Chemistry and Properties of Phenylethynyl Containing Imides

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Introduction

In 1989, the United States National Aeronautics and Space Administration (NASA) and major US aerospace companies embarked upon a $1.6B program to develop the technology for a Mach 2.4 high speed civil transport. Many areas of technology had to be developed such as aerodynamics, propulsion, flight deck and structures and materials. The airframe structures and materials activity began in 1993 and consisted of 8 tasks, one of which was the Composites, Adhesives and Sealants Task. Adhesives, polymeric composites, fuel tank sealants and durable surface treatments for titanium alloys and composites represented enabling technology. Without any one of these, economically viable HSCTs could not be built.

This paper will deal with the development of adhesives and composite matrices for the HSCT. After screening virtually all available candidate resins as adhesives and composites, it became clear that existing materials could not meet the requirements of a Mach 2.4 HSCT. Some of the major requirements for the uncured materials included non-toxic, long shelflife, robust processability and material forms (e.g. unidirectional carbon fiber tape and supported adhesive tape) with good handleability. The cured material in the form of an adhesive or composite had to exhibit high mechanical properties from –54 to 177°C, durability for 60,000 hours at 177°C, environmental stability, solvent resistance under stress and acceptable cost of the final part. Little time was available for the development of adhesives and composite matrices. If material forms and preliminary mechanical properties of adhesives and composites were not available by December 1995, the structure part of the HSCT program would be delayed and this would have a detrimental effect on the program.

Discussion

Because of the initial requirements, especially processability, high molecular weight polymers with high melt viscosities were not considered to be prime candidates. Instead, work focused on endcapping oligomers with reactive groups. The reactive group of choice was the phenylethynyl group because it offered the best overall combination of properties: a wide processing window, long room temperature shelflife and excellent mechanical performance for the cured polymer. Early work with the phenylethynyl group on imide oligomers was reported in 1983. The NASA in-house work began in the latter part of 1992. Many phenylethynyl terminated imide oligomers (PETI) were prepared and characterized. One of the early materials, designated PETI-1, from the reaction of 3,3',4,4'-oxydiphthalic anhydride (ODPA), 3,4'-oxydianiline and 4-(3-aminophenoxy)-4'-phenylethynylbenzophenone (endcapper) at a molecular weight of ~9000 g/mole was available in 1994. This material offered an attractive combination of properties: cured Tg of 249°C, fracture energy (G_{1c}) of 2.38 kJ/m^2, RT thin film tensile

strenth of 113 MPa, modulus of 3.19 GPa and break elongation of 6.8% and excellent stress solvent resistance. The titanium (6Al-4V) adhesive tensile shear strengths were excellent: RT, 51 MPa; 177°C, 26.9 MPa and 177°C after 10,000 hours at 177°C, 26.9 MPa (2). The intermediate modulus carbon fiber (IM7) composite properties of PETI-1 were also excellent. However because of the projected high cost of the endcapper and the questionable availability of ODPA (China was the only source), work progressed to other PETIs. More than 100 PETIs were made and characterized.

One material, designated PETI-5, from the reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), a mixture of 85 mole % of 3,4'-oxydianiline (3,4'-ODA) and 15 mole % of 1, 3-bis(3-aminophenoxy)benzene (1,3-APB) and 4-phenylethynylphthalic anhydride (PEPA) at a molecular weight of 5000 g/mole (see Equation) afforded the best overall combination of properties. Two other oligomers of different molecular weights as depicted in the equation were also prepared. The properties of the 3 oligomers and the cured polymers are presented in Tables 1-5 (3).

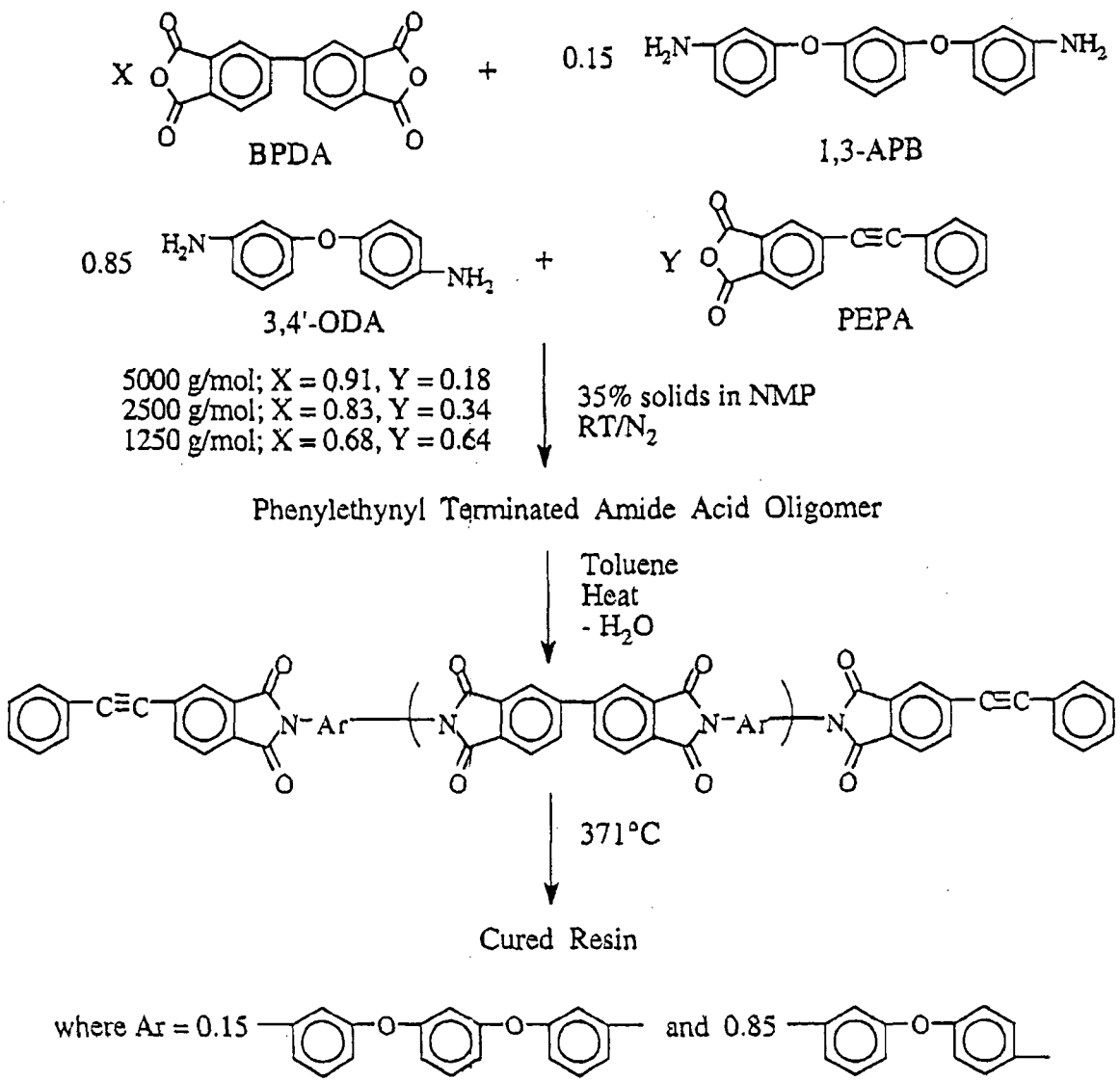

Table 1. Physical Properties of PETI-5 Oligomers

Calculated $\bar{M}_n$ (g/mole)	K_{inh}, dL/g[1]	T_g (T_m), °C[2]		TGA, 5% Wt. Loss, °C[4]
		Initial	Cured[3]	
1250	0.15	170 (320)	288	489
2500	0.20	210 (330)	277	497
5000	0.27	210 (357)	270	503

1. Determined on 0.5% (w/v) NMP solutions of the amide acid at 25°C.
2. Determined on powdered samples by DSC at a heating rate of 20°C/min.
3. Determined on powdered samples cured in a sealed aluminum pan for 1 hr at 371°C.
4. Determined on powdered samples in air at a heating rate of 2.5°C/min.

Table 2. GPC Analysis of PETAA-5 Oligomers

Calculated $\bar{M}_n$ (g/mole)	$\bar{M}_n$, g/mole	$\bar{M}_w$, g/mole	$\bar{M}_z$, g/mole
1250	1946	2931	4202
2500	3044	5559	10870
5000	7914	13865	24260

Table 3. Unoriented PETI-5 Thin Film Tensile Properties*

Calculated $\bar{M}_n$ (g/mole)	T_g (T_m), °C	Test Temp., °C	Str., MPa	Mod., GPa	Elong. @ Break, %
2500	ND (368)	23	151.7	3.5	14
		177	76.6	2.2	43
5000	270	23	129.6	3.1	32
		177	84.1	2.3	83

* Dried through 1 hour at 350°C in air

Table 4. Complex Melt Viscosity at 100 Rad/sec

Calculated $\overline{X}_n$ (g/mole)	Minimum Melt Viscosity, Pa sec	Temp., °C
1250	5	335
2500	90	335
5000	1000	371

Table 5. Adhesive Properties

Calculated $\overline{X}_n$ (g/mole)	Test Temp., °C	Tensile Shear St.[1], MPa	Flatwise Tensile St.[2], MPa
1250	23	36.6	6.9
	177	31.7	4.0
2500	23	46.2	7.6
	177	37.2	5.2
5000	23	48.3	5.2
	177	37.9	3.3

1. Ti(6Al-4V)/Ti single lap shear specimens, 5 volt chromic acid anodized surface treatment
2. Sandwich specimens with Titanium core (3.2V-2Sn, 0.48 cm cell size) and 2024 T-3 facesheets

A more detailed discussion on composite work is presented herein since most of the effort concentrated on composites. IM-7 carbon fiber composites of the 1250 and 2500 g/mole PETI-5 were fabricated from solution coated unidirectional tape in a vacuum press under 0.3 and 0.7 MPa, respectively, with a final step at 371°C for 1 hr. The laminate processing cycle was originally developed for the 5000 g/mole PETI-5 (4). Initially a vacuum was applied and the prepreg was heated to 250°C and held for 1 hr in the press without pressure. At the end of this hold, a 30 cm x 30 cm x 32 ply laminate contained <0.2% volatiles as determined by dynamic TGA. Pressure was then applied and the temperature ramped to 371°C and held for 1 hr. The laminate was then cooled in the press and the pressure and vacuum released when the temperature fell below 100°C.

Other than a reduction of the applied pressure due to the better flow of the 1250 and 2500 g/mole versions as compared to the 5000 g/mole version which used 1.4 MPa, no optimization work was performed. C-scans of the laminates showed good consolidation

with little or no void content. The mechanical properties of composites from the 3 different molecular weight oligomers are presented in Tables 6 and 7.

Table 6. IM-7/PETI-5 Composite Properties

Property	Lay-up	1250 g/mol	2500 g/mol[1]	5000 g/mc
OH Tension St., MPa RT (dry) 177°C (wet)	$(+45,0,-45,90)_{4s}$ (25/50/25)	—	444 436	461 452 (dry
OH Tension St., MPa RT (dry) 177°C (wet)	$(+45,-45,90,0,0,+45,-45,0)_s$ (38/50/12)	—	578 566	557 565 (dry
OHC S., MPa RT (dry) 177°C (wet)	$(+45,0,-45,90)_{4s}$ (25/50/25)	—	342 219	335 238
OHC St., MPa RT (dry) 177°C (wet)	$(+45,-45,90,0,0,+45,-45,0)_s$ (38/50/12)	—	377 263	369 296
OHC St., MPa RT (dry) 177°C (dry) 177°C (wet)	$(\pm45,90,0,0,\pm45,0,0,\pm45,0)_{2s}$ (58/34/8)	431.6 366.2 368.5	458.6 395.2 344.1	450.3 342.7 344.6
CAI St., MPa	$(+45,0,-45,90)_{4s}$ (25/50/25)	244.6	334.5	331.0
CAI Mod., GPa	$(+45,0,-45,90)_{4s}$ (25/50/25)	55.8	57.9	55.9
Microstrain, Πm/m	$(+45,0,-45,90)_{4s}$ (25/50/25)	4377	5908	5986

1. Normalized to 62% fiber volume.

Compression strengths after impact (CAI) were obtained on quasi-isotropic laminates which were impacted at an energy of 6.67 KJ/m. Open hole compression (OHC) data were obtained on three different lay-ups and open hole tension on two. The 2500 and 5000 g/mole PETI-5 composites exhibited comparable OHC (RT dry), CAI strength and modulus, and microstrain regardless of the stiffness of the lay-up. Notably better retention of the OHC (177°C dry) properties of the 58/34/8 lay-up were exhibited by the 2500 g/mole PETI-5 as compared to the 5000 g/mole version. The 1250 g/mole PETI-5 exhibited comparable OHC properties to the 2500 and 5000 g/mole PETI-5, however, the CAI strength and microstrain were lower. Upon analysis, it was determined that the 1250 g/mole PETI-5 laminates had low resin contents (26-28%) due to excessive resin flow during fabrication. Consequently, the laminate properties for the 1250 g/mole version in Table 6 were not normalized. Thus it is not prudent to directly compare the laminate properties of the 1250 g/mole version with the others.

Table 7. IM-7/PETI-5 Composite Properties

Property	Lay-up	1250 g/mol	2500 g/mol[1]	5000 g/mc
0° Compression St., MPa	$(0)_{8t}$	-----	1768	1659
0° Compression Mod., GPa	$(0)_{8t}$	-----	131	133
0° Tension St., MPa	$(0)_{8t}$	-----	2364	2295
0° Tension Mod., GPa	$(0)_{8t}$	-----	149	157
0° Tension Strain, microstrain, μm/m	$(0)_{8t}$	-----	15259	12416
In-Plane Shear Mod., GPa RT (dry) 177°C (dry)	(0/100/0)	-----	5.31 4.28	4.21 3.45
Interlaminar Shear St., MPa RT (dry)	$(0)_{16t}$	-----	130	142
Comp. Interlaminar Shear St., MPa RT (dry) 177°C (wet)	$(0)_{30t}$	-----	95.9 66.4	86.2 46.9
Thermal Cycling, Microcracks/in.[2]	$(\pm45,90,0,0,\pm45,0,0,\pm45,0)_{2s}$ (58/34/8)	0	0	0

1. Normalized to 62% fiber volume.
2. After 200 thermal cycles from -54 to 177°C with a 1 hr hold at each temperature and a heating rate of 8.3°C/min.

Crossply composite (58/34/8) specimens of the 1250 and 2500 g/mole PETI-5 were thermally cycled from -54 to 177°C at a heating rate of 8.3°C/min with a 1 hr hold at –54 and 177°C. The specimens were examined after 100 and 200 cycles under a microscope for microcracks. After 200 cycles, neither specimen exhibited any microcracks.

In general, most of the properties of the cured 2500 g/mole version of PETI-5 were similar to those of the cured 5000 g/mole version apparently because the nature of the cured resins were very similar. The cured 2500 g/mole oligomer was expected to have significantly higher crosslink density than the cured 5000 g/mole oligomer but this did occur. For example in Table 1, the difference in the Tg of cured 2500 and 5000 g/mole oligomers is only 7°C while the difference between the cured 1250 and 5000 g/mole oligomers is 18°C, suggesting a higher crosslink density in the cured 1250 g/mole material. Unfortunately, solution cast films and neat resin moldings were difficult to make from the 1250 g/mole oligomer and therefore quality specimens were not available to obtain certain properties for comparison.

Composite and adhesive work progressed with the PETI-5 5000 g/mole to the fabrication and testing of large parts (1.8 m x 3.0 m curved sandwich panels and skin stringer panels). Even larger parts were planned but the HSCT program was cancelled. PETI-5 5000 g/mole composite structure is currently being considered for use on reusable launch vehicles.

Concurrent with work on PETI-5, imide oligomers containing both pendent and terminal phenylethynyl groups were also under investigation. The monomer to introduce pendent phenylethynyl groups was 1,3-diamino-4'-phenylethynylbenzophenone. Although the combination of terminal and pendent phenylethynyl groups on the same oligomers gave cured resins with Tgs > 300°C, the processability of the oligomers was more difficult than PETI-5. Low molecular weight (~750 g/mole) phenylethynyl containing imide oligomers were investigated for use as resins for transfer molding (5). This work provided an attractive RTM material, designated PETI-298, made from the reaction of BPDA, 75 mole % 1,3-bis(4-aminophenoxy)benzene, 25 mole % 3,4'-ODA and PEPA at a molecular weight of 750 g/mole. This material had a melt viscosity of 0.6-1.3 Pa sec at 280°C for 2 hours and a cured Tg of 301°C. Composites fabricated by RTM were well consolidated and gave high mechanical properties (6).

Summarizing Remarks

A variety of imide oligomers containing phenylethynyl groups have been prepared, characterized and fabricated into adhesive panels and composites. These materials offer a unique combination of properties that includes excellent processability, durability at 177°C, excellent stressed solvent resistance and high mechanical properties. Although the work reported herein pertained primarily to composites, these materials, depending upon the molecular weight of the oligomer, could find application in many other areas such as thin coatings, films and moldings.

References

1. F. W. Harris, A. Pamidimukkala, R. Gupta, S. Das, T. Wu and G. Mock, Polym. Prepr., 24(2), 324 (1983)
2. R.B. Bryant, B. J. Jensen and P. M. Hergenrother, J. Appl. Polym. Sci., 59, 1249 (1996)
3. J. G. Smith Jr., J. W. Connell and P. M. Hergenrother, J. Comp. Matl., 34(7), 614 (2000)
4. T. Hou, B. J. Jensen and P. M. Hergenrother, J. Comp. Matl., 30(10), 109 (1996)
5. J. M. Criss, C. P. Arendt, J. W. Connell, J. G. Smith Jr. and P. M. Hergenrother, SAMPE J., 36(3), 32 (2000).
6. J. G. Smith Jr., J. W. Connell, P. M. Hergenrother and J. M. Criss, Sci. Adv. Matl. Proc. Eng. Series, 46, 000 (2001)