

ADHESIVE AND COMPOSITE PROPERTIES OF A NEW PHENYLETHYNYL TERMINATED IMIDE

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ABSTRACT

A relatively new phenylethynyl terminated imide oligomer (PETI) from the reaction of 2,3,3',4'-biphenyltetracarboxylic dianhydride, 4,4'-oxydianiline and endcapped with 4-phenylethynylphthalic anhydride at a calculated number average molecular weight of 5000 g/mole was evaluated as an adhesive and composite matrix. The asymmetric dianhydride imparts a low melt viscosity to the oligomer and a high glass transition temperature to the cured resin. Preliminary adhesive work with titanium (6Al-4V) adherend gave good room temperature (RT) tensile shear strengths and excellent retention of RT strength at 260°C. Preliminary composite work using unsized IM7 carbon fiber provided moderate to high mechanical properties. The chemistry, mechanical, and physical properties of the new PETI in neat resin, adhesive and composite form are presented.

KEY WORDS: Phenylethynyl Imides, Laminates, Adhesives

1. INTRODUCTION

In the search for new polymers with a unique combination of attractive properties for use as high temperature adhesives and composite matrices, phenylethynyl groups have been placed terminal, pendent, and both terminal and pendent on a variety of oligomers and polymers (1). The

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phenylethynyl groups undergo a thermally induced reaction leading to linear chain propagation, branching and crosslinking without the evolution of by-products. Currently, the phenylethynyl group is the preferred group to place pendent or terminal on molecules particularly for use as structural resins (e.g. adhesives and composite matrices) primarily because oligomers with phenylethynyl groups offer a wide processing window and the cured polymers provide excellent mechanical properties.

For example, the phenylethynyl group technology was used in the development of a new resin, a phenylethynyl terminated imide oligomer designated PETI-5, for use as a composite matrix and adhesive (2-5) in the United States Mach 2.4 high speed civil transport (HSCT) program. This resin was specifically designed to provide the combination of properties required for the HSCT such as acceptable processability, high mechanical properties, excellent solvent resistance under stress and long term durability at 177°C (5). The glass transition temperature (T_g) of cured PETI-5 is 270°C (2). Unidirectional tape and fabric prepreg were used to fabricate composites via autoclave processing. High quality curved skin stringer and curved sandwich subcomponents as large as 1.8 m x 3.1 m were fabricated. Modification of the PETI-5 imide segment and lowering the oligomer molecular weight gave low melt viscosity resins for the fabrication of support structure (e.g. frames, spars, ribs) via resin transfer molding and resin infusion (6). These materials with cured T_gs as high as 330°C were not developed into conventional prepreg forms.

Structural resins with good processability and temperature performance higher than that offered by PETI-5 are needed for various applications in jet engines, advanced high speed aircraft, and space vehicles. For example, high temperature composite structure is needed in future reusable launch vehicles. The higher the temperature performance of polymeric composite substructure on these vehicles, the less thermal protection system required which converts into a significant weight savings. Work is underway to develop new and improved high temperature adhesives and composite matrices for these applications.

Recently, a new asymmetric aromatic dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), was used to make polyimides (7,8) with T_gs higher than the analogous polyimide from the symmetric aromatic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride. Research with the asymmetric dianhydride was extended to reactive oligomers where several new phenylethynyl terminated imide oligomers from the reaction of a-BPDA with various aromatic diamines and endcapped with 4-phenylethynylphthalic anhydride (PEPA) were reported (9-11). One oligomer, in particular, from the reaction of a-BPDA with 4,4'-oxydianiline and endcapped with PEPA at a calculated number average molecular weight (M_n) of 4500 g/mole was of special interest because the cured polymer was tough and had a T_g of 343°C (11). Because of the catenation from the dianhydride, the oligomers have highly irregular structures resulting in relatively low melt viscosities that suggests the fabrication of composites and bonded parts could be performed under relatively low pressures. The work presented herein was conducted to evaluate the processability of a 5000 g/mole oligomer and to obtain preliminary mechanical properties on composites and bonded specimens from the cured oligomer.

2. EXPERIMENTAL

2.1 Starting Materials The following chemicals were obtained from the indicated sources and used without further purification: 4,4'-oxydianiline (4,4'-ODA, Mitsui Petrochemical Ind., m.p.189-190°C), 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA, Ube Industries Ltd., m.p. 195-198°C), 4-phenylethynylphthalic anhydride (PEPA, Daychem Laboratories, Inc., m.p. 152-153.5°C) and N-methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co.). Pasa Jell 107TM was obtained from Products Research and Chemicals Corporation, Semco Division. All other chemicals were used as-received.

2.2 Synthesis of Phenylethynyl Terminated Imide (PETI) Oligomer The phenylethynyl terminated imide oligomer was prepared twice at a calculated \overline{M}_n of ~ 5000 g/mole by reacting a-BPDA (0.912 mole) with 4,4'-ODA (1.000 mole) and endcapping with PEPA (0.176 mole). The first preparation was run on a 0.0764 mole scale for 4,4'-ODA while the second preparation was scaled-up by a factor of 10 (384 g solids and 866 mL of NMP). The diamine was dissolved in NMP at room temperature under nitrogen and the dianhydride and endcapper were added in one portion as a slurry in NMP. The solids concentration was subsequently adjusted to 30% (w/w) with additional NMP. The reaction was stirred for ~24 hrs at ambient temperature under a nitrogen atmosphere and an aliquot subsequently removed to determine inherent viscosity. The amide acid/NMP solution was used to prepare thin films, supported adhesive film, and unidirectional IM-7 carbon fiber tape. Imide oligomer was prepared from the amide acid solution by subsequently fitting the flask with a Dean Stark trap and condenser, adding toluene, and refluxing the solution overnight. Water from cyclodehydration was removed by azeotropic distillation. The imide oligomer was isolated by removing the toluene and adding the reaction mixture to water to precipitate a light colored solid that was washed in warm water. The off-white powder was dried at 200°C in air.

2.3 Film Specimens NMP solution (30% w/w solids) of the oligomer was centrifuged, the decantate doctored onto clean, dry plate glass and dried to a tack-free form in a low humidity air chamber. The film on glass was imidized and cured by heating at 100, 225 and 371°C for 1 hr each in flowing air. The resulting film was transparent, dark orange and fingernail creaseable. Specimens (13 cm long, 0.51 cm wide, 0.005 cm thick) were cut with a JDC Precision Sample Cutter, Thwing-Albert Instrument Company. Thin film tensile properties were determined following the general procedure in ASTM D882 using four specimens per test condition.

2.4 Adhesive Specimens Supported adhesive film with volatile contents of ~2% was prepared by multiple brush coating 112 E-glass having an A-1100 finish with the oligomer solution. Single lap shear adhesive panels containing 4 standard test specimens per panel (bond area 2.54 cm wide x 1.27 cm overlap) using titanium (Ti, 6Al-4V) adherends with a PASA Jell 107TM surface treatment were fabricated in a press by heating to 250°C under contact pressure during 45 min., holding at 250°C under contact pressure for 1 hr, applying 0.34 to 0.69 MPa, heating to 350 or 371°C in air, holding under these conditions for 1 or 2 hr and cooling under pressure. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

2.5 Composite Specimens The NMP oligomer solution with a Brookfield viscosity at 24°C of 24.9 Pa sec was used to coat unsized IM-7 carbon fiber (12k tow) on a prepregging machine. The unidirectional tape (21.6 cm wide) exhibited an areal weight of 135 g/sq. m., resin content of 32% and volatile content of 18%. Laminates were fabricated initially in a stainless steel mold in a vacuum press and later in an autoclave. The vacuum press laminates were sandwiched between a release layer (Release Ease 234 TFP from Airtech International, a teflon coated 1080 style glass fabric) and 2 layers of bleeder (Bleeder Lease C from Airtech International, 7781 style glass fabric containing a silicone release agent) on each side. Autoclave cured laminates used the same release and bleeder system and were bagged in a polyimide film (Thermalimide from Airtech International). In the vacuum press and the autoclave, full vacuum was applied during the entire process cycle starting with heating to 250°C and holding at 250°C for 1 hr. Pressure (1.38 MPa) was subsequently applied and the temperature was increased to 371°C and held for 1 or 2 hr. The laminates were cooled under pressure to about 100°C and the pressure subsequently released. The laminates were ultrasonically scanned (C-scan), cut into specimens, and tested for mechanical properties. Resin content was determined by acid digestion.

Open hole compressive (OHC) strength (Northrop Grumman Test) was determined on 24 ply quasi-isotropic specimens 7.62 cm by 2.54 cm with a 0.64 cm hole in the center (4). Compressive strength (Boeing Test, BSS 7260) was determined on 8 ply unidirectional specimens 5.7 cm by 1.27 cm. Tensile strength (ASTM D3039) was determined on 8 ply unidirectional specimens 15.2 cm by 1.27 cm. Interlaminar shear strength or short beam shear (SBS) strength (ASTM D2344) was determined on 24 ply unidirectional specimens 1.91 cm x 0.64 cm. Four composite specimens were tested under each condition.

2.6 Other Characterization Inherent viscosity (η_{inh}) was obtained on a 0.5% (w/v) solution of the amide acid in NMP at 25°C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the T_g taken at the inflection point of the DT versus temperature curve. Dynamic thermogravimetric analysis (TGA) was performed on a Seiko 200/220 instrument on cured film at a heating rate of 2.5°C/min in air or nitrogen at a flow rate of 15 cm³/min. Brookfield viscosity was obtained on a Brookfield LVT Synchro-Lectric viscometer at 24°C. Rheological measurement was conducted on a Rheometrics System 4 rheometer at a heating rate of 4°C/min. The specimen disk, 2.54 cm in diameter and 1.5 mm thick, was formed by compression molding imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 100 rad/sec while the lower plate was attached to a transducer which recorded the resultant torque. Storage (G') and loss (G'') moduli and complex melt viscosities (η^*) as a function of time (t) were measured at several temperatures.

3. RESULTS AND DISCUSSION

An asymmetric aromatic dianhydride, a-BPDA, was reported in 1973 by Ube Industries, Ltd. (12) and was recently evaluated in a series of new phenylethynyl terminated imide oligomers (9-11). The new PETIs were found to have a unique combination of attractive properties including

low melt viscosities and when cured, high Tgs. This is due to the catenation emanating from the dianhydride that provides highly irregular structures, resulting in decreased intermolecular interactions between the molecules (11). Because of the properties resulting from the unique backbone structure, one of these new PETIs from the reaction of a-BPDA and 4,4'-ODA endcapped with PEPA at a calculated Mn of 5000 g/mole as depicted in Figure 1 was selected for evaluation. This particular oligomer was chosen over others because the diamine is readily available, relatively inexpensive and the properties of the oligomer and cured polymer are very attractive. For example, the cured polymer has a Tg of 343°C and neat resin flexural elongation of 13% (11). As shown in Table 1, two batches of the PETI were prepared on 0.0764 and 0.7640 mole scale based upon 4,4'-ODA. The latter scale used 384 g of reactants and 866 mL of NMP. Although reaction conditions were held constant, the larger reaction gave a higher molecular weight oligomer as indicated by the inherent viscosity. The reason for the difference in molecular weight is unknown. Past work with other PETIs have not shown any effect from a scaling factor.

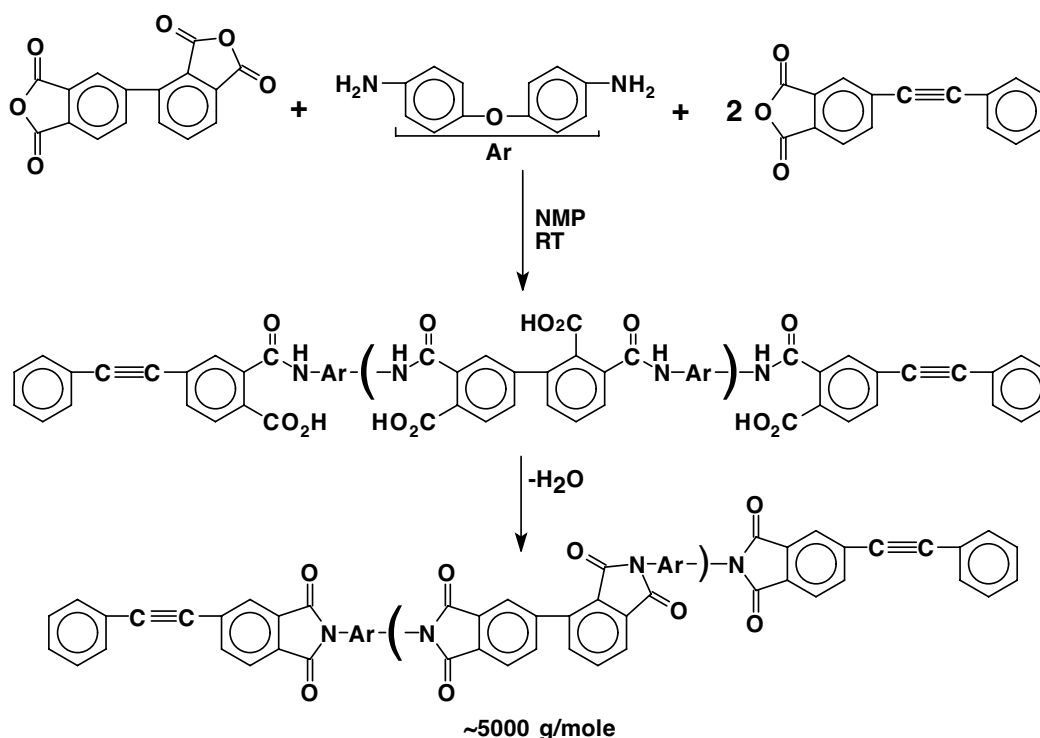


Figure 1. Synthesis of Phenylethynyl Terminated Imide Oligomer

As shown in Table 1, the smaller batch oligomer had a lower inherent viscosity and a slightly lower melt viscosity than the larger batch oligomer. As a reference point, PETI-5 at a calculated Mn of 5000 g/mole had a minimum melt viscosity of 1000 Pa sec at 371°C (13). Surprisingly the smaller batch oligomer (lower inherent viscosity) had an initial Tg higher than that of the larger batch oligomer. This was contrary to what was expected and what was found for different

molecular weight versions (1250, 2500, and 5000 g/mole) of PETI-5 where the lowest molecular weight oligomer had the lowest initial Tg and when cured, the highest Tg (13). Upon curing, the smaller batch oligomer (lower inherent viscosity) had a slightly higher Tg, presumably because the crosslink density was higher than that of the cured larger batch oligomer.

The Tgs of the air-cured films were higher than those of the powder samples cured in a sealed DSC pan. As noted before (2), specimens cured in air have higher Tgs and other properties (e.g. tensile properties) are also higher than those cured in a restricted air environment (e.g. vacuum or a closed mold). The 23°C unoriented thin film tensile properties of the 2 cured oligomers are essentially the same and are considered to be reasonably good. A rheological curve for the smaller batch oligomer in Figure 2 shows a gradual change for the storage modulus (G') and loss modulus (G'') of about 1 decade until about 280°C. The melt fluidity increases rapidly as the temperature approaches 350°C. At 351°C, G' crosses G'' , representing the gel point, and the melt viscosity reaches its minimum value. After 351°C, reaction of the phenylethynyl groups occurs at a faster rate as evident by the increase in G' and G'' . Most of the resin in the specimens during the rheometric test had flowed out from the circular disks to form a cured foam that was extremely tough. By TGA at a heating rate of 2.5°C/min, the cured films showed 5% weight losses at ~513 and 531°C in air and nitrogen, respectively. Weight loss in air did not begin until 450°C. The only data in Table 1 that disagrees with expectations is the 13°C higher initial Tg of the uncured smaller batch oligomer. No reasonable explanation is offered to explain this discrepancy.

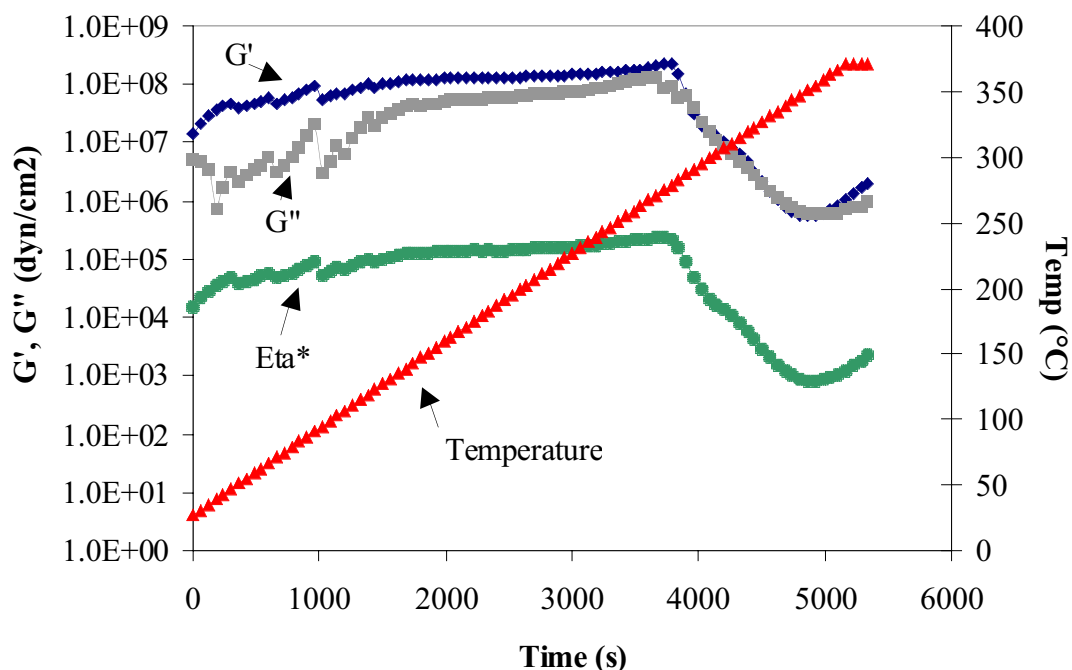


Figure 2. Rheological Curves for the Phenylethynyl Terminated Imide Oligomer

All adhesive and composite work was performed with the larger batch oligomer. Titanium alloy (6Al-4V) adherends were surface treated with PasaJell™ 107 (a hydrosilicic acid/hydrofluoric acid mixture) and tensile shear specimens (single lap shear) were fabricated in a press using a supported film of the oligomer on 112 E-glass carrier. Cure conditions and adhesive properties are given in Table 2. Initially a cure of 1 hr at 371°C under 0.69 MPa was used to fabricate adhesive panels but the tested adhesive

Table 1. Oligomer and Polymer Properties

Reaction size, mole of 4,4'-ODA (total solids, g)	0.0764 (38.4) small batch	0.7640 (384) large batch
Amide Acid Oligomer Inherent Viscosity, dL/g	0.36	0.50
Imide Oligomer Tg, °C	274	261
Temperature of 5 % weight loss of film by TGA, °C	513 (air) 531 (nitrogen)	511 (air) 531 (nitrogen)
Imide Oligomer Melt Viscosity, Pa sec	830 @351°C	960@351°C
Cured Polymer Tg, °C	334 (powder after 1 hr @ 371°C in sealed DSC pan)	326 (powder after 1 hr @ 371°C in sealed DSC pan)
	342 (film after 1 hr @ 371°C in air)	340 (film after 1 hr @ 371°C)
23°C Thin Film Tensile Properties at Break		
Strength, MPa	117.9	112.8
Modulus, GPa	2.61	2.70
Elong., %	12.8	14.3

specimens showed predominantly adhesive failure. The pressure was reduced by 50% and the same heating cycle was used. The resulting specimens had cured bondline thicknesses significantly higher and the strength was lower than specimens made under 0.69 MPa. Next the cure temperature was lowered to 350°C and 0.52 MPa was used. The tested adhesive specimens showed more cohesive failure but still 30-40 % adhesive failure. The tensile shear strengths are respectable even though all specimens failed with 30 % or more adhesive character, indicating that the full strength of the adhesive was not determined. Nevertheless, the strengths at 232°C and 260°C are excellent. The Tg of the tough resin flash (resin that flowed out of the bondline) from an adhesive specimen bonded in a press at 350°C for 1 hr was 326°C. When specimens were fabricated with a cure of 2 hr at 350°C, the strength at all test temperatures dropped relative to those cured for 1 hr at 350°C. The resin flash of the specimens bonded for 2 hr at 350°C had a Tg of 327°C, essentially the same as that from the flash of a 1 hr cure at 350°C. In general, the oligomer showed excellent flow in adhesive panel fabrication providing a low porosity bond area

(from microscopic inspection) and a dark brown, very tough, flash. The strengths are expected to improve substantially with improvement in the surface treatment.

Table 2. Tensile Shear Properties

Cure Conditions	Test Temp., °C	Tensile Shear Strength, MPa	Avg. Cured Bondline Thickness, mm	Comments
1 hr @ 250°C, apply 0.69 MPa, heat to 371°C, hold 1 hr	25	28.4	0.11	Mostly adhesive failure
1 hr @250°C, apply 0.34 MPa, heat to 371°C, hold 1 hr	25	24.8	0.18	Mostly adhesive failure
1 hr @ 250°C, apply 0.52 MPa, heat to 350°C, hold 1 hr.	25	31.2	0.13	Mixed failure
1 hr @ 250°C, apply 0.52 MPa, heat to 350°C, hold 1 hr	25	34.0	0.15	Mixed failure
	177	31.0	0.16	
	232	25.8	0.15	
	260	19.7	0.15	
1 hr @270°C, apply 0.52 MPa, heat to 350°C, hold 2 hr	25	28.2	0.15	Mixed failure
	177	26.8	0.15	
	232	20.4	0.16	

Composite work was performed using unidirectional tape prepared from the solution coating of unsized IM7 (intermediate modulus) carbon fiber. The tape contained 18% volatiles (NMP and water due to cyclodehydration of the amide acid to the imide). During the composite fabrication process, the volatiles are readily removed by B-staging the layup at 250°C under vacuum. Composite fabrication was performed initially in a vacuum press and then later in an autoclave. The first 24 ply 7.62 cm x 7.62 cm, unidirectional laminate fabricated in the vacuum press under 0.69 MPa for 1 hour at 371°C exhibited significant porosity. Precompaction of several plies during the layup would be expected to alleviate much of this porosity but this is generally not done on small laminates. Therefore future laminates were fabricated under 1.38 MPa at 371°C for 1 to 2 hr. All of these laminates were well-consolidated as shown by C-scan. When individual specimens were dropped on a hard surface, they rang like dropping a piece of steel. Other laminates were cured in an autoclave under the same conditions as in a vacuum press except the hold time at 371°C was 2 hr. A schematic of the cure profile in the autoclave is shown in Figure 3.

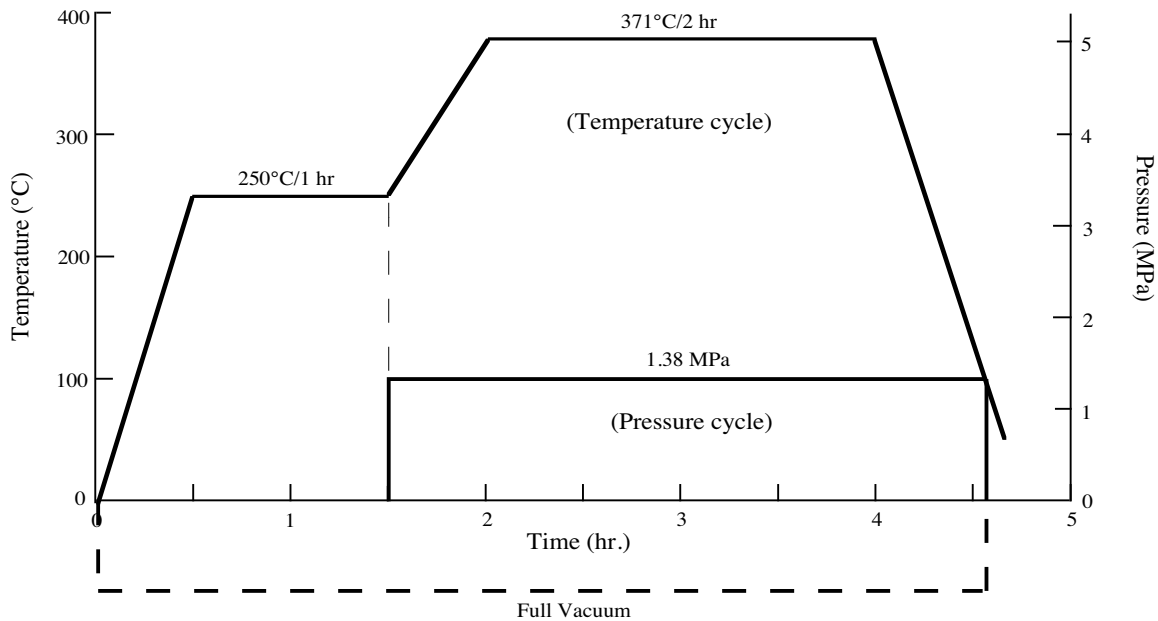


Figure 3. Cure Cycle for Laminate Fabrication

Information on the laminate layup and size is given in Table 3 while the mechanical properties are presented in Table 4. Resin contents were on the low side varying from about 28 to 30.5 %. Laminates were well-consolidated as evidenced from C-scans and optical microscopy of test specimens. As shown in Table 4, SBS specimens from the initial 24 ply unidirectional laminate press cured for 1 hr at 371°C under 1.38 MPa gave relatively high 23°C strength but at 232°C, pronounced thermoplastic failure occurred. By DSC, the SBS specimens had a T_g of only 250°C (lower than the oligomer in Table 1) indicating incomplete cure and perhaps presence of solvent, even though the final cure was 1 hr at 371°C. When a piece of a SBS specimen was heated in the DSC to 370°C, quenched and rerun, a T_g of 288°C was obtained. A piece of the SBS specimen was then cured in the DSC cell for 1 hour at 371°C to give a T_g of 326°C, providing further evidence for incomplete cure. A 23°C SBS strength of 113.8 MPa for an incompletely cured laminate is surprising. Laminates for SBS specimens were then fabricated in a press under 1.38 MPa at 371°C for 2 hr. SBS specimens from these laminates gave T_gs ~ 324°C. As seen in Table 4, the SBS strength at 23°C is less than that obtained for the incompletely cured laminate but the strengths at 177 and 232°C are significantly better. The retention of 23°C values was 63% when tested at 232°C. Autoclave curing minimizes air exposure and therefore requires a longer cure time than curing in air. This is more pronounced with this PETI than observed for other PETIs and PETI-5 (3,4). As a result, all the remaining laminates were cured in an autoclave for 2 hr at 371°C. Since the air cured film (see Table 1) had a T_g of 340°C, the advantageous effect of curing in air is obvious.

Table 3. Laminate Information

Mechanical Test	Layup	Laminate size	Test specimen size
Interlaminar shear strength (short beam shear strength, SBS)	[0 ₂₄]	7.62 cm x 7.62 cm	1.91 cm x 0.64 cm
0° Tensile strength	[0 ₈]	15.2 cm x 10.2 cm	15.2 cm x 1.27 cm
0° Compressive strength	[0 ₈]	15.2 cm x 10.2 cm	5.7 cm x 1.27 cm
Open hole compressive strength (OHC)	[+45/0/-45/90] _{3S}	15.2 cm x 10.2 cm	7.62 cm x 2.54 cm (0.64 cm hole in center)

The 0° tensile strength was lower than expected. As a comparison, PETI-5/IM7 laminates gave 0° tensile strength at 23°C of 2295 MPa (4). However much work had been done on optimizing the quality of the PETI-5 unidirectional tape and the laminate fabrication conditions. The tape used to fabricate the laminates reported herein was not of high quality (e.g. non-uniform in thickness, some fiber misalignment). In addition, the resin had excessive flow during laminate fabrication that caused fiber wash and waviness and in some cases, thinner test specimens than desired.

The 0° compressive strength at 23°C is reasonably good while the value at 177°C is poor because of premature failure in the test tabs. For reference, PETI-5/IM7 laminates gave 0° compressive strength at 23°C of 1661 MPa (4). The OHC strengths were high with excellent retention (91.5 %) of RT strength at 177°C. Laminates of PETI-5/IM7 with the same layup gave 335 MPa at RT and 237.8 MPa at 177°C (4). Although only 4 specimens were tested at 177°C, it appears as though the new PETI provides better retention of OHC strength at 177°C than that of PETI-5. Overall, the laminates of the new PETI showed good to excellent properties. Better quality tape and optimization of the cure conditions are expected to provide laminates with superior properties.

Table 4. Laminate Mechanical Properties

Mechanical property	Test Temperature, °C	Average Value
SBS strength, MPa (cured 1 hr @ 371°C in a press)	23	113.8
	177	40.7 (thermoplastic)
	232	thermoplastic failure
SBS strength, MPa (cured 2 hr @ 371°C in a press)	23	86.9
	177	62.5
	232	50.6
0° Tensile strength *, MPa (modulus, GPa)	23	1634 (185)
	232	1448 (145)
	288	1314 (135)
0° Compressive strength*, MPa	23	1420
	177	724 (tab failure)
OHC strength*, MPa	23	293.0
	177	268.2

*Cured 2 hr @ 371°C in an autoclave

4. CONCLUSIONS

A new PETI oligomer was evaluated in preliminary adhesive and laminate work. The neat resin properties of the cured oligomer were excellent. The oligomer had a surprisingly low melt viscosity that enabled the fabrication of small adhesive panels and laminates under relatively low pressure. The adhesive specimens showed high retention of RT tensile shear strength at 232°C and 260°C. Laminate properties were good to excellent with the OHC specimens displaying high RT values and excellent retention of RT strength at 177°C.

5. ACKNOWLEDGEMENT

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The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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7. BIOGRAPHIES

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