

# **POLYIMIDES BASED ON ASYMMETRIC DIANHYDRIDES (II) (a-BPDA VS a-BTDA) FOR RESIN TRANSFER MOLDING (RTM)**

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## **ABSTRACT**

A new series of low-melt viscosity imide resins (10-20 poise at 280°C) were formulated from asymmetric 2,3,3',4'-benzophenone dianhydride (a-BTDA) and 4-phenylethynylphthalic endcaps, along with 3,4'-oxydianiline, 3,3'-methylenedianiline and 3,3'-diaminobenzophenone, using a solvent-free melt process. a-BTDA RTM resins exhibited higher glass transition temperatures ( $T_g$ 's = 330-400°C) compared to those prepared by asymmetric 2,3,3',4'-biphenyl dianhydride, (a-BPDA,  $T_g$ 's = 320-370°C). These low-melt viscosity imide resins were fabricated into polyimide/T650-35 carbon fiber composites by a RTM process. Composites properties of a-BTDA resins, such as open-hole compression and short-beam shear strength, are compared to those of composites made from a-BPDA based resin at room temperature, 288°C and 315°C. These novel, high temperature RTM imide resins exhibit outstanding properties beyond the performance of conventional RTM resins, such as epoxy and BMI resins which have use-temperatures around 177°C and 232°C for aerospace applications.

KEY WORDS: Polyimides, Resin Transfer Molding (RTM), Advanced Composites

## **1. INTRODUCTION**

Polyimides have been used as matrix resins in lightweight polymer matrix composites for high temperature applications that exceed the capability of epoxies (177 °C) and bismaleimides, BMI, (232 °C) for decades [1]. Most notably, PMR-15 [2] polyimide was successfully fabricated into a composite outer bypass duct for the F-404 engine as a replacement for the titanium duct, leading to a 30% cost savings and 12% weight savings. Other PMR-type polyimides, prepared from diester diacid derivatives of dianhydrides, diamines and terminated with reactive endcaps, such as AFR-PE-4 [3-4], all require the use of an alcohol solvent for processing. On the other hand, Avimid N<sup>®</sup> [5] and PETI-5 [6] resins are prepared in high boiling N-methyl-2-pyrrolidinone (NMP), resulting in solvent residuals that can cause difficulties during composite fabrication. All these polyimide composites rely on the use of prepregs, either by labor intensive hand lay-up or by automated tow placement equipments, for fabrication of large and/or more complicated geometries and structures. In recent years, significant efforts have been devoted to the development of solvent-free, low-melt viscosity (10-30 poise) imide resins that are amenable to resin transfer molding (RTM) to enable an estimated 30% reduction in manufacturing cost.

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Several approaches have been used with the goal of developing RTM processable imide resins that exceed the 232°C (450°F) performance capability of the state-of-the-art bismaleimides; for example, Cytec's 5270-1 BMI resin. Maverick Corporation has developed low-melt viscosity resins by using the diester diacid of benzophenonetetracarboxylic dianhydride (BTDE) along with the nadic ester endcap, but substituting 4,4'-methylenedianiline (MDA) in PMR-15 with a combination of a flexible 4,4'-[1,3-phenylene-bis(1-methylethylidene)] (i.e. Bisaniiline M) and rigid *m*-phenylenediamine (*m*-PDA), using a lower molecular weight formulation [7]. These RTM processable PMR-type polyimides exhibited low-melt viscosities (3-10 poise) as recorded by a Brookfield viscometer at 260°C. They also displayed glass transition temperatures ( $T_g$ 's) in the range of 260-300°C, making them suitable for 260°C (500°F) applications.

Researchers at NASA Langley have developed a low-melt viscosity PETI-298 ( $T_g = 298^\circ\text{C}$ ) imide resin [8], based on symmetrical 3,3',4,4'-biphenyl dianhydride (s-BPDA) and 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB), 3,4'-oxydianiline (3,4'-ODA) and terminated with 4-phenylethynylphthalic anhydride (PEPA). PETI-298 displayed a wider processing window, similar to other polyimides terminated with PEPA endcaps, which also imparted better thermal oxidative stability than the same materials prepared with the nadic endcap [9]. To raise the use temperature while maintaining low-melt viscosity, PETI-330 ( $T_g = 330^\circ\text{C}$ ) was formulated using asymmetrical 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), PEPA endcap and a mixture of 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) and *m*-phenylenediamine (*m*-PDA) [10]. PETI-330 (based on a-BPDA) displayed better property retention at 288°C than PETI-298 (derived from s-BPDA), due to its higher  $T_g$  and corresponding softening temperature [11-12]. To further enhance the high temperature capability, PETI-375 [13] was developed using the same monomers as PETI-330 except that 2,2'-bis(trifluoromethyl)benzidine (BTBZ) was used in place of *m*-phenylenediamine. The use of BTBZ raised the resin  $T_g$  to 375°C, but also significantly increased resin cost, due to the high cost of BTBZ. PETI-298, PETI-330 and PETI-375 have all been processed by resin transfer molding (RTM) to yield composites with excellent mechanical properties and low void content suitable for aerospace applications between 260-315°C. However, these imidized oligomers were made in NMP, and after the oligomers were precipitated out of water, they still required drying in a forced air oven at 135°C for 24 h in order to remove residual NMP. Such multi-step processes to produce imidized powder are time consuming and costly.

We have previously reported a simpler and more cost effective approach to prepare low-melt viscosity imide resins ( $\eta^* = 10\text{-}30$  poise at 280°C for 1 h) by a solvent free, melt imidization process (Fig. 1), using either asymmetric 2,3,3',4'-biphenyl dianhydride (a-BPDA) [14] or asymmetric 2,3,3',4'-oxydiphthalic anhydride (a-ODPA) [15], kinked aromatic diamines and 4-phenylethynylphthalic anhydride (PEPA) as the endcap. In this paper, we extend the same melt processing approach to formulate new resins from asymmetric 2,3,3',4'-benzophenone

dianhydride (a-BTDA) and either 3,4'-oxydianiline (3,4'-ODA) or 3,3'-methylenedianiline (3,3'-MDA), or 3,3'-diaminobenzophenone (3,3'-DABP), along with the PEPA endcap. The mechanical properties of composites fabricated by RTM from these a-BTDA based resins are compared to those fabricated from a-BPDA based resins and commercial BMI-5270-1.

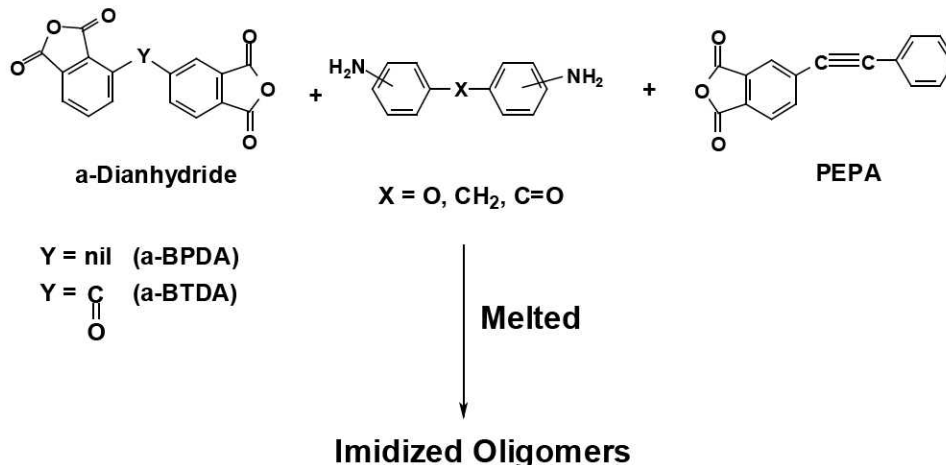


Figure 1. Synthesis of imide resins based on asymmetric dianhydrides

## 2. EXPERIMENTAL

### 2.1 Resin Preparation and Characterization

The a-BTDA used in this study was prepared by Suzuki coupling according to the method described in US patent No. 7,381,849 [16]. A specific asymmetrical dianhydride (either a-BTDA or a-BPDA), 4-phenylethynylphthalic anhydride (PEPA) and the respective diamine were melted above 200°C for 1 h to form the corresponding phenylethynyl terminated imide oligomers. The resulting solids were then ground into powders. The absolute viscosities of these imide oligomers were measured using a digital Brookfield viscometer. The rheology was measured by a Ares Rheometer manufactured by TA Instruments, using the parallel plate geometry with 1 g of imidized powder at a ramp rate of 4°C/min and frequency at 10 rad/sec.

### 2.2 Composite Fabrication

Composite panels were fabricated using a high temperature RTM process [17]. The panels were fabricated from T650-35, 8 harness satin weave (8HS) carbon fabrics with a polyimide high temperature size (HTS), using an 8-ply quasi-isotropic lay-up [+45/0/90/-45]<sub>s</sub>. After the tool and the injector were preheated to approximately 288°C for 1 hr, 600 g of resin was injected into the preforms and held under 1.38 MPa of hydrostatic pressure, using a low-cost high temperature injector developed by M&P Technologies. The composites were cured at 371°C (700°F) for 2 h

and then further post-cured in an oven at 343°C (650°F) for 8 h to enhance the mechanical properties at elevated temperatures.

### 3. RESULTS AND DISCUSSION

#### 3.1 Physical properties and viscosity profiles of neat resins

The imide resins formulated with a-BPDA, 4-phenylethynylphthalic anhydride and either 3,4'-oxydianiline (3,4'-ODA), 3,3'-methylenedianiline (3,3'-MDA) or 3,3'-diaminobenzophenone (3,3'-DABP) exhibited  $T_g$ 's of 370°C, 330°C and 320°C, respectively, after post-cure at 370°C (700°F) for 16 h (Table 1). Therefore, they are designated as RTM370, RTM330 and RTM320 in reference to their  $T_g$ 's

Table 1. Physical Properties of Imide Resins Based on a-BPDA and PEPA

Resin	Dianhydride	Diamine	Oligomer Min. $\eta$ @280 °C by Brookfield <sup>1</sup> (Poise)	Cured Resin $T_g$ /NPC <sup>2</sup> byTMA <sup>4</sup>	Cured Resin $T_g$ /PC <sup>3</sup> @ 371°C by TMA <sup>4</sup>
RTM370	a-BPDA	3,4'-ODA	11	342°C	370°C
RTM330	a-BPDA	3,3'-MDA	6.0	288°C	330°C
RTM320	a-BPDA	3,3'-DABP	7.0	319°C	320°C

<sup>1</sup> Absolute viscosity measured by Brookfield Viscometer at 280°C.

<sup>2</sup> NPC = No Post-cure

<sup>3</sup> PC = Post-cured at 371°C (700°F) for 16 h.

<sup>4</sup> TMA =Thermal mechanical analysis heated at 10°C/min, using expansion mode.

On the other hand, the corresponding resin formulation based on a-BTDA displayed  $T_g$ 's in the range of 330-400°C after post-cure at 343°C (650°F) for 16 h (Table 2). A lower post-cure temperature of 343 °C was chosen to prevent occasional softening of the resin surface at 371°C. Surprisingly, the formulation based on a-BTDA/3,3'-DABP/PEPA exhibited exceedingly high  $T_g$  of 400°C, even though its corresponding a-BPDA/3,3'-DABP/PEPA resin only displayed a  $T_g$  of 320°C. There is no obvious explanation for this other than the possibility that carbonyl group in a-BTDA imparts rigidity to the polymer backbone, thus increasing the rotational energy barrier during the glass transition phase.

Table 2. Physical Properties of a-BTDA/PEPA Resins/Composites

Dianhydride	Diamine	Cured Resin $T_g$ /PC <sup>1</sup> @ 650°F By TMA <sup>2</sup>	Composites $T_g$ /PC <sup>1</sup> @ 343°F By DMA <sup>3</sup>
a-BTDA	3,4'-ODA	330 °C	---
a-BTDA	3,3'-MDA	335 °C	---
a-BTDA	3,3'-DABP	400 °C	405°C (380°C) <sup>3</sup>

<sup>1</sup> PC = Post-cured at 650°C (343 °F) for 16 h.

<sup>2</sup> TMA = Thermal mechanical analysis heated at 10°C/min, using expansion mode.

<sup>3</sup>  $T_g$  = 405°C based on  $\tan \delta$  by Dynamic mechanical analysis (DMA).

$T_g = 380^\circ\text{C}$  based on the onset decline of storage modulus  $G'$ .

### 3.2 Melt-viscosity profile of a-BPDA and a-BTDA imide oligomers

Based on a previous study, it is known that imide oligomers containing methylenedianiline usually exhibit a very short pot-life [18]. This is due to the presence of methylene ( $-\text{CH}_2-$ ) unit, which is believed to produce a benzylic free radical that can promote further crosslinking at elevated temperature [19], and give rise to the increase in melt viscosity. Therefore, in this continued study, composite fabrications were confined to the imide resins derived from two asymmetric dianhydrides (a-BPDA and a-BTDA) with 3,3'-diaminobenzophenone (3,3'-DABP), and the resulting mechanical properties will be compared to that of RTM370 resin formulated from a-BPDA/3,4'-ODA/PEPA. The melt viscosities of a-BPDA/3,3'-DABP/PEPA (Fig. 2) and a-BTDA/3,3'-DABP/PEPA resins prepared in small batches (10g) (Fig. 3), range from 10-20 poise which are clearly amenable to resin transfer molding (RTM).

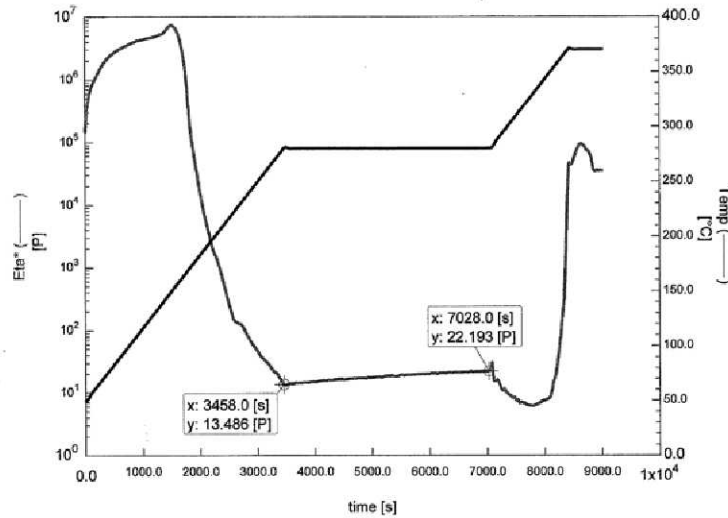


Figure 2. Rheology of a-BPDA/3,3'-DABP/PEPA resin

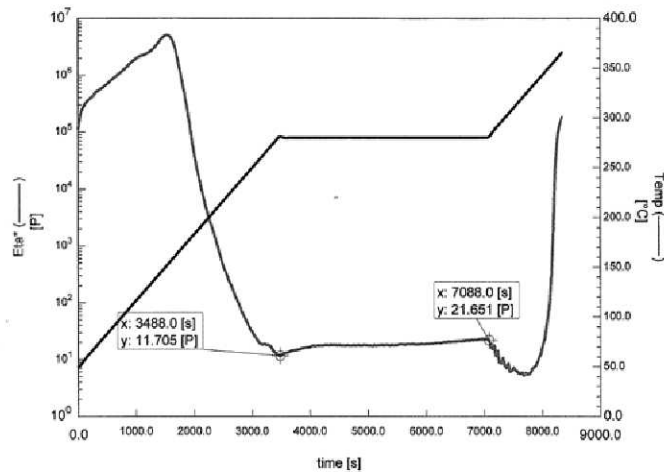


Figure 3. Rheology of a-BTDA/3,3'-DABP/PEPA resin (small batch)

However, there are discrepancies on the viscosity and especially on the pot-life between large and small batches of a-BTDA resins. During the preparation of a large batch of a-BTDA/3,4'-ODA/PEPA (600g), the resin flowed over the top of the container, due to a tremendous exothermic reaction, and the resulting resin displayed a much higher viscosity and shorter pot-life than the corresponding small 10g batch (Fig. 4). The rapid exotherm might have over-heated the reactive PEPA endcap and induced some initial crosslinking. Also, the a-BTDA used in the large batches contained < 0.5% of unknown impurity, which might contribute to the shorter pot-life.

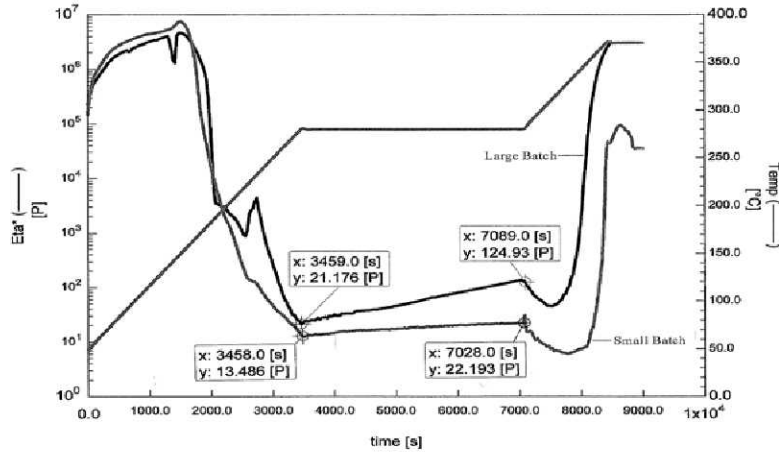


Figure 4. Rheology of a-BTDA/3,4'-ODA/PEPA (large batch vs small batch)

### 3.3 Thermo-oxidative stability of a-BTDA based RTM imide resins

The a-BTDA resins formulated with 3,3'-diaminobenzophenone (3,3'-DABP), 3,4'-oxydianiline (3,4'-ODA) 3,3'-methylenedianiline (3,3'-MDA) and the PEPA endcap were subjected to isothermal aging at 288°C (550°F) for 1000 h. Surprisingly, these a-BTDA based imide resins showed lower weight loss than PMR-15 (Fig. 5), probably due to the presence of the more stable phenylethynyl endcap as compared to the aliphatic nadic endcap in PMR-15.

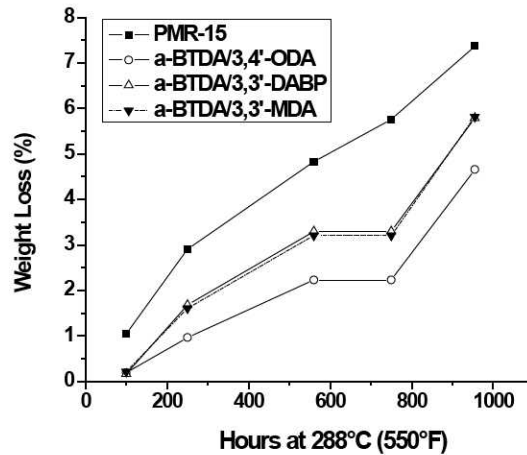




Figure 5. Isothermal aging of a-BTDA based RTM imide resins

**3.4 Durability of RTM370 (a-BPDA/3,4'-ODA/PEPA) composites.**

As reported previously, RTM370 displayed high  $T_g$  and excellent mechanical properties when manufactured by RTM, using T650-35 fabrics with UC309 epoxy sizing [14]. For this study to evaluate the durability RTM370, composites were fabricated with T650-35 fabrics with high temperature polyimide sizing to improve interfacial bonding between matrix and fiber, and thereby, enhance high temperature performance. The RTM370 resin flow was very good, and the injection was completed in 30 min. The void content of the RTM370/T650-35 composite was 1.1%, and the fiber volume was 56%. As shown in Table 3, after 1000 h of isothermal aging at 288°C (550°F), RTM370 composites retained 85% and 76% of their initial open-hole compression strength at room temperature and 288°C, respectively. Furthermore, these composites also maintained 71% of their original short-beam shear strength after thermal aging.

Table 3. Durability of RTM370 (a-BPDA/3,4'-ODA/PEPA)/T650-35/8HS/HT Sizing)

Property	Initial Properties $T_g = 370^\circ\text{C}^1$		Aging 500 hrs @288°C		Aging 1000 hrs @288°C	
	RT	288°C	RT	288°C	RT	288°C
OHC <sup>2</sup> Strength (MPa)	269	241	287	244	230	184
OHC <sup>2</sup> Modulus (GPa)	44	48	47	44	46	45
SBS <sup>3</sup> Strength (MPa)	60	29	54	41	43	41

<sup>1</sup>  $T_g = 370^\circ\text{C}$  based on  $\tan \delta$  by Dynamic Mechanical Analysis (DMA).

$T_g = 350^\circ\text{C}$  based on the onset decline of storage modulus  $G'$ .

<sup>2</sup> OHC = open-hole compression strength.

<sup>3</sup> SBS = short-beam shear strength

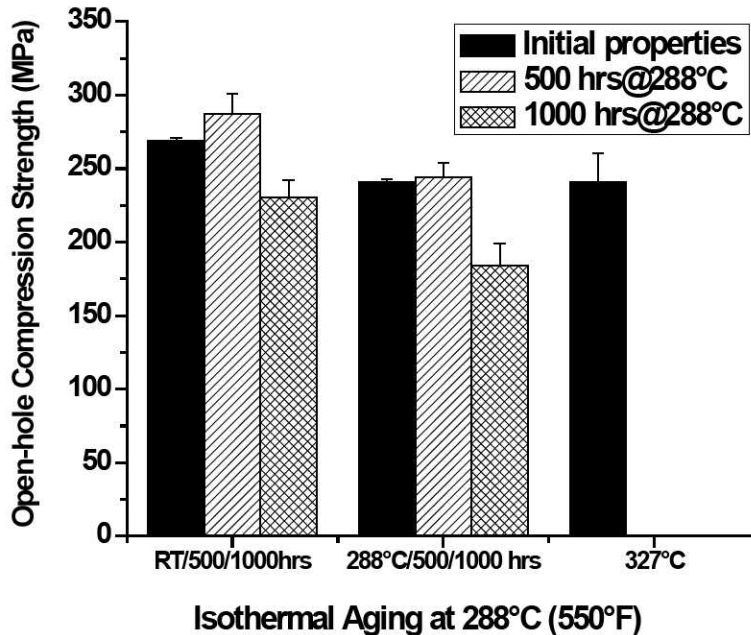


Figure 6. Open-hole compression strength of RTM370 composites

aged at 288°C (500°F) for 1000 h

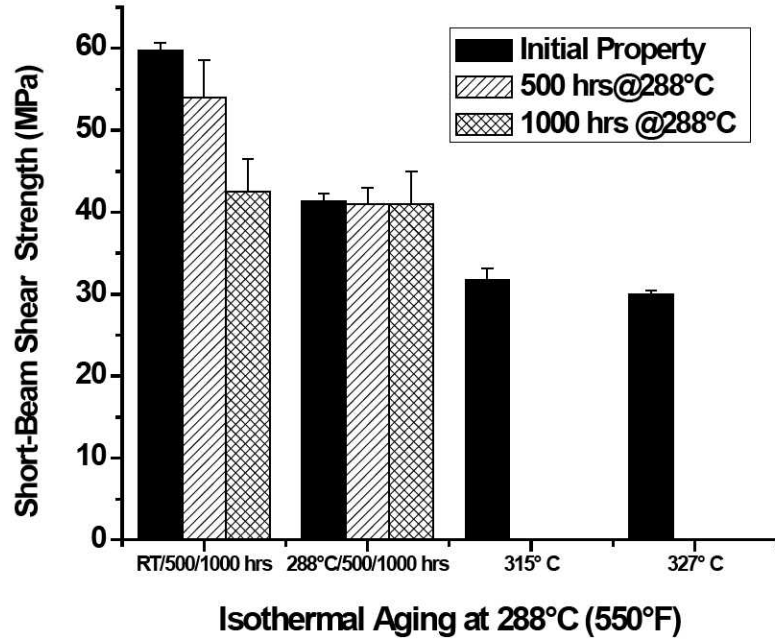


Figure 7. Short-beam shear strength of RTM370 composites aged at 288°C (500°F) for 1000 h

### 3.5 Characterization and mechanical properties of a-BPDA and a-BTDA composites

Another two sets of polyimide composites were fabricated by the RTM from imide resins derived from 3,3'-diaminobenzophenone (3,3'-DABP) with either a-BPDA or a-BTDA, using the PEPA endcap. The a-BPDA/3,3'-DABP/PEPA composite ( $T_g = 330^\circ\text{C}$ ) had a void content of 1.2% and fiber volume of 53%; however, it delaminated when subjected to post-cure at  $343^\circ\text{C}$  ( $650^\circ\text{F}$ ). The cause of the delamination is still under investigation. Furthermore, due to the presence of 0.5% of an unknown impurity in the a-BTDA and the exotherm during resin preparation, the large batch of a-BTDA/3,3'-DABP/PEPA resin exhibited a short pot-life. The high viscosity and the short pot-life resulted in the fabrication of a non-uniform composite panel, which only yielded enough high quality composite to machine short-beam shear (SBS) test specimens, instead of larger open-hole compression samples. Therefore, only SBS data for these two composites are presented in Table 4 in comparison to RTM370 and BMI-5270-1. While the initial SBS for a-BTDA/3,3'-DABP/PEPA is not as high as that of RTM370, the composite retained very good properties at elevated temperature due to its high  $T_g$  of  $400^\circ\text{C}$ .



Table 4 Composite Properties<sup>1</sup> of Polyimide Resins Based a-Dianhydrides

Dianhydride	Daimine	Test Temp.	SBS <sup>2</sup> Strength (MPa)	OHC <sup>3</sup> Strength (MPa)	OHC Modulus (GPa)
<b>a-BPDA (RTM370)</b>	<b>3,4' -ODA (T<sub>g</sub>=370°C)</b>	<i>RT</i>	60	269	44
		288°C	41	241	48
		315°C	32	231	46
		327°C	30	241	48
<b>a-BPDA</b>	<b>3,3' -DABP (T<sub>g</sub> = 330°C)</b>	<i>RT</i>	35	---	---
		288°C	29	---	---
		315°C	23	---	---
		327°C	22	---	---
<b>a-BTDA</b>	<b>3,3' -DABP (T<sub>g</sub> = 405°C)</b>	<i>RT</i>	36	---	---
		288°C	34	---	---
		315°C	29	---	---
		327°C	30	---	---
<b>BMI-5270-1</b>	<b>BMI-5270-1 (T<sub>g</sub> =300°C)</b>	<i>RT</i>	37	245	51
		288°C	14	148	38
		315°C	---	---	---
		327°C	---	---	---

<sup>1</sup> Composite made from T650-35/8HS/HT polyimide sizing

<sup>2</sup> SBS = Short-Beam Shear Strength

<sup>3</sup> OHC = Open-hole compression

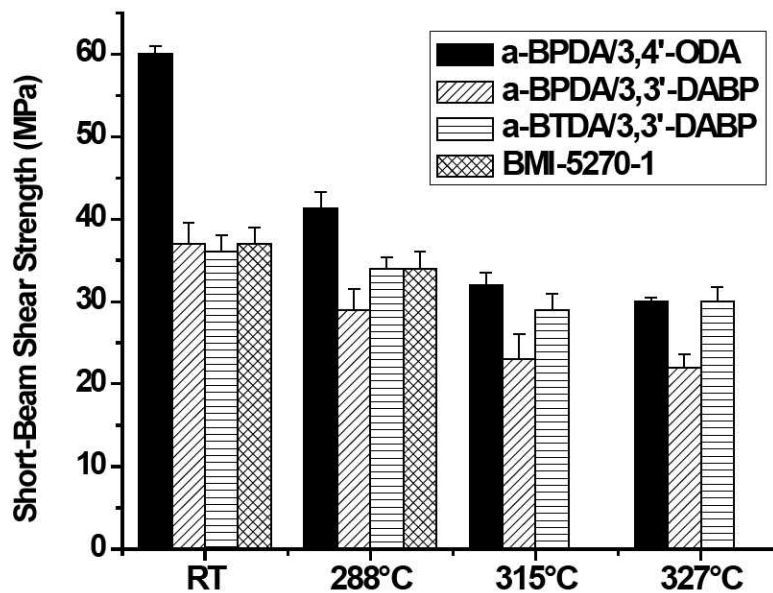


Figure 7. Comparison of short-beam shear strength of RTM imide resins based on a-BPDA and a-BTDA vs BMI-5270-1

## 4. CONCLUSION

A new series of imide resins (10-20 poise) were developed based on a-BTDA and formulated with 3,3'-diaminobenzophenone, 3,3'-methylenedianiline (3,3'-MDA) and 3,4'-oxydianiline (3,4'-ODA), using the 4-phenylethynyl endcap (PEPA). These resins displayed low-melt viscosities (10-20 poise) that are amenable to fabrication by low-cost resin transfer molding (RTM). These a-BTDA imide resins displayed better thermo-oxidative stability than PMR-15 after isothermal aging at 288°C (550°F) for 1000 h. However, a-BTDA/3,3'-DABP/PEPA resin produced on large scale batch (600g) has a shorter pot-life than those made in a small batch (10g), probably due to an impurity or partial curing of PEPA during an exotherm that occurred in the melt formulation of a-BTDA resin. Although the initial short-beam shear (SBS) strength of a-BTDA/3,3'-DABP/PEPA composites are not as high as that of a-BPDA/3,4'-ODA/PEPA (RTM370) composites, it maintains good short-beam shear property at 288°C, due to its high  $T_g$  of 405°C. In comparison of RTM imide resins based on asymmetric dianhydrides studies so far, RTM370 composites based on BPDA/3,4'-ODA/PEPA showed the best overall mechanical performance. In essence, RTM370 composites exhibited excellent mechanical properties, especially toughness, up to 327°C (620°F). Additionally, isothermal aging of RTM370 composites at 288°C (550°F) for 1000 h also confirmed their outstanding property retention, i.e. RTM370 maintained 85% and 76% of its initial open-hole compression strength at room temperature and 288°C, respectively. Its short-beam shear strength also showed 71% property retention.

This work demonstrates an efficient new method for producing high  $T_g$ , low-melt viscosity imide resins without the use of solvents. Most of these high-flow imide resins based on asymmetric dianhydrides (a-BPDA, a-BTDA and a-ODPA) were successfully processed into high quality composites with outstanding high temperature performance and property retention at 288-327°C (550-620°F). This work also represents a major break through in high temperature RTM resins as compared to conventional epoxy and bismaleimide resins currently used in aerospace industries.

## 5. ACKNOWLEDGEMENTS

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