

Polyimide Composites Based on Asymmetric Dianhydrides (a-ODPA vs a-BPDA)

Kathy C. Chuang NASA Glenn Research Center, Cleveland, OH 44135
Jim M. Criss M&P Technologies, Inc. Marietta, GA 30068
Eric A. Mintz Clark Atlanta University, Atlanta, GA 30314

ABSTRACT

Two series of low-melt viscosity imide resins (2-15 poise at 260-280°C) were formulated from either asymmetric oxydiphthalic anhydride (a-ODPA) or asymmetric biphenyl dianhydride (a-BPDA) with 4-phenylethynyl endcap (PEPA), along with 3,4'-oxydianiline, 3,4'-methylenedianiline, 3,3'-methylenedianiline or 3,3'-diaminobenzophenone, using a solvent-free melt process. These low-melt viscosity imide resins were fabricated into polyimide/T650-35 carbon fabric composites by resin transfer molding (RTM). Composites from a-ODPA based resins display better open-hole compression strength and short beam shear strength from room temperature to 288 °C than that of the corresponding a-BPDA based resins. However, due to the lower T_g 's of a-ODPA based resins (265-330°C), their corresponding composites do not possess 315 °C use capability while the a-BPDA based composites do. In essence, RTM 370 ($T_g = 370$ °C), derived from a-BPDA and 3,4'-ODA and PEPA, exhibits the best overall property performance at 315 °C (600 °F).

1. INTRODUCTION

Polyimide resins have been used as matrices in lightweight carbon fiber reinforced composites for use as replacements for metallic components in the aerospace propulsion and airframe components, due to their outstanding heat resistance and high strength to weight ratio. The development of polyimide composites started with thermoplastic polyimides, such as Avimid N[®] [1] in N-methyl-2-pyrrolidinone (NMP), which is very stable, but difficult to process. Later PMR-15 [2] and PMR-II-50 [3] were developed to improve processability, using an alcohol solution of monomer reactants of dianhydride ester acid and diamines along with the nadic endcap, in order to control the molecular weight of the polyimides and, ultimately, increase the use temperature to 288-315°C (550-600°F) for aircraft engine applications.

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During 1980's, NASA Langley introduced PETI-5 [4], an imide oligomer terminated with 4-phenylethynyl anhydride (PEPA), developed under High Speed Civil Transport (HSCT) Program for long-term 177 °C airframe application. The PEPA endcap provided a wider processing window than the nadic endcap. The recently developed HFPE [5,6] or AFR-PE-4 [7,8] resins are variations of PMR-II-50 based on 6F-dianhydride, with the nadic endcap being replaced with the phenylethynyl group to improve processability and high temperature stability. All of these polyimide resins have been incorporated into carbon fiber prepregs for composite processing which requires hand lay-up or tow-preg placement for complex structure fabrication. In addition, the NMP or alcohol contained in the prepregs must be removed during processing. Therefore, it would produce significant cost savings (~30%), if the polyimide could be adapted to low-cost manufacturing process, such as resin transfer molding (RTM), similar to what is used for epoxy and bismaleimide (BMI) composite fabrication in the aerospace industry.

Along these lines, PETI imide research efforts in the 1990's were focused on imide oligomers with lower molecular weights than PETI-5 (~5000 g/mol) to reduced resin's melt viscosity to enable processing by RTM. This led to the development of PETI-298 ($T_g = 298$ °C) derived from 3,3',4,4'-biphenyl dianhydride (s-BPDA), a mixture of 3,4'-oxydianiline (3,4'-ODA) and 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) along with the PEPA endcap. PETI-298 displayed a low melt viscosity (complex viscosity, $\eta^* = 6-10$ poise at 280 °C) adaptable to RTM processing [9]. Recent work has shown that when 2,3,3',4'-biphenyl dianhydride (a-BPDA) was used in place of the commercially available 3,3',4,4'-biphenyl dianhydride (s-BPDA), the resulting polyimides exhibited increased solubility, reduced viscosity and higher glass transition temperatures than the s-BPDA based polyimides [10-12]. NASA Langley developed PETI-330 ($T_g = 330$ °C) [13] formulated from a-BPDA (0.53 mole), PEPA (0.94 mole), 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB, 0.5 mole) and 1,3-phenylenediamine (0.5 mole) to raise the use temperature above 300 °C. PETI-330 exhibited a low complex melt viscosity (η^*) of 1.8-3.0 Pa.s (18-30 poise) at 280 °C, which is amenable to low-cost resin transfer molding (RTM), and, once cured, retained better mechanical properties at 288 °C (550 °F) [14] than the corresponding PETI-298. To further enhance the high temperature capability, PETI-375 [15] 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 it also increased resin cost substantially, because of 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 hours in order to remove residual NMP.

We have previously reported a simpler and more cost effective approach to prepare low-melt viscosity imide resins ($\eta = 10-30$ poise at 280 °C for 1 hr) by a solvent free, melt process (Fig. 1), using asymmetric biphenyl dianhydride (a-BPDA) with kinked aromatic diamines and end capped with 4-phenylethynylphthalic anhydride (PEPA) [16]. RTM370, based on a-BPDA/3,4'-ODA/PEPA, exhibits a steady complex viscosity (η^*) of 6.4-17 poise when held at 280 °C for 1 h. (Fig. 2), which is very amenable to RTM. The glass transition temperatures (T_g) of a-BPDA based RTM resins, after post cure at 343 °C for 16 hrs, ranged from 330-350 °C as determined by thermal mechanical analysis (TMA) (Table 1). The corresponding composites

displayed T_g 's between 337-360 °C as measured by dynamic mechanical analysis (DMA) (Table 2). In this paper, we extend the melt processing approach to formulate new resins from asymmetric 3,4' -oxydiphthalic anhydride (a-ODPA) with either 3,4' -oxydianiline (3,4' -ODA), 3,4' -methylenedianiline (3,4' -MDA), 3,3' -methylenedianiline (3,3' -MDA) or 3,3' -diaminobenzophenone (3,3' -DABP), along with the PEPA endcap to afford a new series of low-melt viscosity imide oligomers. The mechanical properties of composites fabricated by RTM from these a-ODPA based resins are compared to those made from the best performing a-BPDA based resin (RTM370) and commercial BMI-5270-1.

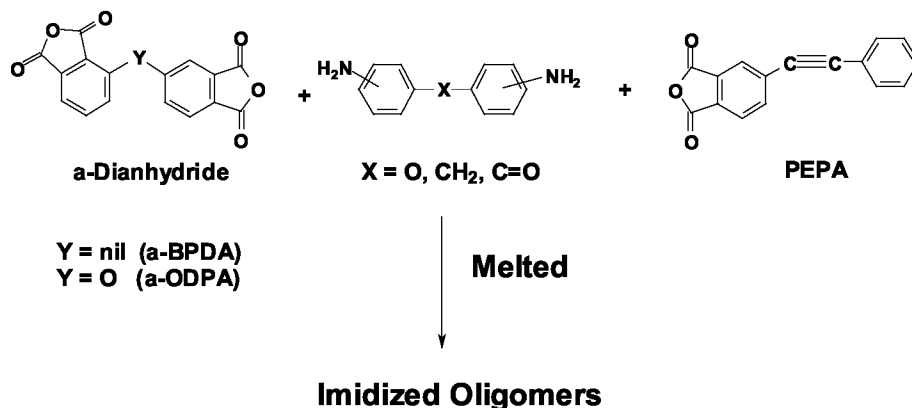


Figure 1 Synthesis of imide resins based on asymmetric dianhydrides

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

Resin	Dianhydride	Diamine	Oligomer Min. η @280 °C by Brookfield ¹ (Poise)	Cured Resin T_g (°C) NPC ² by TMA ⁴	Cured Resin T_g (°C) PC ³ @ 650°F By TMA ⁴
RTM370	a-BPDA	3,4' -ODA	6.5	342	370
RTM350	a-BPDA	3,4' -MDA	7.4	338	350
RTM330	a-BPDA	3,3' -MDA	1.5	288	330

¹ Absolute viscosity measured by Brookfield Viscometer at 280 °C.

² NPC = No Post cure

³ PC = Post cured at 343 °C (650 °F) for 16 hrs.

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

Table 2 T_g 's of Polyimide/T650-35 Composites based on a-BPDA and PEPA

Resin	Dianhydride	Diamine	T_g (°C) by DMA ¹ NPC ²	T_g (°C) by DMA PC ³ @ 343°C (650 °F)
RTM370	a-BPDA	3,4' -ODA	324	356
RTM350	a-BPDA	3,4' -MDA	314	337
RTM330	a-BPDA	3,3' -MDA	334	361

¹DMA= Dynamic Mechanical Analysis were performed at 5 °C/min heating rate, using single cantilever.

²NPC = No post cure. ³PC = Post cured at 343 °C (650 °F) for 8 hrs.

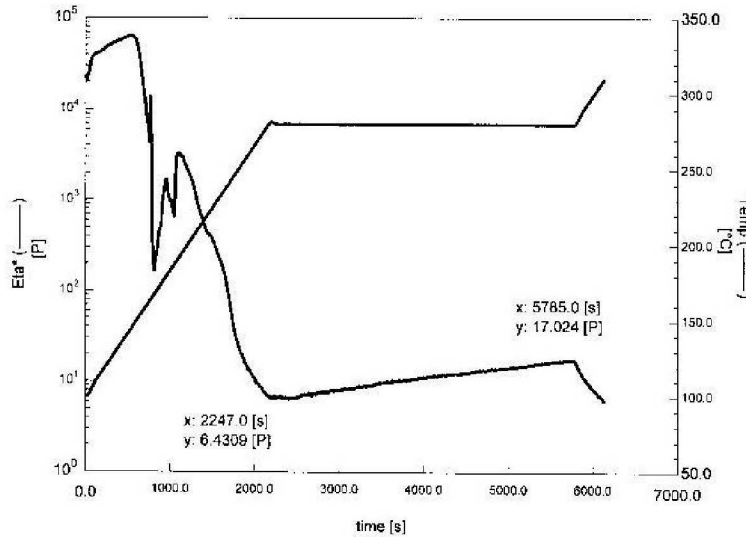


Figure 2 Rheology of α -BPDA/3,4'-ODA/PEPA imide oligomer

2. EXPERIMENTAL

2.1 Resin Preparation and Characterization

The α -ODPA used in this study was prepared according to the method of Li *et al.* [17]. A specific asymmetrical dianhydride (either α -ODPA or α -BPDA), 4-phenylethynylphthalic anhydride (PEPA) and the respective diamine were melted above 200 °C for 1 hour to form the corresponding phenylethynyl endcapped 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 performed in the parallel plate geometry with 1 g of imidized powder at a ramp rate of 4 °C/min and frequency at 10 rad/sec, using a TA Instruments Ares Rheometer.

2.2 Composite Fabrication

Composite panels were fabricated using a high temperature RTM process developed in our laboratories [18]. The panels were made from T650-35, 8 harness satin weave (8HS) carbon fabrics with an 8 ply quasi-isotropic lay-up [+45/0/90/-45]_s. After the tool and the injector were preheated to approximately 288 °C for 1 hr, 600 g of the resin was injected at 288 °C at a rate of 200 cc/min. into the performs at 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 hrs and then further post cured in an oven at 343 °C (650 °F) for 8 hrs in order to enhance the mechanical properties at elevated temperatures.

3. RESULTS AND DISCUSSION

3.1 Physical properties and viscosity profiles of neat resins

The a-ODPA imide oligomers display very low absolute viscosity ($\eta = 2.5\text{-}4.0$ poise) at $280\text{ }^{\circ}\text{C}$ as measured with a Brookfield viscometer (Table 3). The T_g of cured resin made from 3,4' - ODA is higher than that of the resin prepared from 3,4' -MDA, due to a higher rotational barrier in the crosslinked polymers caused by the larger bond angle angle (123 °) in the ether linkage (-O-) as compared to 110 ° in the methylene linkage (-CH₂-), as determined by the computer modeling [19]. The resin containing 3,3' -MDA has a lower T_g than the corresponding resin derived from 3,4' -MDA, because of the dual *m*-cattination instead of a combination of one *m*- and one *p*- linkages. Furthermore, the 3,3' -DABP based resin exhibits a higher T_g than the 3,3' -MDA based resin, because the planar sp² bonding in carbonyl group (C=O) is more rigid than the sp³ tetrahedral bonding of the methylene group in the diamine. The addition of an ether linkage (-O-) in a-ODPA apparently provides more flexibility in the polyimide backbone, and consequently the cured a-ODPA resins display lower T_g 's ($266\text{-}330\text{ }^{\circ}\text{C}$), relative to a-BPDA based resins ($T_g = 330\text{-}370\text{ }^{\circ}\text{C}$ (Table 1).

Table 3 Physical Properties of Imide Oligomers/Resins Based on a-ODPA and 4-PEPA

Dianhydride	Diamine	Oligomer Min. η @ $280\text{ }^{\circ}\text{C}$ by Brookfield ¹ (Poise)	Cured Resin T_g ($^{\circ}\text{C}$) NPC ³ By TMA	Cured Resin T_g ($^{\circ}\text{C}$) PC ⁴ @ 650°F By TMA ⁵
a-ODPA	3,4' -ODA	3.5	296	329
a-ODPA	3,4' -MDA	4.0	270	294
a-ODPA	3,3' -MDA	2.5	273	266
a-ODPA	3,3' -DABP	3.0	270	297

¹ Absolute viscosity measured by Brookfield Viscometer at $280\text{ }^{\circ}\text{C}$.

² Complex viscosity measured by Aries Rheometer, using parallel plates.

³ NPC = No Post cure

⁴ PC = Post cured at $343\text{ }^{\circ}\text{C}$ ($650\text{ }^{\circ}\text{F}$) for 16 hrs.

⁵ TMA =Thermal mechanical analysis heated at $10\text{ }^{\circ}\text{C}/\text{min}$, using expansion mode.

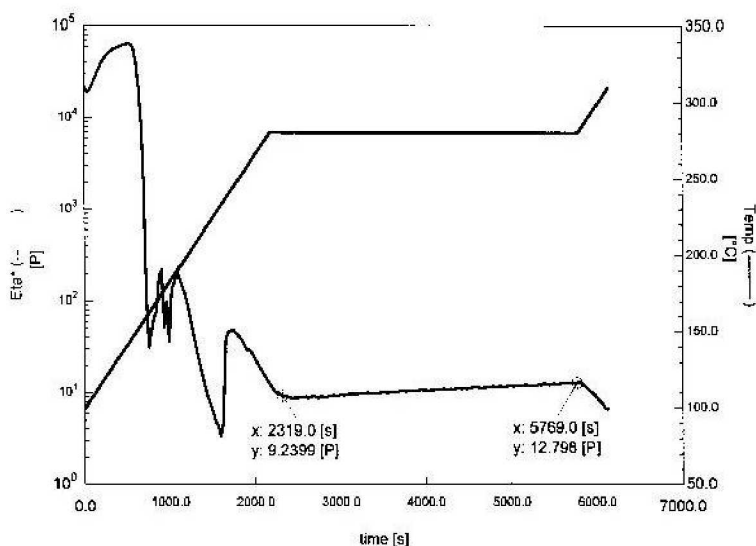


Figure 3 Rheology of a-ODPA/3,4' -ODA/PEPA imide oligomer

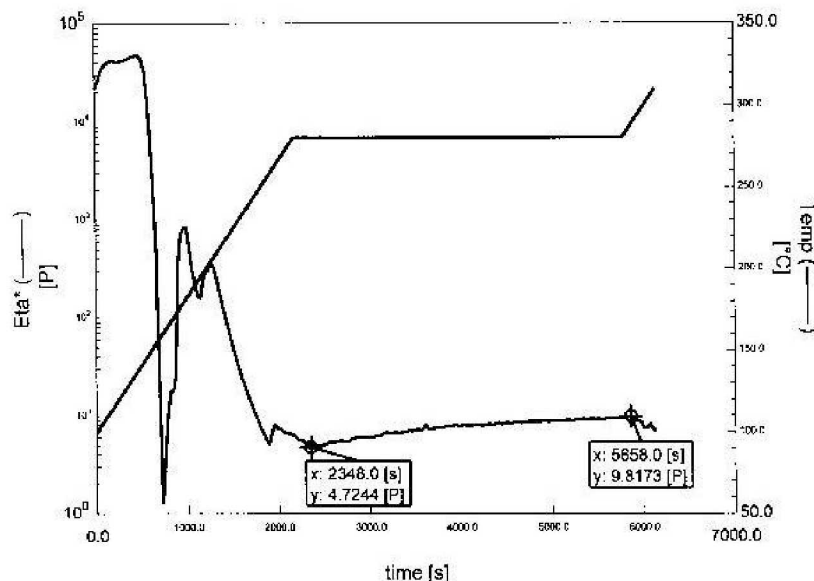


Figure 4 Rheology of a-ODPA/3,3' -DABP/PEPA imide oligomer

Previous rheological studies have shown that the pot-life of a-BPDA based resins containing 3,4' -MDA, and 3,3' -MDA are shorter than those of the corresponding resin derived from 3,4' -ODA, and resulted in poor composite quality [20]. Therefore, composites were fabricated for evaluation from resins formulated from a-ODPA, PEPA endcap and either 3,4' -ODA or 3,3' -DABP, which maintained a steady complex viscosities in the range of 5-15 poise when held at 280 °C for 1 hr. This low melt-viscosity profile is amenable for RTM processing (Fig. 3 and Fig. 4).

3.2 Characterization and mechanical properties of a-ODPA polyimide/T650-35 composites

T650-35 carbon fabric composites were fabricated by a high temperature RTM process from resins derived from a-ODPA, PEPA endcap and either 3,4' -ODA and 3,3' -DABP. The composite panels were then post cured at 343 °C (650 °F) for 8 hrs to improve high temperature mechanical properties and afforded T_g 's of 324 °C and 298 °C, respectively (Table 4).

Table 4 T_g 's of Polyimide/T650-35 Composites based on a-BPDA and PEPA

Dianhydride	Diamine	T_g (°C) by DMA PC ³ @ 343°C (650 °F)
a-ODPA	3,4' -ODA	324
a-ODPA	3,3' -DABP	298

¹DMA= Dynamic Mechanical Analysis were performed at 5 °C/min heating rate, using single cantilever

²NPC = No post cure.

³PC = Post cured at 343 °C (650 °F) for 8 hrs.

As listed in Table 5 and Table 6 for comparison, composites fabricated from the a-ODPA/3,4' - ODA/PEPA resin display better open-hole compression strength , both at room temperature and at 288 °C, than the a-BPDA/3,4' -ODA/PEPA resin. In general, a-ODPA based resins exhibit slightly better or comparable short beam shear strength than a-BPDA based resins up to 288 °C. The presence of the ether linkage(-O-) in a-ODPA seems to impart toughness to the composites. However, the composites containing flexible a-ODPA yield lower T_g's (298-329°C) and lower thermal oxidative stability than a-BPDA based composites (T_g = 330-370 °C), as evidence by the microvoids present in the photomicrograph of the a-ODPA/3,4' -ODA/PEPA composite (Fig. 5) after post cure at 343 °C (650 °F) for 8 hrs. As a result, the a-BPDA based composites exhibit outstanding mechanical properties at 315 °C (600°F) while a-ODPA based composites have already softened at temperatures above 288 °C, due to the limitation of their T_g's (Fig. 6, Fig. 7 and Fig. 8).

Table 5 Composite Properties of T650-35 carbon fabrics/a-ODPA Imide Resins

Property	Test Temp. (°C)	Diamine 3,4' -ODA T _g = 329 °C	Diamine 3,3' -DABP T _g = 298 °C	BMI-5270-1
OHC Strength, (MPa)	23	306	327	245
	232	---	---	---
	288	281	221	148
OHC Modulus, (GPa)	23	51	53	51
	232	---	---	---
	288	49	53	38
SBS Strength, (MPa)	23	70	58	37
	232	56	46	---
	288	33	36	14

OHC = Open-Hole Compression
SBS = Short Beam Shear Strength

**Table 6 Composite Properties of T650-35 carbon fabrics and Imide Resins
Based on a-BPDA/PEPA vs BMI-5270-1**

Property	Test Temp. (°C)	RTM370 3,4' -ODA	RTM350 3,4' -MDA	RTM330 3,3' -MDA	BMI-5270-1
OHC Strength (MPa)	23	306	285	252	245
	288	223	216	220	148
	315	166	199	185	---
OHC Modulus (GPa)	23	50	43	43	51
	288	47	44	45	38
	315	42	45	50	---
SBS Strength (MPa)	23	62	58	57	37
	288	43	32	38	14
	315	32	31	33	---

OHC = Open-Hole Compression
SBS = Short Beam Shear Strength



Figure 5 Photomicrographs of a-ODPA/3,4' -ODA/PEPA composites after post cured at 343 °C for 8 hrs

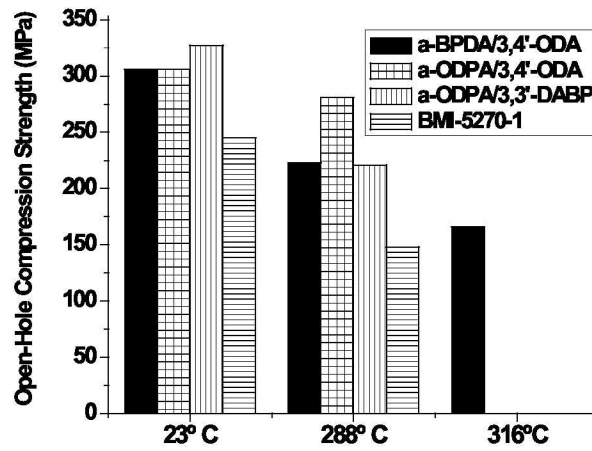


Figure 6 Open-hole compression strength of T650-35/a-ODPA based composites vs a-BPDA/3,4' -ODA/PEPA (RTM370) composite

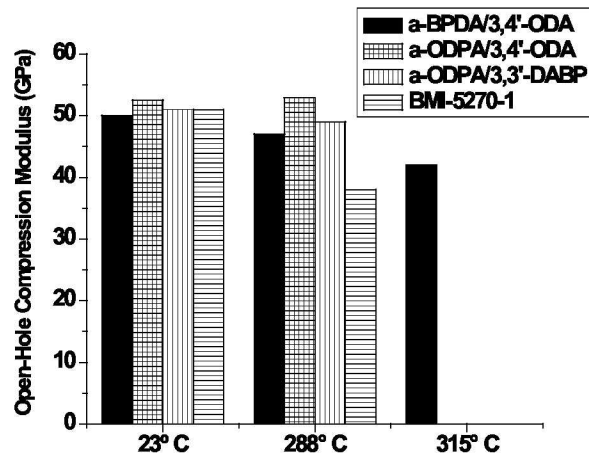


Figure 7 Open-hole compression modulus of T650-35/a-ODPA based composites vs a-BPDA/3,4' -ODA/PEPA (RTM370) composite

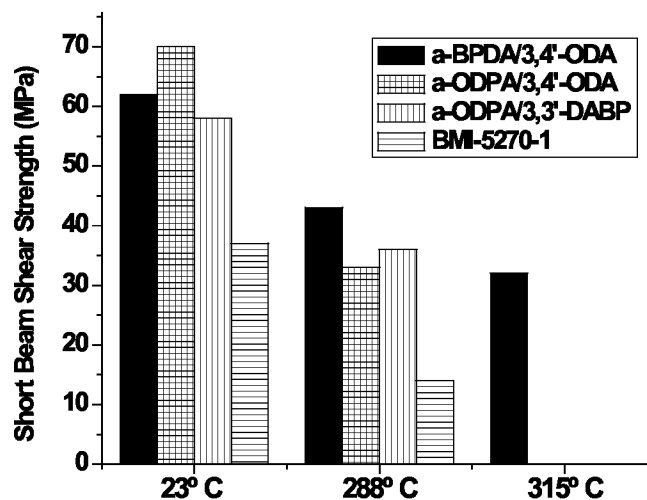


Figure 8 Short Beam Shear Strength of T650-35/a-ODPA based composites vs a-BPDA/3,4' -ODA/PEPA (RTM370) composite

4. CONCLUSION

A new series of imide resins having low-melt viscosity and high temperature capability were developed. High quality composites were successfully fabricated from these resins using a low-cost high temperature injector developed by M&P Technologies. The imide resins ($\eta < 5$ poise at 280 °C) were prepared from 2,3,3',4' -oxydiphthalic anhydride (a-ODPA) and 4-phenylethynylphthalic anhydride (PEPA) endcap along with either 3,4' -oxydianiline (3,4' -ODA), 3,4' -methylenedianiline, 3,3' -methylenedianiline or 3,3' -diaminobenzophenone (3,3' -DABP) in a melt, without the use of a solvent. Resins based on a-ODPA/3,4' -ODA/PEPA and a-ODPA/3,3' -DABP/PEPA were infused into T650-35 fabric performs to fabricate composite panels by resin transfer molding (RTM), with T_g 's of 324 °C and 298 °C, respectively. The composite fabricated from a-ODPA/3,4' -ODA/PEPA resin exhibited outstanding open-hole compression strength, exceeding a-BPDA/3,4' -ODA/PEPA resin, up to 288 °C (550 °F). However, the a-ODPA based composites tend to soften and lose their mechanical properties above 288 °C, due to their lower T_g 's as compared to RTM370 based on a-BPDA/3,4' -ODA/PEPA ($T_g = 370$ °C). The ether linkage in a-ODPA imparts flexibility and toughness to the polyimide composites, but it also lowers the T_g 's and thermo-oxidative stability of the corresponding imide resins. Overall a-BPDA/3,4' -ODA/PEPA imide resin exhibits low-melt viscosity and is amenable to low-cost RTM. RTM370 also demonstrates the best overall mechanical properties and high temperature property retention up to 315 °C (600 °F), exceeding the performance of conventional RTM resins, such as epoxy for 177 °C use and bismaleimide (BMI) for 232°C application in the aerospace industry. This work developed and demonstrated a new method for synthesizing imide resins using no solvents. The imide resins were successfully RTM processed into high quality composites with outstanding high temperature performance. It represents a major breakthrough in imide resin synthesis methodology.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- 1) H. H. Gibbs, *J. Appl. Polym. Sci.*, **35**: 297 (1979)
- 2) T. T. Serafini, P. Delvigs, and G. R. Lightsey, *J. Appl. Polym. Sci.*, **16(4)**, 905 (1972)
- 3) T. T. Serafini, R. D. Vannucci, and W. B. Alston, NASA TM X-71894 (1976)
- 4) P. M. Hergenrother, *SAMPE J.*, **36(1)**, 30 (2000)
- 5) K. C. Chuang, and J. E. Waters, *Soc. Adv. Mat. Pro. Eng. Ser.*, **40(1)**, 1113 (1995)
- 6) Kathy C. Chuang, Cheryl L. Bowman, Thomas K. Tsotsis, Cory P. Arendt, *High Perform. Polym.*, **15(4)**, 459 (2003)
- 7) B. P. Rice, *HITEMP Review 1997*, paper 8, NASA CP-10192 (1997)
- 8) F. E. Arnold, T. Gibson, B. Price, R. Trejo, A. Drain, A. Jacques, *High Temple Workshop XXVII*, Sedona, AZ, paper L (2007)
- 9) J. G. Smith, Jr., J. W. Connell, P. M. Hergenrother, R. Yokota, J. M. Criss, *Soc. Adv. Mat. Pro. Eng. Ser.*, **47(1)**, 316 (2002)
- 10) R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa, and R. Sato, *High Perform. Polym.*, **13**, 861 (2001)
- 11) M. Hasegawa, Z. Shi, R. Yokota, F. He, and H. Ozawa, *High Perform. Polym.*, **13**, 355 (2001)
- 12) P. M. Hergenrother, K.A. Waton, J. G. Smith, Jr., J.W. Connell, and R. Yokota, *Polymer*, **43**, 5077 (2002)
- 13) J. W. Connell, J. G. Smith Jr., P. M. Hergenrother, and J. M. Criss, *Soc. Adv. Mat. Pro. Eng. Ser.*, **48**, 1076 (2003)
- 14) J. W. Connell, J. G. Smith, Jr., J. M. Criss, *High Perform. Polym.*, **15**, 375 (2003)
- 15) J. W. Connell, J. G. Smith Jr., P. M. Hergenrother, J. M. Criss, *Proceeding of 49th Int'l Soc. Adv. Mat. Pro. Eng. Symp.* May 16-20, Long Beach, CA (2004), CD version
- 16) K. C. Chuang, J. M. Criss, Jr., E. A. Mintz, B. Shonkwiler, D. A. Scheiman, B.N. Nguyen, L. S. McCorkle, D. Hardy-Green, *Proceedings of 50th Int'l Soc. Adv. Mat. Pro. Eng. Symp.*, May 1-5, Long Beach, CA (2005), CD Version
- 17) Q. Li, X. Fang, Z. Wang, L. Gao, M. Ding, *J. Polymer Science, Part A: Polymer Chemistry*, **41**, 3249, (2003)
- 18) J. M. Criss, M.A. Meador, K.C. Chuang, J. W. Connell, J. G. Smith, Jr., P. M. Hergenrother, E. A. Mintz, *Soc. Adv. Mat. Pro. Eng. Ser.*, **48**, 1063 (2003)
- 19) J. W. Kang, K. Choi, W. H. Jo, S. L. Hsu, *Polymer*, **39(26)**, 7079 (1998)
- 20) K. C. Chuang, J. M. Criss, E. A. Mintz, D. A. Scheiman, B.N. Nguyen, L. S. McCorkle, *Proceedings of 51th Int'l Soc. Adv. Mat. Pro. Eng. Symp.*, June 3-7, Baltimore, MD (2007)