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Phenylethynyl containing imide oligomers

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Abstract

As part of a program to develop high performance/high temperature adhesives and composite matrices for a Mach 2.4 high speed civil transport, imide oligomers containing phenylethynyl groups were investigated. Phenylethynyl groups were placed on the ends of oligomers of different molecular weights (1250, 2500 and 5000 g/mol), pendent along the backbone of oligomers and both pendent and terminal on oligomers. Many different compositions of phenylethynyl containing imide oligomers had been previously prepared and evaluated before selecting the composition based upon 3,3′,4,4′-biphenyltetracarboxcylic dianhydride (BPDA), 3,4′-oxydianiline (3,4′-ODA) and 1,3-bis(3-aminophenoxy)benzene (APB) for extensive work. 4-Phenylethynylphthalic anhydride (PEPA) was used to place phenylethynyl groups on the ends of the oligomers and 3,5-diamino-4′-phenylethynylbenzophenone (DPEB) was used to introduce pendent phenylethynyl groups along the oligomeric backbone. Upon heating above 300°C, the phenylethynyl groups react to provide chain extension, branching and cross-linking. Several of these materials exhibited excellent properties as adhesives and composite matrices. The chemistry, processability and properties of the oligomers, the cured polymers, bonded specimens and composites from phenylethynyl containing oligomers are presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Phenylethynyl groups; Imide oligomers; Composite matrices

1. Introduction

In 1993, intensive work was initiated jointly by industry and NASA to develop adhesives and composites for a Mach 2.4 high-speed civil transport (HSCT). These materials represent enabling technology for an economically viable HSCT. Adhesives and composite matrices must exhibit a favorable combination of attractive properties. Good handlability, long shelf life and safety (non-toxicity) are required for each material form. The materials must exhibit robust processability in forming large structures, which implies volatileless or low volatile systems or materials amenable to acceptable volatile management during the fabrication of a part. The final part would be required to exhibit high mechanical properties over a temperature range of −54 to 177°C and upon exposure to cyclic temperature and stress while being exposed to aircraft fluids and moisture. The time at 177°C was projected to be 60 000 h or 6.7 years. No micro-cracking in the bonded area or composites is allowed because of the long time at 177°C and the anticipated degradative effect cracks would eventually have on mechanical properties. The various material forms should be amenable to different fabrication methods such as automated tape placement, resin transfer molding, resin infusion and conventional high temperature autoclave curing. In addition, the final large components consisting primarily of sandwich (honeycomb core) and skin stringer construction must be economically acceptable.

At the beginning of the adhesive and composite work, available candidates were screened to determine if they possessed the proper combination of initial properties to suggest that they may perform in this demanding application. All commercially available and some advanced experimental resins were screened and were found to exhibit shortcomings. Due to the accelerated HSCT program schedule, it was of extreme importance that promising adhesives and composite matrices be developed in a timely manner to avoid delays in certain portions of the program. Past experience had shown that moderate to high molecular weight thermoplastics such as linear polyimides were generally difficult to compression mold because of the high melt viscosity. In addition, linear thermoplastics under stress are generally sensitive to aircraft fluids. Thermosetting materials such as the PMR-15 type polyimides had poor toughness and damage tolerance and they micro-cracked upon cyclic stress and temperature exposure. The approach to develop the adhesives and composite resin matrices that was selected concerned imide oligomers containing reactive groups. Imide oligomers were chosen over other oligomeric families

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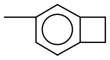
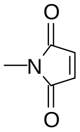
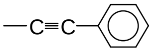
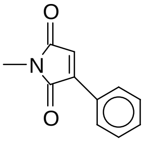
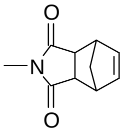
Table 1
Representative end-groups considered for oligomers leading to polymers for long term use at 177°C

Reactive group		Cure Temperature (°C)	Concerns
$-O-C\equiv N$	Cyanate	200–300	Poor thermal stability
	Benzocyclobutene	220–250	Poor thermal stability
	Maleimide	230–250	Poor thermal stability
$-OCF=CF_2$	Trifluorovinylether	250	Small processing window, unknown thermal stability
$-C\equiv H$	Ethynyl	250	Small processing window, unknown thermal stability
	Phenylethynyl	350–370	High cure temperature, excellent long term stability at 177°C
	Phenylmaleimide	370	High cure temperature, unknown thermal stability
	Nadimide	350–370	Cyclopentadiene evolution, low toughness

because of the availability of monomers and the excellent mechanical and thermal properties of polyimides. The reactive groups considered are presented in Table 1.

Of these groups, the phenylethynyl group was selected based upon past work where this group had been placed along the backbone of various polymers and subsequently thermally reacted to provide cross-links [1–4]. Phenylethynyl groups had also been placed on the ends of imide oligomers and subsequently thermally reacted to afford materials with attractive properties [5,6]. The phenylethynyl group offers certain distinct advantages over other reactive groups. It has adequate chemical and temperature stability to withstand relatively harsh synthetic conditions (e.g. aromatic nucleophilic displacement reactions as used to prepare poly(arylene ether)s). It demonstrates versatility insomuch that it can be used on a variety of different families of oligomers (e.g. arylene ether, benzimidazole and phenylquinoxaline) [7–9]. Oligomers containing phenylethynyl groups afford excellent shelf life, exhibit a broad processing window, cure without volatile evolution and upon curing provide polymers with an excellent combination of properties [10]. The attractive features offered by oligomers and polymers containing the phenylethynyl group have been recognized and explored by several researchers as evidenced by the amount of work reported [11–29].

The primary purpose of this paper is to review the chemistry, processability and properties of the oligomers, the cured polymers, the bonded specimens and the composites from phenylethynyl containing imide oligomers. Work has concentrated on the oligomers from the reaction of 3,3′,4,4′-biphenyltetracarboxclic dianhydride (BPDA), 3,4′-oxydianiline (3,4′-ODA) and 1,3-*bis*(3-aminophenoxy)benzene (APB) because this oligomeric backbone offered the best combination of properties of the many oligomers evaluated. 4-Phenylethynylphthalic anhydride (PEPA) was used to terminate the imide oligomers and 3,5-diamino-4′-phenylethynylbenzophenone (DPEB) was used to place phenylethynyl groups randomly along the oligomeric backbone. Phenylethynyl containing imide oligomers were evaluated where phenylethynyl groups were placed on the ends of the oligomers (PETI), pendent along the oligomeric chain that was endcapped with phthalic anhydride (PPEI) and pendent and terminal on the oligomers (PTPEI). Various molecular weights of these oligomers were evaluated. Because of the HSCT program schedule and the attractive properties offered by the oligomer from the reaction of BPDA, 3,4′-ODA, APB and PEPA at a calculated molecular weight of 5000 g/mol, it was selected as the leading candidate for use in the HSCT program. This material has been designated PETI-5 and in less than 3 years, has progressed far beyond the laboratory scale. PETI-5/IM-7 unidirectional tape has been prepared on about a 5000 kg scale and supported adhesive film has been produced on about a 300 m^2 level. The chemistry, processability and properties of the oligomers, the cured polymers, bonded specimens and composites from phenylethynyl containing oligomers are presented.

2. Experimental

2.1. Starting materials

The following chemicals were obtained from the indicated sources and used without further purification: 3,4′-ODA, Mitsui Petrochemical Ind., Ltd., m.p. 84–85°C; APB, Mitsui Petrochemical Ind, Ltd., m.p. 107–109°C; BPDA, m.p. 305–307°C, Chriskev Co., Inc.; PEPA, Daychem Laboratories, Inc., m.p. 152–153°C; DPEB, Daychem Laboratories, Inc., m.p. 154–156°C, phthalic anhydride (PA, Aldrich Chemical Co., m.p.132–134°C) and *N*-methyl-2-pyrrolidinone (NMP, Fluka Chemical Co.).

2.2. Synthesis of phenylethynyl containing imide oligomers

The oligomers were prepared by initially dissolving the appropriate quantities of diamines (3,4′-ODA, APB and in some cases DPEB) in NMP at room temperature under nitrogen. The dianhydride (BPDA) and endcappers (PEPA or PA, as required) were added in one portion as a slurry in NMP to the stirred solution of diamines. The solids concentration was subsequently adjusted to ~35% (w/w) with additional NMP. A mild exotherm is observed during the first few minutes of reaction. The moderately viscous solutions of the amide acid oligomers were stirred for ~24 h at ambient temperature under nitrogen. In all cases, an aliquot was subsequently removed to determine inherent viscosity and for gel permeation chromatographic analysis (GPC) to assess molecular weight and molecular weight distribution. The amide acid/NMP solution was used to prepare thin films, supported adhesive tape, and unidirectional IM-7 carbon fiber prepreg. Imide oligomer was prepared from the amide acid solution by subsequently adding toluene and refluxing the solution under a Dean Stark trap overnight under nitrogen. The imide oligomers precipitated from solution during the imidization process. The pale yellow powders were isolated by adding the reaction mixture to water, washing in warm water and then methanol. The yellow powders were dried at 200°C in air to a constant weight to obtain yields >95%.

2.3. Films

NMP solutions (30–35% w/w solids) of the amide acid oligomers were centrifuged, the decantate doctored onto clean, dry plate glass and dried to a tack-free form in a low humidity chamber. The films on glass were imidized and cured by heating at 100, 225 and 350°C for 1 h each in flowing air. Thin film tensile properties were determined according to ASTM D882 using four specimens per test condition.

2.4. Molded specimens

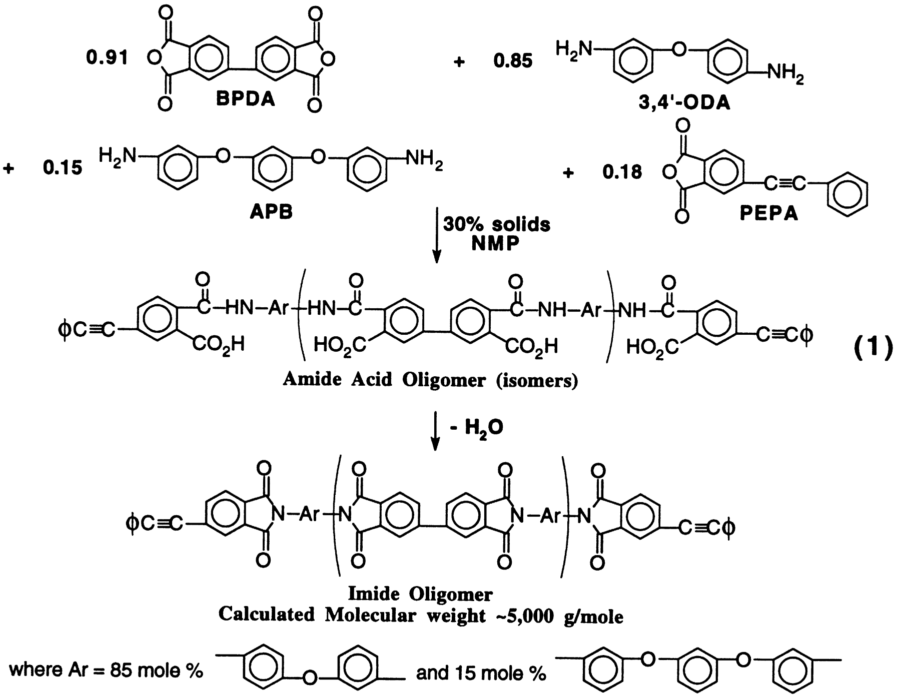
Powdered imide oligomers were compression molded in stainless steel molds under 0.34–1.4 MPa by heating to 350 or 371°C for 1 h. Miniature compact tension specimens ($1.6 \times 1.6 \times 0.95\ cm^3$ thick) and in some cases larger specimens ($5.1 \times 5.1 \times 0.95\ cm^3$) were machined from the moldings and subsequently tested to determine fracture toughness (K_{Ic}, critical stress intensity factor) according to ASTM E399 using four specimens per test condition. G_{Ic}, (critical strain energy release rate) was calculated using the mathematical relationship $G_{Ic} = (K_{Ic})^2/E$, where E is the modulus of the material.

2.5. Adhesive specimens

Supported adhesive films with volatile contents of ~2% were prepared by solution coating 112 E-glass with an A-1100 (γ-aminopropyltriethoxysilane) finish with the amide acid NMP oligomeric solutions followed by stage-drying to final temperatures of about 220°C. Several coats were required to attain the proper film thickness. In some cases, supported film was obtained from Cytec Fiberite, Inc. (Harve de Grace, MD). Standard lap shear adhesive specimens (bond area 2.54 cm wide × 1.27 cm overlap) using titanium (Ti, 6Al–4V) adherences with a chromic acid anodized (5V) surface treatment were fabricated in an autoclave at 350°C under 0.34 MPa for 1 h. Tensile shear adhesive strengths were determined according to ASTM D1002 using four specimens per test condition. Flatwise tensile specimens were fabricated from titanium honeycomb (3V–2.5Sn, 0.48 cm cell size) with a chromic acid anodized (5V) surface treatment and titanium (6Al–4V) facesheets in an autoclave at 350°C under 0.34 MPa for 1 h. Flatwise tensile strengths were determined according to ASTM C297 using four specimens per test condition.

2.6. Composite specimens

NMP solutions (30–35% solids) of the amide acid oligomers were used to coat unsized IM-7 carbon fiber (12K tow, Hexcel, Inc.) on a prepregging machine. The unidirectional tapes (21.6 cm wide) exhibited resin contents ranging from 30–36%, volatile contents of ~12–19%, and fiber areal



Scheme 1.

weights of ~145 g/m^2. Laminates were fabricated in a vacuum press under 76.2 cm of mercury during the entire process cycle by heating to 250°C over ~1 h period and holding at 250°C for 1 h. Pressure (0.7–1.4 MPa) was then applied and the temperature was ramped up over a 0.5 h period to 371°C and held for 1 h. The laminates were cooled under pressure to about 100°C and the pressure subsequently released. The composite panels were ultrasonically scanned (C-scanned), cut into specimens, and tested for mechanical properties according to ASTM procedures. In some cases, large laminates were fabricated in an autoclave under slow heating rates with the same temperatures and hold times as previously described.

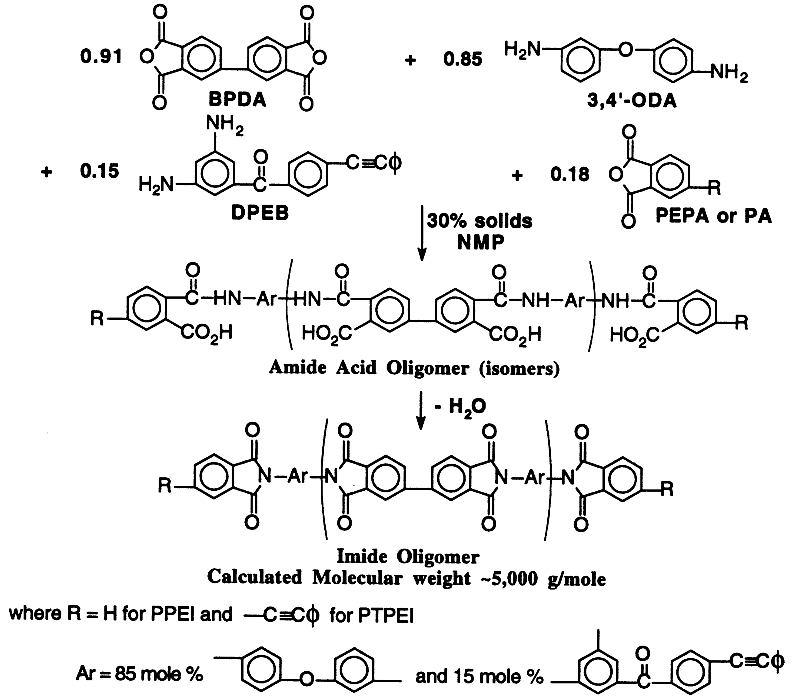
2.7. Other characterization

Inherent viscosities (h_{inh}) were obtained on 0.5% (w/v) solutions of the amide acids 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 glass transition temperature (T_g) taken at the inflection point of the DT versus temperature curve. Rheological measurements were conducted on a single specimen on a Rheometrics System 4 rheometer. Sample specimen disks, 2.54 cm in diameter and 1.5 mm thick, were prepared 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 10 rad/s while the lower plate was attached to a transducer which recorded the resultant torque. Storage (G') and loss (G'') moduli as a function of time (t) were measured at several temperatures. GPC was performed on a Waters 150C system equipped with a model 150R differential viscosity detector and a differential refractive index detector. GPC analyses were performed on dilute solutions of the amide acids in freshly distilled NMP containing 0.02 M lithium bromide. The analyses were performed using a two column bank consisting of a linear Waters Styragel HT 6E column covering the molecular weight range of 10^3–10^7 g/mol in series with a Styragel HT 3 column covering the molecular weight range of 10^2–10^4 g/mol. A universal calibration curve was generated with Polymer Laboratories narrow molecular weight distribution polystyrene standards having molecular weights ranging from 500 to 2.75×10^6 g/mol.

3. Results and discussion

3.1. Synthesis and properties of phenylethynyl containing oligomers

The various oligomers were prepared in a manner by adding an NMP slurry of the anhydride(s) to a stirred NMP solution of the diamines. The anhydride(s) can also be added, as fine powder but will tend to clump if stirring is not adequate or the addition rate is too fast. Depending upon the size of the reaction, a mild exotherm is observed. A one-liter reaction at about 35% (w/w) solids content will exotherm to about 40°C. The exotherm for a larger reaction is slightly higher and persists longer. Obviously the



(2)

Scheme 2.

exotherm can be controlled by the slow addition of the anhydride(s) or by cooling the reaction. The reaction is stirred for about 24 h at ambient temperature under nitrogen to allow the amide acid oligomers to equilibrate (molecular weight equilibration). Based upon BPDA, 3,4′-ODA, APB, PEPE, DPEB and PA, the reaction scheme for the preparation of the 5000 g/mol phenylethynyl terminated amide acid and imide oligomer (PETI-5) is presented in Scheme 1 and the reaction scheme for the preparation of the pendent phenylethynyl amide acid and imide oligomer (PPEI) and the pendent/terminal phenylethynyl amide acid and imide oligomer (PTPEI) is represented in Scheme 2.

The NMP amide acid solutions were used to prepare thin supported adhesive film and unidirectional IM-7 carbon fiber tape. The amide acid oligomers were converted to the imide oligomers by adding toluene to the NMP solutions and refluxing with stirring overnight under a Dean Stark trap. The imide oligomers precipitate from solution during the imidization process. They were isolated and subsequently dried at 200°C.

The amide acid oligomeric solutions exhibited excellent stability. As shown in the GPC curves in Fig. 1 for an NMP solution (30% solids) of phenylethynyl terminated amide acid oligomer at 5000 g/mol, aging at 5 and 23°C for up to 275 days caused only a slight decrease in molecular weight. The GPC curves in Fig. 2 for the 5000 g/mol amide acid and imide oligomers of PETI-5 show the molecular weights to be very similar with M_n of 5438 and 5759 g/mol, M_w of 13 020 and 12 700 g/mol and M_z of 30 770 and 26 910 g/mol, respectively.

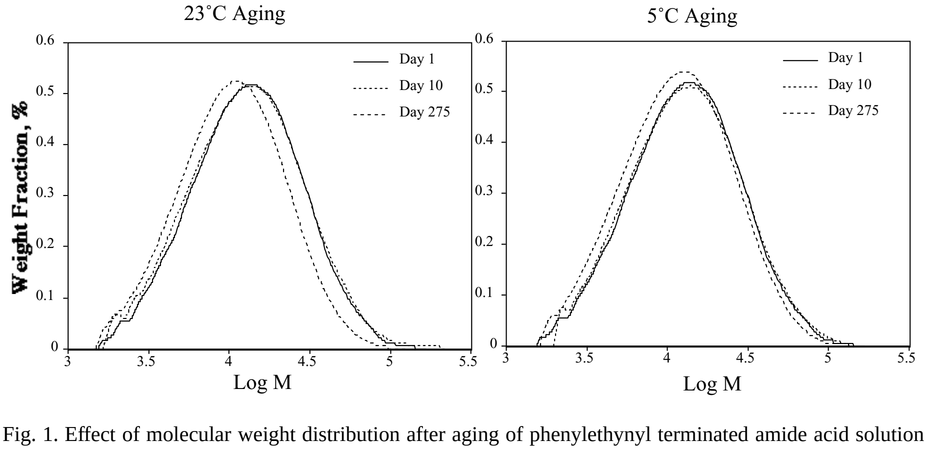


Fig. 1. Effect of molecular weight distribution after aging of phenylethynyl terminated amide acid solution.

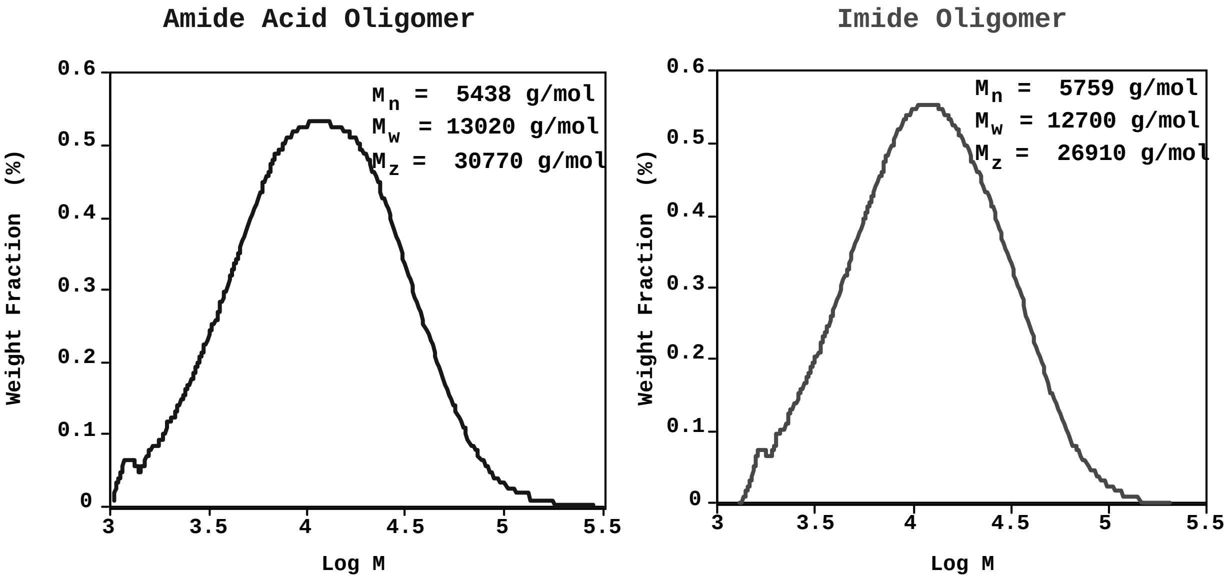


Fig. 2. Molecular weight distribution of PETI-5 oligomers.

In the PETI-5 series, calculated molecular weights (M_n) of 1250, 2500 and 5000 g/mol were prepared to determine the effect molecular weight had on the properties of the oligomers and the cured polymers. As shown in Table 2, the initial T_g for the 1250 g/mol imide oligomer is lower than the T_gs for the 2500 and 5000 oligomers as expected. The T_gs for the cured oligomers show the lower molecular weight cured oligomers have higher T_gs than the highest molecular weight cured oligomer presumably due to higher cross-link density. The melt viscosities show a dramatic effect of molecular weight where the 1250 g/mol imide oligomer has a melt viscosity significantly lower than the 2500 and 5000 g/mol imide oligomers. More comprehensive properties on the 1250, 2500 and 5000 g/mol oligomers are published elsewhere [29].

The properties of cured polymers from PETI-5, PPEI and PTPEI are presented in a series of tables. The mol% ratios of phenylethynyl groups in PETI-5, PPEI and PTPEI oligomers of about 5000 g/mol are 0.18, 0.15 and 0.34, respectively. The location of the phenylethynyl group may have an effect on reactivity. In Table 3, PETI-5 had the lowest cured T_g and also the lowest melt viscosity while PPEI with similar molar ratio of phenylethynyl groups had a cured T_g 9°C higher and also a higher melt viscosity. The melt viscosity of PTPEI oligomer may be deceptively high because of some reaction of the phenylethynyl groups during the measurement. The density of phenylethynyl groups in PTPEI is high which can allow for more frequent collision and reaction, thereby increasing the molecular weight and accordingly melt viscosity. With the higher phenylethynyl group concentration in PTPEI, the T_g of the cured polymer is higher than that of cured PETI-5 or PPEI because of higher cross-link density. The unoriented thin film tensile properties of solution cast films that were stage-cured through 1 h at 350°C in air are presented in Table 4. No definitive differences are present in the tensile strength and modulus values. The elongation of the PETI-5 film is significantly higher than that of the other films. The high toughness of cured PETI-5 is also evident in fracture energy (G_{Ic}, critical strain energy release rate) measurements on compact tension specimens where PETI-5, PPEI and PTPEI had values of 4795, 2070 and 1320 J/m, respectively. The high film elongation and the high compact tension fracture toughness of PETI-5 suggest that the

Table 2
Physical properties of PETI-5 of different molecular weights

Calculated $\bar{M}_n$ (g/mol)	η_{inh} (dl/g)[a]	T_g (T_m) (°C)[b]		Imide minimum melt viscosity (Pa s) (temperature in °C)
		Initial	Cured[c]	
1250	0.15	170 (320)	288	500 (335)
2500	0.20	210 (330)	277	9000 (371)
5000	0.27	210 (357)	270	100 000 (371)

[a] Determined on 0.5% (w/v) NMP solution of the amide acid at 25°C.

[b] Determined on powdered sample by DSC at a heating rate of 20°C/min.

[c] Determined on powdered sample cured in a sealed aluminum pan for 1 h at 371°C.

Table 3
Physical properties of phenylethynyl containing imide oligomers

Oligomer	η_{inh} (dl/g)[a]	T_g (T_m) (°C)[b]		Imide minimum melt viscosity (Pa s) (temperature in °C)
		Initial	Cured[c]	
PETI-5	0.27	210 (286)	270	100 000 (371)
PPEI	0.31	209	279	600 000 (371)
PTPEI	0.32	231 (282)	313	1 150 000 (371)

[a] Determined on 0.5% (w/v) NMP solution of the amide acid at 25°C.
[b] Determined on powdered sample by DSC at a heating rate of 20°C/min.
[c] Determined on powdered sample cured in a sealed aluminum pan for 1 h at 371°C.

thermally induced curing of the phenylethynyl groups proceeds predominantly in linear chain extension rather than the formation of a network structure. However some network structure must be present to explain the excellent stressed solvent resistance in cured PETI-5 films [10], moldings, bonded panels and composites [30]. Composites were exposed under stress to aircraft fluids such as hydraulic and deicing fluids, paint stripping solvents, alkaline cleaning solutions and jet fuel.

3.2. Adhesive properties

Supported adhesive films (also referred to as tapes) of the 1250, 2500 and 5000 g/mol PETI-5 oligomers and PPEI and PTPEI oligomers were prepared by coating 112 E-glass (A-1100 finish) with the NMP amide acid solutions. After drying, the film volatile contents were ~2%. Titanium (6Al–4V) to titanium (5V chromic acid anodized surface treatment) single lap shear specimens primed with the amide acid of the 5000 g/mol PETI-5 were fabricated by heating in an autoclave to 350°C for 1 h under 0.34 MPa. As presented in Table 5, essentially equivalent tensile shear strengths were obtained for the 2500 and 5000 g/mol PETI-5 at both test temperatures whereas the 1250 g/mol PETI-5 exhibited lower strengths. The lower strengths were partly due to excessive flow during fabrication resulting in thin glueline bond thicknesses. Failure modes for the tested specimens at 23°C were generally >95% cohesive while at 177°C the failure modes were about 75% cohesive. Both the 1250 and 2500 g/mol PETI-5 exhibited higher flatwise tensile strengths than the 5000 g/mol version presumably due to better flow.

Table 4
Unoriented thin film tensile properties

Oligomer	Test temperature (°C)	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
PETI-5	23	129.6	3.1	32
	177	84.1	2.3	83
PPEI	23	117.2	3.9	7
	177	64.1	2.6	9
PTPEI	23	139.3	3.4	10
	177	78.6	2.2	9

Titanium tensile shear specimens (5V chromic acid anodized surface treatment) of PPEI and PTPEI were fabricated under the same conditions as PETI-5 except a pressure of 1.4 MPa was used instead of 0.34 MPa. The supported adhesive films of PPEI and PTPEI exhibited less flow at elevated temperature than PETI-5 films. The PPEI specimens gave tensile shear strengths of 29.6 and 28.3 MPa at 23 and 177°C, respectively with about 75% cohesive failure. PTPEI specimens gave a tensile shear strength of 34.5 MPa at 23°C with 80% adhesive failure.

3.3. Composite properties

Carbon fiber unidirectional tapes were prepared by coating IM-7 fiber with the NMP amide acid solutions of PETI-5, PPEI and PTPEI on a prepregging machine. The tapes contained ~30–36% resin content with ~12–19% volatiles (NMP and water) to avoid splitting and to provide tack and drape. The composite processing cycle is presented in Fig. 3.

Initially a vacuum was applied and the tape lay-up was heated to 250°C and held for 1 h in the press without pressure. At the end of this hold, about 0.2% volatiles remained in the lay-up as determined by weight loss measurements at 350°C. Pressure was then applied while increasing the temperature to 371°C where it was held for 1 h under pressure. At the end of the 1 h hold, the composite was cooled and the pressure and vacuum released when the temperature was below 100°C. The composites generally exhibited excellent C-scans indicating good consolidation with little or no void content. Two important properties of composites, open hole compressive strength (OHC) and compressive strength after impact (CAI, impact level of 6.67 kJ/m), are presented in Table 6. The data is not normalized because the resin content of the composites from the 1250 g/mol PETI-5 oligomer was low (about 29%). Composite properties are generally not normalized unless the fiber volume is within a range of about 56–62%. Although the test description for an OHC specimen describes a crossply (e.g. 42/50/8 with 42% of the plies in the zero direction, actual lay-up $(+45/-45/90/0/0/+45/-45/0/0/+45/-45/0)_s$) specimen 30.5 cm in length and 3.8 cm wide with a 0.64 cm hole in the center, the dimensions of the

Table 5
Adhesive properties of PETI-5 oligomers

Calculated $\bar{M}_n$ (g/mol)	Test temperature (°C)	Tensile shear stress (MPa)	Flatwise tensile stress (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

specimens used in this work were 7.6 cm in length and 2.54 cm wide with a 0.64 cm diameter hole in the center. Industry has showed that comparable results are obtained from the smaller specimen. The CAI specimen is nominally 32 ply quasi-isotropic lay-up (25/50/25 with 25% of the plies in the zero direction, actual lay-up $(+45/0/-45/90)_s$) 15.2 by 10.2 cm. The specimen is impacted at an impact level of 6.67 kJ/m and the residual compressive strength is tested. Composites from the 1250 and 2500 g/mol PETI-5 oligomers gave values similar to those of composites from the 5000 g/mol PETI-5. However the 1250 and 2500 g/mol PETI-5 oligomers exhibited significantly better processability (more flow at less pressure) than the 5000 g/mol oligomer. The improvement in moldability of the lower molecular weight versions of PETI-5 is in agreement with what is expected based upon the melt viscosity data in Table 2. More extensive composite properties on the 1250, 2500 and 5000 g/mol PETI-5 composites are published elsewhere [29].

The composites of PETI-5 (5000 g/mol), PPEI and PTPEI whose properties are presented in Table 6 had comparable fiber volumes of about 58%. The OHC strengths of PTPEI composites are much higher than those of PPEI or PETI-5 presumably because of a higher modulus arising from higher cross-link density although this was not reflected in the modulus of thin films as reported in Table 4. The CAI strength of PTPEI is significantly lower than that of PETI-5 or PPEI for several reasons such as the lower toughness of the resin as evident in the fracture energy previously reported and also because of poorer interaction with the fiber. Composites with a favorable combination of properties are desired rather than a composite that may have an unusually high value in a particular test.

Thermal cycling tests were performed on fairly stiff crossply laminates with a 58/34/8 lay-up (58% of the plies are in the zero direction, actual lay-up $(+45/-45/90/0/0/+45/-45/0/0/+45/-45/0)_s$). Small composites were thermally cycled from −54 to 177°C at a heating rate of 8.3°C/min with a 1 h hold at −54 and 177°C. The composites were examined after 200 cycles under a microscope for microcracks. PETI-5 and PPEI composites showed no microcracks whereas the PTPEI composites microcracked.

4. Conclusions

Solutions of phenylethynyl containing amide acid oligomers were readily prepared and the amide acid solutions of PETI-5 were shown to exhibit excellent shelf-life stability. The amide acid solutions were used to prepare supported adhesive films and IM7 unidirectional tapes. These were subsequently employed in the fabrication of adhesive specimens and composites. PETI-5 adhesive specimens gave excellent strengths, significantly higher than those of PPEI and PTPEI specimens. PETI-5 and PPEI composites had comparable properties and a better combination of mechanical properties than that of PTPEI composites. PETI-5 oligomers of 1250, 2500 and 5000 g/mol provided high adhesive and composite properties with the lower molecular

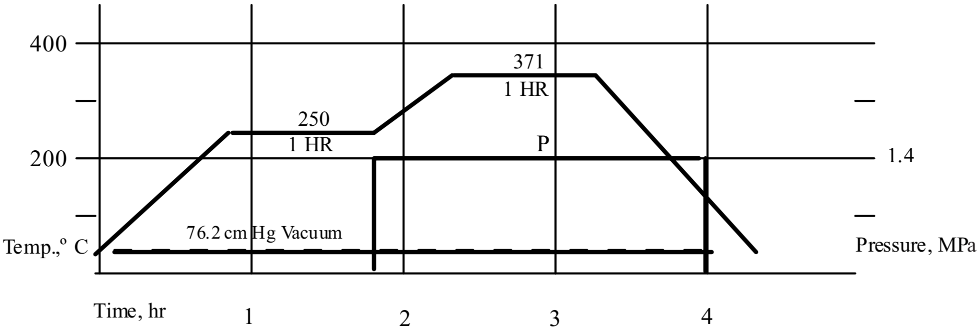


Fig. 3. Composite processing cycle.

Table 6
Preliminary composite properties (all oligomers at M_n of about 5000 g/mol)

Property	Lay-up	PETI-5	PPEI	PTPEI
OHC (MPa)	42/50/8			
RT dry		393	397	462
177°C		317	308	366
CAI (MPa)	25/50/25	324	296	241

weight oligomers exhibiting better compression moldability than the higher molecular weight version.

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