for 3 h at room temperature under nitrogen. The amide acid/NMP solutions were used for preparation of prepreg tapes and prepreg fabrics. The imide oligomers with different molecular weight (calc. ~1600 ($n = 2$), ~2500 ($n = 4$), and ~5250 g/mol ($n = 10$)) were synthesized through the amide acid route in NMP. Detailed descriptions regarding the synthesis of the imide oligomer were reported elsewhere [6–8]. Oligomer characterization is presented in Table 1. The dynamic rheological behaviors of the imide oligomers were determined by a Rheometrics RDS-II dynamic rheometer at a heating rate of 3°C/min. The compacted resin disk was loaded in parallel plates with 7.9 mm diameter. The top plate was oscillated at a fixed strain of 10%, and a fixed frequency of 10 Hz. Melt viscosity of a neat PETI-5 ($M_w \sim 5000$ g/mol) resin was also evaluated for direct comparison.

Table 1.
Physical properties of imide oligomers

	Tri-A PI $n = 2$	Tri-A PI $n = 4$	Tri-A PI $n = 10$	LaRC™ PETI-5*
Molecular weight (calc.), M_n	∼1600	∼2500	∼5250	∼5000
Imide oligomer T_g, (°C)**	189	230	237	210
Imide oligomer minimum melt viscosity (Pa s)	3.4 (336°C)	124 (347°C)	1750 (369°C)	1000 (371°C)
Cured polymer T_g, (°C)** ***	351	341	308	270

* J. G. Smith, Jr., J. W. Connell and P. M. Hergenrother, *J. Comp. Mater.* **34** (7), 614–628 (2000).
** Estimated on powdered samples by DSC at a heating rate of 10°C/min.
*** Cured at 370°C for 1 h.

Table 2.
Unidirectional prepreg and UD-composite properties

	$n = 2$	$n = 4$
Molecular weight (calc.), M_n	∼1600	∼2500
Prepreg solids (wt%)	36.4	30.4
Prepreg volatiles (wt%)	15.6	15.3
Carbon fiber	T800H 12K (445TEX)	
Carbon fiber areal weight (g/m^2)	240	
Prepreg areal weight (g/m^2)	365	350
Composite fiber fraction (vol%)	64.2	69.6
Composite porosity (vol%)	0.8	4.0

2.2. Processing of composites

It is known that the lower molecular weight oligomer had the lower melting point and melt viscosity, when cured, the higher T_g, and lower fracture toughness, because of the higher crosslink density [4]. In this study, the unirectional (UD) composites with the ∼1600 ($n = 2$), and ∼2500 g/mol ($n = 4$) oligomers were fabricated, and mechanical properties were investigated. In this paper, the term Tri-A PI (1600), and Tri-A PI (2500) are used to describe the ∼1600 and ∼2500 g/mol version of the imide oligomers. The amide acid/NMP solutions were impregnated into T-800H carbon fiber (12K/bundle, Toray, Japan). The properties of the UD prepreg tapes and imide oligomers are summarized in Table 2. UD composites were cured in an autoclave. In order to obtain a well-consolidated T800/Tri-A PI composite, the solvent (NMP) and reaction by-products (H_2O) should be removed before applying pressure [3]. For the purpose, the prepreg was held at 250°C for 0.5 h. Subsequently, pressure (0.3 MPa) was applied and the temperature was increased to 370°C and held for 1 h.

Plain fabric composites were also fabricated from prepreg route. The amide acid/NMP solutions were impregnated into Toray T-800 carbon fiber (12K/bundle) plain fabrics. The properties of the fabric prepreg are summarized in Table 3. Plain

Table 3.
Plain fabric prepreg and composite properties (imide oligomer, $n = 4$, $M_n \sim 2500$)

Cure temperature (°C)*	360	370	380
Carbon fiber		T800H 12K (445TEX)	
Carbon cloth areal weight (g/m^2)		318	
Number of fiber bundles (/inch)		9 (for warp and fill)	
Prepreg solids (wt%)		36	
Prepreg volatiles (wt%)		14	
Prepreg areal weight (g/m^2)		432	
Composite architecture		0°/90° plain woven fabric	
Composite fiber fraction (vol%)	66.7	68.7	65.2
Composite resin contents (wt%)	25.4	22.7	27.0
Composite porosity (vol%)	1.7	3.3	1.7

* Cured for 1 h under 5.5 MPa in a hot press.

fabric composites were cured in a hot press. The solvent (NMP) and reaction by-products (H_2O) were removed at 250°C for 40 min, and pressure (5.5 MPa) was applied. The temperature was increased to 360, 370, and 380°C and held for 1 h. The effect of cure temperature on the composite properties was also investigated.

2.3. Evaluation of mechanical properties

2.3.1. Unidirectional composites. Dynamic mechanical analyses (DMA) for the UD composites were performed on Rheometrics RSA II. A beam specimen along 0° direction (2 mm in width, 1.1 mm in thickness, 56 mm in length) was prepared, and three-point bending load with 48 mm span width was applied at a fixed strain of 0.02% and a fixed frequency of 1 Hz under a constant heating rate of 3.75°C/min. The storage (E') and loss (E'') moduli, and tan δ were measured as a function of temperature. DMA analysis for unidirectional IM7/PETI-5 composite was also conducted for direct comparison.

Short beam shear strength (SBS, ASTM D2344) was determined on 12-ply specimens (12 mm length, 6.35 mm width, 2.2 mm thickness) at 25, 177, and 300°C. Five or three composite specimens were tested under each condition. Short beam shear tests were conducted on a mechanical testing machine (Model 4482, Instron, USA) under a constant displacement rate of 1.27 mm/min. Specimens were held for 5 min after reaching the test temperature. Tensile strength (NHT, SACMA SRM-4R94) was determined on 6-ply unidirectional (0°) specimens (320 mm length, 12.7 mm width, 1.1 mm thickness) at 25, 177, 250, and 300°C. Tensile tests for the Tri-A PI (2500) composite were conducted on a servo-hydraulic testing machine (Model 8501, Instron, USA) under a constant displacement rate of 1.0 mm/min. Specimens were held for 20 min after reaching the test temperature with heating rate of 5°C/min. Tensile Young's modulus of each specimen was determined using strain gages bonded on the both sides of a specimen. Three-point flexural strengths (ASTM D790) were determined on the Tri-A PI and IM7/PETI-5 unidirectional composite specimens (70 mm length, 12.7 mm width, 1.1 mm thickness) with span width of 25 mm at 25, 177, 250, and 300°C. Two or three specimens were tested for tensile and flexural tests under each condition.

2.3.2. Plain woven fabric composites. Tensile strength (NHT, SACMA SRM-4R94) was determined on 7-ply fabric (0°/90°) specimens (300 mm length, 25.4 mm width, 2.0 mm thickness). On the other hand, compressive strength (NHC, SACMA SRM-1R94) was determined on 15-ply fabric (0°/90°) specimens (80 mm length, 12.7 mm width, 4.0 mm thickness, without tabs). For compressive and tensile testing, two or three specimens were tested under each condition, and mechanical tests were performed at 25, 177, 250, and 300°C. Open hole compressive (OHC) strength at 25°C was determined on 14-ply fabric (0°/90°) specimens (80 mm length, 25.4 mm width, 4.0 mm thickness) with a 6.35 mm hole in the center.

3. RESULTS AND DISCUSSION

3.1. Rheological properties of imide oligomers

The dynamic rheological behaviors of the imide oligomers are shown in Fig. 2. The minimum viscosities were 3.4, 124, and 1750 Pa s for the Tri-A PI (1600), Tri-A PI (2500), and Tri-A PI (5250), respectively, which corresponded to the viscosities reported for PETI-5 (5.0, 90, and 1000 Pa s for M_w ~ 1250, ~2500, and ~5000) [4]. On the other hand, the onset temperature of melting (apparent melting point) of Tri-A PI (5250) is approximately 300°C, which is much lower than that of PETI-5 (M_w ~ 5000, m.p. ~335°C). This is due to difference in imide oligomer crystallinity between Tri-A PI and PETI-5. It should be noted that the melt viscosities above 310°C are not stable because of the phenylethynyl group reaction,

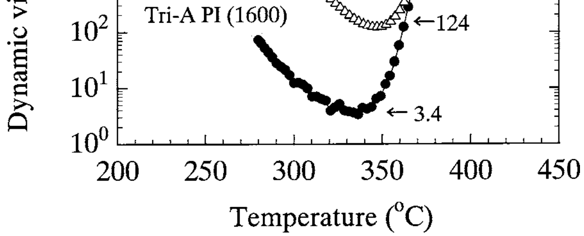
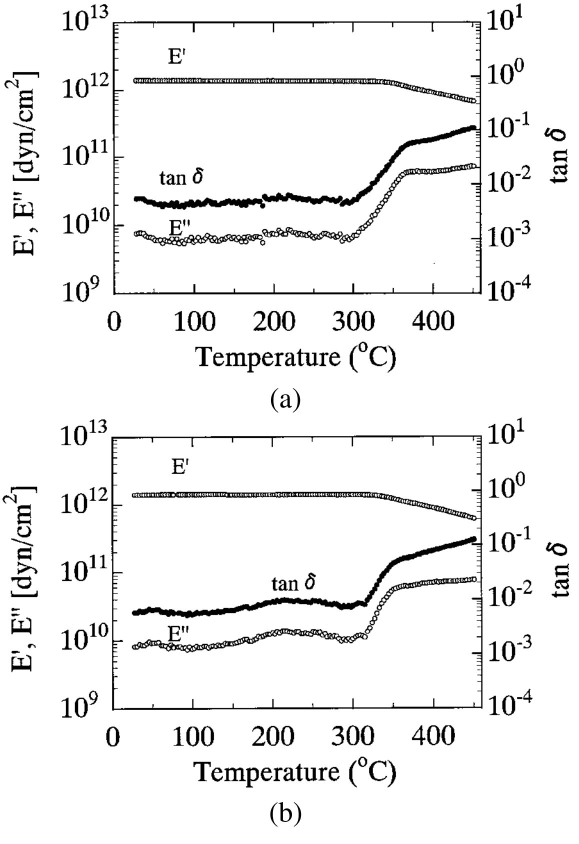


Figure 2. Dynamic viscosities of the Tri-A PI (M_w ~ 1600, ~2500, ~5250) and LaRC™ PETI-5 (M_w ~ 5000) imide oligomers.

and the melt viscosity below 310°C is more important for composite processability than the minimum viscosity. Therefore, it is understood that Tri-A PI exhibits excellent processability in comparison with PETI-5.

3.2. Mechanical properties

3.2.1. Unidirectional composite. Figure 3 shows a DMA trace of the unidirectional T800/Tri-A PI composites. The storage modulus (E'), loss modulus (E''), and $\tan\delta$ 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 340°C and 320°C for the Tri-A PI (1600) and Tri-A PI (2500) composites, respectively. Because of the 0° unidirectional composites, the distinct peak in loss modulus (E') was not observed. The DMA trace of the IM7/PETI-5 composite is shown in Fig. 4, and the estimated T_g was approximately 260°C. The Tri-A PI composites exhibit higher glass transition temperature due to irregular structure and higher cross link density derived from lower molecular weight in comparison with the PETI-5 composite.



(a)

(b)

Figure 3. Dynamic Mechanical Analysis (DMA) trace of the unidirectional T800/Tri-A PI composites (a) Tri-A PI ($M_w \sim 1600$), (b) Tri-A PI ($M_w \sim 2500$).

Short beam shear (SBS) strengths for the T800/Tri-A PI (1600) and T800/Tri-A PI (2500) composites are shown in Table 4. The literature data for the IM7/PETI-5 (5000) composites are cited in Table 4 [3]. The SBS strength of the Tri-A PI (1600) composite is superior to those of the T800/Tri-A PI (2500) composite above 177°C, which attributes to higher glass transition temperature. The T800/Tri-A PI (1600) composite exhibits much higher SBS strength and plastic deformation resistance above 177°C as compared with the IM7/PETI-5 (5000) composite.

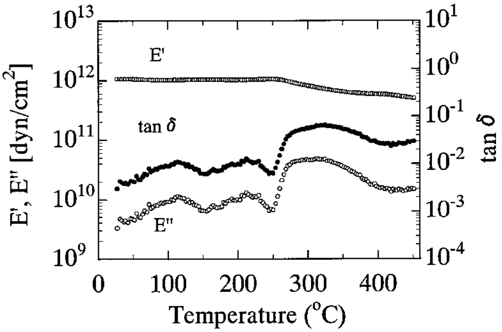


Figure 4. Dynamic Mechanical Analysis (DMA) trace of the unidirectional IM7/PETI-5 composites.

Table 4.
Mechanical properties of UD-composites

Mechanical properties	Temp. (°C)	T800H/Tri-A PI (1600)	T800H/Tri-A PI (2500)	IM7/PETI-5
Molecular weight (calc.), M_n		~1600	~2500	~5000
Composite fiber fraction (vol%)		64.2	69.6	62
Composite porosity (vol%)		0.8	4.0	1–2
SBS strength (MPa)	25	124.1	123.6	106.5*
	177	87.7	83.1	62.8*
	250	60.9	plastic	—
	300	plastic	plastic	—
0° Tensile strength (MPa)	25	—	2672	2929*
	177	—	2735	—
	250	—	2364	—
	300	—	2504	—
Young's modulus (GPa) (Tensile test)	25	—	190	—
	177	—	190	—
	250	—	190	—
0° Flexural strength (MPa)	25	2151	2194	1448
	177	1865	1440	921
	250	1657	1434	256
	300	1280	863	129

*T. H. Hou, B. J. Jensen and P. M. Hergenrother, *J. Comp. Mater.* **30** (1), 109–122 (1996).

Tensile and flexural strengths of the composites are also shown in Table 4. The T800/Tri-A PI composite exhibits excellent tensile and flexural strengths. Degradation in tensile strength was not significant up to 300°C. In spite of high crosslink density due to lower molecular weight, the T800/Tri-A PI composites exhibit excellent mechanical properties with high glass transition temperature. It is supposed that the irregular and asymmetric structure as well as flexible endcapper (PEPA) contribute to the excellent mechanical properties such as fracture toughness, and elongation to failure.

3.2.2. Plain woven fabric composite. Mechanical properties such as tensile (NHT) strength, compressive (NHC) strength, and open hole compressive (OHC) strength were summarized in Table 5. During the compressive tests for the composite cured at 360°C, local fracture at the loading edge of the specimen occurred before interlaminar fracture (namely, brooming fracture); therefore, the actual compressive strengths of the composite are supposed to be higher than the values shown in Table 5.

In spite of the plain fabric configuration, the composites exhibit excellent mechanical properties up to 300°C. The composite cured at 360°C has the most excellent mechanical properties. The composite cured at 360°C exhibits the least crosslink density, and the most flexible crosslink structure among the matrix. It is supposed that the flexible crosslink structure contributes to good mechanical properties, such as toughness and elongation, resulting in better compressive and tensile strengths.

Table 5.
Mechanical properties of plain fabric composite

Mechanical properties	Temp. (°C)	T800H/Tri-A PI ($M_w \sim 2500$)	T800H/Tri-A PI ($M_w \sim 2500$)	T800H/Tri-A PI ($M_w \sim 2500$)
Cure temperature (°C)		360	370	380
Composite fiber fraction (vol%)		66.7	68.7	65.2
Composite porosity (vol%)		1.7	3.3	1.7
NHT strength (MPa)	25	939	838	866
	177	988	843	849
	250	838	846	803
	300	784	788	771
Young's modulus (GPa)	25	80	81	79
(Tensile test)	177	80	81	79
	250	74	79	75
NHC strength (MPa)	25	545*	465	412
	177	435*	386	395
	250	386*	308	325
	300	301*	233	253
OHC strength (MPa)	25	289	287	288

* Brooming fracture at the loading edge of the specimen.

4. CONCLUSIONS

Preliminary studies for processing and mechanical properties of carbon fiber reinforced composites with the 1600 and 2500 g/mol version imide oligomers were conducted. The following conclusions were reached:

(1) Processing of the composites by routing prepreg consolidation was almost established.

(2) The onset temperature of melting (apparent melting point) of Tri-A PI (M_w 5250 g/mol) is much lower than that of PETI-5 (M_w5000 g/mol). This is due to difference in imide oligomer crystallinity.

(3) In spite of higher crosslink density due to lower molecular weight (<2500 g/mol), the T800/Tri-A PI composites exhibit excellent mechanical properties at elevated temperature with high glass transition temperature (>320°C).

(4) It is supposed that the flexible imide structure (irregular and asymmetric) derived from a-BPDA, and the chain extension derived the phenylethynyl group reaction contribute to the excellent mechanical properties.

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