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Imide oligomers containing pendent and terminal phenylethynyl groups

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As part of a programme to develop high performance/high temperature structural resins for aeronautical applications, imide oligomers containing pendent and terminal phenylethynyl groups were prepared, characterized and the cured resins evaluated as adhesives and composite matrix resins. As a means of controlling the molecular weight between reactive sites (i.e. crosslink density), varying amounts of phenylethynyl groups were distributed randomly along the imide oligomer whose calculated number-average molecular weight was 5000 g mol^{-1}. Upon thermal cure at 350–371°C for 1 h in air, the phenylethynyl group undergoes a complex reaction resulting in chain extension, branching and crosslinking. The products depend upon several factors such as the relative concentration of phenylethynyl groups, molecular mobility of the growing polymer and conformational restrictions and have been postulated to be predominantly highly conjugated polyenes. In general, the cured resins have a favourable combination of properties including good thermal stability, solvent and moisture resistance and good toughness. The amide acid oligomer solutions were processed into thin films, adhesive tape and carbon fibre prepreg. Neat resin plaques were fabricated from imide oligomer powder by compression moulding. The maximum processing pressure was 1.4 MPa and the cure temperature varied from 350–371°C for 1 h for the composites, adhesive panels and neat resin mouldings. The properties of the cured imide oligomers containing pendent and terminal phenylethynyl groups are compared with those of cured oligomers of similar composition and molecular weight which contain either terminal or pendent phenylethynyl groups. Published by Elsevier Science Ltd.

(Keywords: imide oligomers; pendent and terminal phenylethynyl groups; high performance/high temperature resins)

INTRODUCTION

As part of a continuing effort to develop high performance/high temperature structural resins for aeronautical applications, imide oligomers containing latent thermally reactive groups have been under investigation. Aromatic polyimides are a class of thermally stable high performance polymers which are used in a variety of applications.The polymers are usually prepared via an amide acid intermediate by the reaction of an aromatic diamine with an aromatic dianhydride in a polar aprotic solvent. The amide acid is subsequently cyclodehydrated, either chemically or thermally, to afford the corresponding imide polymer[1,2]. The polymers typically exhibit high melt viscosities and, as a consequence, processability by compression and injection moulding is often difficult or unachievable. Melt flow can be enhanced by the incorporation of more flexible units such as arylene ether segments within the polymer backbone, by controlling the molecular weight and by endcapping; however, certain properties such as the modulus and glass transition temperature (T_g) are compromised.

An attractive approach to improve the melt processability of imide oligomers while retaining a high T_g and modulus has involved the incorporation of latent thermally reactive groups. Examples of latent thermally reactive groups (temperature, °C, of exothermic peak as measured by differential scanning calorimetry at a heating rate of 20°C min^{-1}) include maleimide (180), benzocyclobutene (200), ethynyl (250), nadimide (316), and phenylethynyl (350). The phenylethynyl group is desirable since by the proper choice of the oligomer backbone a wide processing window can be obtained. Upon thermal cure, the phenylethynyl group undergoes a complex reaction involving chain extension, branching, and crosslinking, without the evolution of volatiles to afford materials exhibiting a favourable combination of physical and mechanical properties. There are several ways to incorporate phenylethynyl groups into amide acid or imide oligomers. To date, a variety of imide oligomers/polymers containing phenylethynyl groups either pendent to the chain or at the chain ends have been prepared (*Figure 1*)[3-29]. The phenylethynyl containing oligomers exhibit good processability by either solution casting of the amide acid or compression moulding of the imide powder. Upon thermal cure, significant increases in the T_g relative to the uncured oligomer are observed. In addition, mechanical properties are improved without significant reduction in thermal stability.

High fracture energies and high elongations to break of unoriented thin films have been obtained for the polymers from the thermally cured phenylethynyl terminated imide oligomers (PETIs) prepared at a calculated $\overline{M}_n$ of 5000–9000 g mol^{-1} [15,16,18-21]. Prior to curing, the imide oligomers are brittle and will not form creasable films, particularly at $\overline{M}_n$s below ~9000 g mol^{-1}. The

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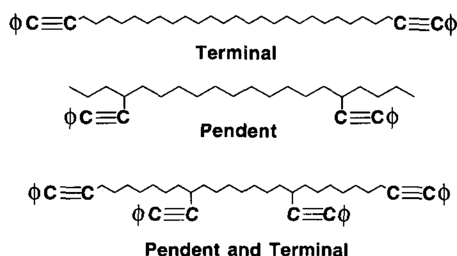


Figure 1 Phenylethynyl containing oligomers

high elongations exhibited by thin films of cured PETIs as well as the high fracture toughness are characteristics of linear thermoplastics not thermosets. Since the cured PETIs exhibited such a high toughness, it was postulated that increasing the crosslink density would produce a resin with improved mechanical properties (i.e. high T_g and modulus) while maintaining moderate toughness. One approach to obtaining a higher crosslink density was to reduce the overall chain length between the crosslink sites by preparing PETIs of lower $\overline{M}_n$. However, PETIs prepared at a calculated $\overline{M}_n$ of 1500 g mol^{-1} were extremely brittle prior to curing with some exhibiting crystalline melts at high temperature and consequently poor processability[20,21].

An alternative approach to increasing the crosslink density was to prepare oligomers containing both pendent and terminal phenylethynyl groups whereby the distance between reactive sites could be controlled by the number of pendent phenylethynyl groups distributed along the backbone. This would effectively increase the crosslink density of the cured resin while retaining processability and reasonable toughness after curing. The work reported herein concerns the synthesis, characterization, and preliminary evaluation of imide oligomers containing pendent and terminal phenylethynyl groups and the corresponding thermally cured polymers. In an attempt to better understand the relationship between phenylethynyl content and configuration on cured resin properties, properties from oligomers containing both pendent and terminal phenylethynyl groups (PTPEI) are compared with those of imide oligomers of comparable molecular weight containing either terminal (PETI) or pendent (PPEI) phenylethynyl groups.

EXPERIMENTAL

Starting materials

3,5-Diamino-4′-phenylethynylbenzophenone (DPEB, m.p. 154–156°C) was prepared as previously described[29]. 4-(3-Aminophenoxy)-4′-phenylethynylbenzophenone (APEB, m.p. 137–139°C) was obtained from Daychem Laboratories, Inc. 3,4′-Oxydianiline (3,4′-ODA, Mitsui, m.p. 84°C) and 1,3-bis(3-aminophenoxy)benzene (APB, Mitsui Toatsu, m.p. 107–109°C) were used as received. 4,4′-Oxydiphthalic anhydride (ODPA, Occidental) was recrystallized from acetic anhydride/glacial acetic acid (m.p. 229°C). 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA, Ube Industries Ltd, m.p. 305–308°C), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA, Allco, m.p. 227°C), pyromellitic dianhydride (PMDA, Aldrich, 282–284°C), 4-phenylethynylphthalic anhydride (PEPA, Imitec, m.p. 152°C) and high purity *N*-methyl-2-pyrrolidinone (NMP, Fluka) were used as received.

Terminal phenylethynyl imide oligomers

PETI oligomers were prepared as previously described[20,21].

Pendent phenylethynyl imide oligomers

PPEI oligomers were prepared as previously described[29].

Pendent and terminal phenylethynyl imide oligomers

PTPEI oligomers with a calculated number-average molecular weight ($\overline{M}_n$) of 5000 g mol^{-1} were prepared by reacting various aromatic dianhydrides with 3,4′-ODA, DPEB and in some cases APB and endcapping with PEPA. *Scheme 1* is representative of the experimental procedure used to prepare the PTPEI oligomers.

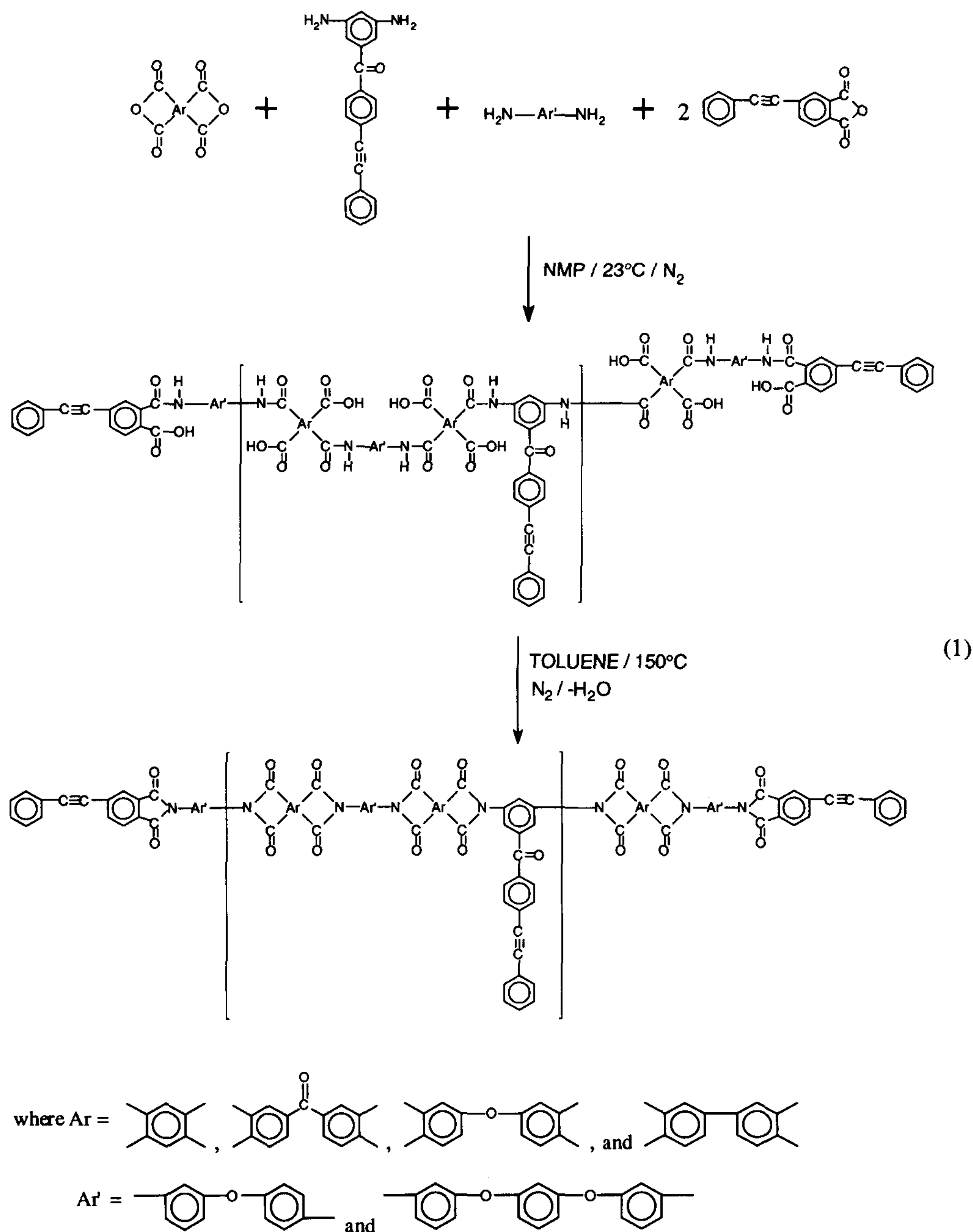
Into a flame-dried 100 ml three necked round-bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed 3,4′-ODA (3.722 g, 0.0186 mol), DPEB (1.0246 g, 0.0033 mol) and 8 ml NMP. After dissolution, a slurry of BPDA (5.8502 g, 0.0199 mol) and PEPA (0.9847 g, 0.0040 mol) in 9 ml of NMP was added and washed in with an additional 9 ml of NMP to afford a 30.1% solids content (w/w) solution. The reaction mixture was stirred at room temperature ~24 h under a nitrogen atmosphere. An aliquot of the pendent and terminal phenylethynyl amide acid (PTPEAA) solution was removed to determine the inherent viscosity and to cast a thin film. Toluene (60 ml) was added to the remaining PTPEAA solution and the temperature was increased and maintained at ~180°C for ~16 h under a nitrogen atmosphere. Water was removed by azeotropic distillation using a Dean Stark trap. As cyclodehydration occurred, the imide precipitated from solution. The mixture was cooled, the PTPEI oligomer was poured into water, isolated by filtration, washed in hot water, and then in warm methanol, and dried under vacuum at 220°C to provide a tan powder. The T_g of the uncured as-isolated PTPEI oligomer (differential scanning calorimetry, d.s.c., 20°C min^{-1}) was 226°C with a transient crystalline melt temperature (T_m) at 283°C and the exothermic onset and peak occurred at 348°C and 406°C, respectively. Following the general procedure above, amide acid solutions were prepared on a 0.50 molar scale.

Films

NMP solutions (~30% w/w solids) of the pendent/terminal phenylethynyl amide acid (PTPEAA) oligomers were centrifuged, the decantates were doctored onto clean, dry plate glass and dried to tack-free forms in a low humidity chamber. The films on glass were dried in flowing air at 100, 225, and 350°C for 1 h each. Unoriented thin film tensile properties were determined according to ASTM D882 using four specimens per test condition.

Moulded specimens

Powdered imide oligomers (approximately 8.5 g) were compression moulded in a 3.2 cm^2 stainless steel mould by heating to 371°C under 1.4 MPa and holding for 1 h. Miniature compact tension specimens (1.6 cm × 1.6 cm × 0.95 cm thick) were machined from the mouldings and subsequently tested to determine their fracture toughness (K_{Ic}, critical stress intensity factor) according to ASTM E399 using four specimens per test condition. Fracture energy (G_{Ic}, critical strain energy release rate) was



Synthesis of PTPEIs

Scheme 1

calculated using the mathematical relationship $G_{Ic} = (K_{Ic})^2/E$, where E is the tensile modulus of the material.

Adhesive specimens

Adhesive tape was prepared by a multiple coating of 112E glass with an A-1100 finish with a 20% (w/w) NMP solution of the PTPEAA oligomer ($\overline{M}_n = 5000\,\mathrm{g\,mol^{-1}}$) and subsequently stage-dried to 225°C in a forced air oven after each coat. A-1100 is an aminopropyltriethoxysilane sizing. The sizing does not appear to affect adhesive performance. Heat cleaned 112E glass has given the same adhesive performance as 112E glass with an A-1100 finish. After the appropriate thickness had been obtained, the tape was dried to 250°C to a final volatile content of ~2%. Titanium (Ti, 6Al-4V) tensile shear specimens with either chromic acid anodized (5V) or PASA-Jell 107 (Products Research and Chemical Corp., Semco Division) surface treatments were fabricated in a press at 350°C under various pressures for 1 h. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition. Chromic acid anodized (5V) Ti adherends were provided by The Boeing Company.

Composite specimens

NMP solutions (35% solids w/w) of PTPEAA oligomers were used to coat unsized IM-7 carbon/graphite fibre (Hexcel Corp., formerly Hercules, Inc.) on a multipurpose tape machine to afford unidirectional tape with resin contents ranging from 33–35% and volatile

contents of 20–22%. The solutions had Brookfield viscosities at room temperature ranging from 20 000 to 30 000 centipoise. Laminates of different dimensions and fibre orientations were fabricated in a vacuum press using stainless steel moulds by heating to 371°C under 1.4 MPa and holding for 1 h. The composite panels were ultrasonically scanned (C-scanned), cut into specimens, and tested for various mechanical properties according to ASTM procedures.

Gel permeation chromatography

Gel permeation chromatography (g.p.c.) was performed on a Waters 150C g.p.c. equipped with a model 150R differential viscosity detector and a differential refractive index detector. G.p.c. analyses were performed on dilute solutions of the PTPEAAs in freshly distilled NMP containing 0.02 M phosphorus pentoxide. 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 to 10^7 g mol^{-1} in series with a Styragel HT 3 column covering the molecular weight range of 10^2 to 10^4 g mol^{-1}. 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^{-1}. In all cases duplicate runs were performed.

Other characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) solutions in NMP at 25°C. Differential scanning calorimetry (d.s.c.) was conducted on a Shimadzu DSC-50 thermal analyser at a heating rate of 20°C min^{-1} with the melting point taken at the minimum of the endothermic peak (T_m) and with the glass transition temperature (T_g) taken at the inflection point of the ΔT vs temperature curve. Dynamic thermogravimetric analyses (t.g.a.) were performed on a Seiko 200/220 instrument on powder samples at a heating rate of 2.5°C min^{-1} in air. Brookfield viscosity was obtained on a Brookfield LVT Synchro-Lectric viscometer at 23°C.

RESULTS AND DISCUSSION

Pendent/terminal phenylethynyl imide oligomers were prepared at a calculated $\overline{M}_n$ of 5000 g mol^{-1} via the amide acid in NMP by the reaction of an aromatic dianhydride with a stoichiometric excess of aromatic diamine(s), consisting of the appropriate quantity of DPEB, 3,4′-ODA and in some cases APB, and endcapped with PEPA (equation (1)). These materials are random co-oligomers with varying amounts of pendent phenylethynyl groups distributed randomly along the oligomer backbone and at the chain ends. The η_{inh} of the PTPEAA oligomers ranged from 0.21 to 0.36 dl g^{-1}. Portions of the PTPEAAs were used to cast films and the remaining solution cyclodehydrated to the imide via azeotropic distillation with toluene. As imidization occurred, the PTPEI oligomers precipitated from solution.

The initial T_g of the uncured oligomers (d.s.c., 20°C min^{-1}) ranged from 209 to 231°C with transient T_ms ranging from 274 to 284°C (*Table 1*). The exothermic onset and peak attributed to the reaction of the phenylethynyl group occurred at ~350 and ~410°C, respectively, and was comparable to that of PETI and PPEI oligomers[19,22,29]. For comparative purposes, similar data for PETI-5 and PPEI-1 are included in *Table 1*. PETI-5 and PPEI-1 are imide oligomers with a calculated $\overline{M}_n$ of 5000 g mol^{-1}, PETI-5 contains only terminal phenylethynyl groups while PPEI-1 contains only pendent phenylethynyl groups and is endcapped with phthalic anhydride (PA). The exact compositions and the phenylethynyl content are listed in *Table 1*. After a cure at 350°C for 1 h in a sealed d.s.c. pan, the T_gs of

Table 1 Characterization of pendent and terminal phenylethynyl imide oligomers

Imide oligomer[a]	η_{inh} (dl g^{-1}, amide acid)[b]	T_gi (T_m, °C)[c]	T_gc (°C)	Temp. of 5% weight loss in air (°C)[d]	
				Initial	Cured
1	0.36	ND[e]	ND	446	481
2	0.28	269	296	451	487
3	0.30	ND	260	447	487
4	0.21	223 (274)	310	463	502
5	0.32	231 (282)	313	465	532
6	0.26	209 (278)	300	478	–
7	–	224	283	496	496
8	0.29	224 (284)	289	499	511
PETI-5	0.27	210 (286)	249	505	503
PPEI-1	0.31	240	279	–	505

[a] 1, 0.90 3,4′-ODA/0.10 DPEB/PMDA/PEPA (~29 mol% phenylethynyl)
2, 0.90 3,4′-ODA/0.10 DPEB/BTDA/PEPA (~29 mol% phenylethynyl)
3, 0.90 3,4′-ODA/0.10 DPEB/ODPA/PEPA (~29 mol% phenylethynyl)
4, 0.90 3,4′-ODA/0.10 DPEB/BPDA/PEPA (~28 mol% phenylethynyl)
5, 0.85 3,4′-ODA/0.15 DPEB/BPDA/PEPA (~33 mol% phenylethynyl)
6, 0.85 3,4′-ODA/0.15 DPEB/BPDA/3-APEB (~32 mol% phenylethynyl)
7, 0.75 3,4′-ODA/0.15 APB/0.10 DPEB/BPDA/PEPA (~28 mol% phenylethynyl)
8, 0.70 3,4′-ODA/0.15 APB/0.15 DPEB/BPDA/PEPA (~34 mol% phenylethynyl)
PETI-5 0.85 3,4′-ODA/0.15 APB/BPDA/PEPA (~18 mol% phenylethynyl)
PPEI-1 0.85 3,4′-ODA/0.15 DPEB/BPDA/PA (~15 mol% phenylethynyl)

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

[c] Determined by d.s.c. at a heating rate of 20°C min^{-1}; i = initial T_g of as-isolated oligomer; c = cured in sealed d.s.c pan/350°C/1 h

[d] Determined by t.g.a. at a heating rate of 2.5°C min^{-1}

[e] ND = not detected

the PTPEIs increased ~30–90°C with respect to the as-isolated oligomers, and no melting endotherms or reaction exotherms were evident in the cured polymers. The trend of the T_gs based on the dianhydride of the thermally cured PTPEI oligomers containing 10 mol% of DPEB was PMDA > BPDA > BTDA > ODPA. A similar trend has been observed for other polyimides. For a given pair of PTPEI oligomers (imides 4 and 5 and imides 7 and 8), increasing the pendent phenylethynyl content (DPEB) from 10 to 15 mol% (total phenylethynyl content of 28 to 33 mol%, respectively) resulted in an increase of 3–6°C in the cured T_g.

The effect of heating rate upon the thermal transitions of the PTPEI oligomers was investigated by d.s.c. at heating rates of 5–50°C min^{-1} in a sealed pan. As the heating rate increased for the imide-8 oligomer as shown in *Table 2*, the initial T_g and T_m increased from 218 to 232°C and from 275 to 294°C, respectively. The exothermic onset and peak maximum also increased from 324 to 400°C and from 370 to 462°C, respectively. Similar results were obtained for PETI oligomers[20,21]. The T_g of the imide-8 oligomer cured in a sealed d.s.c. pan at 350°C for 1 h decreased from 300 to 294°C as the heating rate increased from 5 to 20°C min^{-1}. Similar results were obtained for the PETIs cured at 350°C for 1 h[20,21]. When the imide-8 oligomer was cured in a sealed d.s.c. pan at 371°C for 1 h, the T_g of the cured polymer was ~305°C and was relatively unaffected by increasing the heating rate from 5 to 20°C min^{-1}. PETI-5 exhibits a T_g of 270°C (via d.s.c. at 20°C min^{-1}) after a 1 h cure at 371°C[20,21].

Films

Unoriented thin films cast from NMP solutions of the amide acid and cured in flowing air to 350°C for 1 h were transparent orange, tough and flexible with T_gs ranging from 290 to 313°C (*Table 3*). The film T_gs were typically greater than those of the polymers cured in a sealed d.s.c. pan. This phenomenon has been observed previously for PETIs, and has been attributed to exposure to air in comparison to that of curing the oligomer in a sealed d.s.c. pan, mould or under vacuum, where the exposure to air is limited[20,21].

The room temperature tensile strength and modulus were ~139 MPa and 3.4 GPa, respectively, with ~50% retention of tensile strength and ~57% retention of tensile modulus at 200°C. Similar results were obtained for PETI-5 (0.85 3,4′-ODA/0.15 APB/BPDA/PEPA) (*Table 3*). However, the % elongation to break of the PTPEI films were significantly lower than that of PETI films. This difference was attributed to the higher cross-link density of the PTPEI. PPEI-1 exhibited the highest modulus at both 23 and 177°C, which is surprising since this material has the least amount of phenylethynyl groups (15 mol%). The phenylethynyl content of PETI-5 is ~18 mol%, while that of the PTPEI materials is ~25–30 mol%.

Mouldings

The fracture toughness (K_{Ic}) of PETI-5 ($\overline{M}_n$ of 5000 g mol^{-1}) specimens compression moulded at 350°C under 1.0 MPa for 1 h was 3877 Pa m$^{1/2}$ and the fracture energy (G_{Ic}) was 4795 J m^{-2} (*Table 4*)[20,21]. The

Table 2 Effect of heating rate on thermal transitions of imide-8

			Exothermic peak		Cured T_g (°C)	
Heating rate (°C min^{-1})	T_gi (°C)	T_m (°C)	Onset (°C)	Max (°C)	350°C	371°C
5	218	275	324	370	300	303
10	220	277	333	401	295	308
20	223	285	337	420	294	305
50	232	294	400	462	–	–

Table 3 Unoriented thin film tensile properties

Imide oligomer[a]	T_g (°C)[b]	Test temp. (°C)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
4	306	23	141.3	3.41	20
		177	83.4	2.04	27
		200	73.8	2.06	30
5	318	23	139.3	3.43	10
		177	78.6	2.22	9
		200	68.3	1.84	17
7	290	23	130.3	3.41	12
		177	74.5	2.07	34
		200	63.4	1.90	25
8	301	23	140.7	3.39	15
		177	77.2	2.12	24
		200	68.3	1.97	28
PETI-5	249	23	129.6	3.11	32
		177	84.1	2.33	84
		200	64.1	1.91	69
PPEI-1	279	23	117.2	3.90	7
		177	64.1	2.62	9

[a] See *Table 1* for oligomer compositions
[b] Determined by d.s.c. at 20°C min^{-1} on film samples cured at 100, 225, 350°C for 1 h each in flowing air

high K_{Ic} and G_{Ic} values of PETI-5 and other PETIs, like the high elongation to break of unoriented thin films, are more typical of linear thermoplastics than thermosets. Apparently the cure reaction of PETIs results in a significant amount of chain extension. The incorporation of phenylethynyl groups both terminal and pendent to the oligomer chain, lowers the K_{Ic} and G_{Ic} values as compared to those of the PETIs. The K_{Ic} of imide-5 ($\overline{M}_n$ of $5000\,g\,mol^{-1}$) specimens compression moulded at 371°C under 1.4 MPa for 1 h was 1318 Pa m$^{1/2}$ and the G_{Ic} was 511 J m^{-2}. Flash from the moulding of imide-5 exhibited a T_g of 312°C. By replacing 15 mol% of 3,4'-ODA with APB in the oligomer composition, the K_{Ic} of imide-8 ($\overline{M}_n$ of $5000\,g\,mol^{-1}$) specimens compression moulded at 371°C under 1.4 MPa for 1 h was 1919 Pa m$^{1/2}$ and the G_{Ic} was 566 J m^{-2}. Flash from the moulding of imide-8 exhibited a T_g of 302°C. The fracture toughness of PPEI-1 falls in between that of PETI-5 and PTPEI-5 and 8, albeit closer to those of the latter. Compression strength after impact in a composite is related to some degree to neat resin fracture toughness. Studies have shown that the neat resin fracture toughness should be at least 700 J m^{-2}, to obtain reasonable compression strength after impact in a composite[30].

Table 4 Fracture toughness

Imide oligomer	T_g (°C)	K_{Ic} (Pa m$^{1/2}$)	G_{Ic} (J m^{-2})
5	313	1318	511
8	301	1919	566
PETI-5	270	3877	4795
PPEI-1	279	2066	1090

Table 5 Preliminary 23°C Ti tensile shear strengths of Imide-5

Processing conditions	Tensile shear strength (MPa)	Failure mode (% cohesive)
PASA Jell		
371°C/0.34 MPa/1 h	17.2	15
371°C/0.69 MPa/1 h	21.4	40
371°C/1.4 MPa/1 h	20.7	0
300°C/1.4 MPa/0.5 h, 350°C/1.4 MPa/1 h	27.6	0
Chromic acid anodized (5 V)		
350°C/1.4 MPa/1 h	34.5	20

η_{inh} (NMP, 0.5%, 25°C, AA) = 0.30 dl g^{-1}
Tape volatile content ~2%, cured T_g (d.s.c., 20°C min^{-1}) = 313°C

Adhesives

Ti-to-Ti tensile shear specimens with PASA Jell or CAA (5 V) surface treatments were fabricated at 371°C for 1 h under 0.34 to 1.4 MPa using imide-5. The 23°C strengths ranged from 17.2 to 27.6 MPa with predominantly adhesive type failure presumably due to incompatibility of the resin with the PASA-Jell surface treatment (*Table 5*). Tensile shear strengths of 34.5 MPa were obtained for Ti adherends with CAA (5 V) surface treatment; however, the failure mode was still predominantly adhesive.

Ti-to-Ti tensile shear specimens of imide-8 fabricated at 350°C under 1.4 MPa for 1 h exhibited a strength of 34.5 psi at 23 and 177°C with ~50 to 75% cohesive failure, respectively (*Table 6*). Specimens tested at 232 and 260°C retained ~80 and ~50% of room temperature properties, respectively. This was unexpected since the T_g of the cured polymer was 289°C. Unstressed lap shear specimens exposed to hydraulic fluid and jet fuel for 72 h at ambient temperature exhibited a slight decrease in tensile shear strengths when tested at 23, 177, and 200°C. However after a 72 h water boil, the strength decreased ~20% at 23°C and ~25% at 177 and 200°C, presumably due to some degradation of the surface (interface) and not the polymer.

PETI-5 Ti-to-Ti tensile shear specimens (PASA-Jell 107 surface treatment) fabricated under 0.7 MPa for 1 h at 350°C exhibited strengths of 49.0 and 29.7 MPa when tested at 23 and 177°C, respectively, with 100% cohesive failures[20,21]. PPEI-1 Ti-to-Ti adhesive specimens fabricated under 1.4 MPa for 1 h at 350°C exhibited tensile shear strengths of 27 MPa at 23°C and 28.3 MPa at 177°C with predominantly cohesive failures[29].

Composites

Carbon fibre reinforced composites of imide-5 and Imide-8 ($\overline{M}_n$ of $5000\,g\,mol^{-1}$) were fabricated from solution coated unsized IM-7 carbon graphite fibre using the cure cycle originally developed for PETI-5 shown in

Table 6 Tensile shear strengths of imide-8 after unstressed solvent exposure

Solvent exposure (72 h)	Test temp. (°C)	Tensile shear strength (MPa)	Failure mode (% cohesive)
Control (no exposure)	23	34.5	50
	177	34.5	75
	200	32.4	90
	232	27.6	100
	260	17.9	50
Water boil	23	26.9	5
	177	26.2	70
	200	24.1	80
Hydraulic fluid (Chevron Hyjet IV)	23	32.4	15
	177	29.6	75
	200	29.6	85
Jet fuel (JP-5)	23	33.1	20
	177	31.7	80
	200	30.3	85

η_{inh} (NMP, 0.5%, 25°C, AA) = 0.30 dl g^{-1}, T_g = 289°C
Tape volatile content ~2%

Figure 2[31]. Laminates were fabricated from unidirectional tapes prepared from two different batches of each oligomer. Typically, the tapes contained ~33–35% resin content and ~20% volatiles (NMP and water) to provide tack and drape. During the first stage of the processing cycle, virtually all of the NMP and water from imidization were removed prior to application of pressure[31].

IM-7 laminate properties of two PTPEIs (imide-5 and imide-8) are presented in *Table 7*. For comparative purposes, the properties of PETI-5 and PPEI-1 are included. It should be noted that laminate properties of PETI-5 have been optimized whereas those of PPEI-1 and PTPEIs are preliminary. All of the laminates were fabricated using the cure cycle as shown in *Figure 2*. The laminates generally exhibited excellent C-scans indicating good consolidation and void contents were typically <1.5%. The fibre volume of all laminates tested ranged from 57 to 66%.

The flexural strengths and moduli of imide-5, PETI-5 and PPEI-1 are comparable at 23 and 177°C. Imide-8 exhibited lower strengths at 23 and 177°C, but the moduli are comparable. Imide-8 exhibited high short beam shear strength at 23°C, but only ~50% retention of 23°C values at 177°C. PPEI-1 exhibited the highest short beam shear strength at 177°C of all the composites involved in this study. Imide-8 exhibited identical open hole compressive strengths and compression strengths after impact as PETI-5 at both ambient and elevated temperatures. This is surprising since imide-8 has a T_g of 289°C and contains ~33 mol% phenylethynyl groups, while PETI-5 has a T_g of 270°C and contains 18 mol% phenylethynyl groups. Imide-5 exhibited higher open hole compressive strengths than PETI-5 at 23 and 177°C wet, however compression strength after impact is lower. It is interesting to note that PETI-5 and PPEI-1 have comparable CAIs, yet PETI-5 has a significantly higher neat resin fracture toughness. This is because CAIs reflect a complex interaction of several components, one of which is neat resin fracture toughness. Even imide-5 has a reasonable CAI, yet it had a low neat resin fracture toughness. Therefore it can be concluded that the increase in phenylethynyl crosslink density relative to that of PETI-5 translated to an improvement in composite compression properties (i.e. OHC strength), while maintaining reasonably good damage tolerance (i.e. CAI).

Gel permeation chromatographic analyses

G.p.c. analyses were performed on as-prepared amide acid solutions of imide-5 and imide-8, to assess molecular weight and molecular weight distribution. The data for duplicate runs of the two PTPEAAs are presented in *Table 8*. In general, the g.p.c. information agreed well with the calculated molecular weight, and the amide acid oligomer exhibited a Gaussian molecular weight distribution with a polydispersity of ~2. The reproducibility between duplicate runs was excellent.

To assess the effect of aging amide acid oligomer solution on changes in molecular weight distribution, solutions (35% solids) were stored at 5°C and at room temperature, and analyses were performed periodically over an 80-day period. The effect of aging imide-5 PTPEAA solution on intrinsic viscosity and $\overline{M}_n$ is

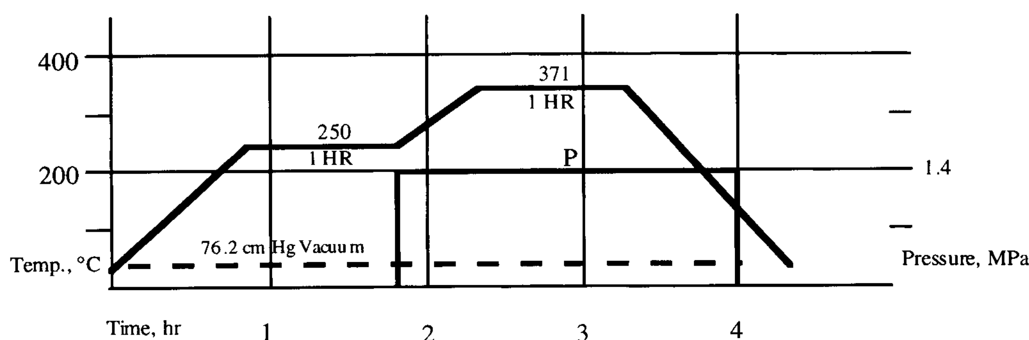


Figure 2 Laminate processing cycle

Table 7 IM-7 Laminate properties[a]

Property	Lay-up	Test temp. (°C)	Imide-5	Imide-8	PETI-5[b]	PPEI-1[c]
Flexural strength (MPa)	Uni	23	1786	1669	1787	1795
		177	1380	1200	1442	1513
Flexural modulus (GPa)	Uni	23	142	138	145	148
		177	138	131	134	142
Short beam	Uni	23	–	124.1	106.6	93.1
Shear strength (MPa)		177	–	62.7	62.8	73.1
Open hole compression strength (MPa)[d]	$\{\pm45/90/0/0 \pm 45/0/0 \pm 45/0\}_{2s}$	23	448	–	429	397
		177 (wet)	366	–	318	308
Compression strength after impact (MPa)[d]	Quasi-isotropic	23	242	–	317	297

[a] Composite cured 1 h at 371°C/1.4 MPa
[b] Ref. 31
[c] Ref. 29
[d] Normalized to 62% fibre volume

presented in *Figures 3* and *4*, respectively. After 20 days at room temperature, the intrinsic viscosity dropped from ~0.255 to 0.243. This trend continued and after 80 days at room temperature the intrinsic viscosity was ~0.225 (*Figure 3*). When stored at 5°C, the intrinsic viscosity changed from 0.255 to 0.250 dl g^{-1} over the same period. The $\overline{M}_n$ followed a trend similar to that exhibited by the intrinsic viscosity and dropped from ~5900 to 5100 g mol^{-1} after 80 days at room temperature. The sample stored at 5°C exhibited a change in $\overline{M}_n$

Table 8 Summary of g.p.c. analyses of PTPEAAs

Sample	$\overline{M}_n$ (g mol^{-1})	$\overline{M}_W$ (g mol^{-1})	$\overline{M}_z$ (g mol^{-1})	Polydispersity	Intrinsic viscosity (dl g^{-1})
PTPEAA-5	7451	13 600	23 480	1.8	0.253
	7565	13 510	23 670	1.8	0.250
PTPEAA-8	7238	15 180	33 910	2.1	0.254
	7144	15 570	33 440	2.2	0.260

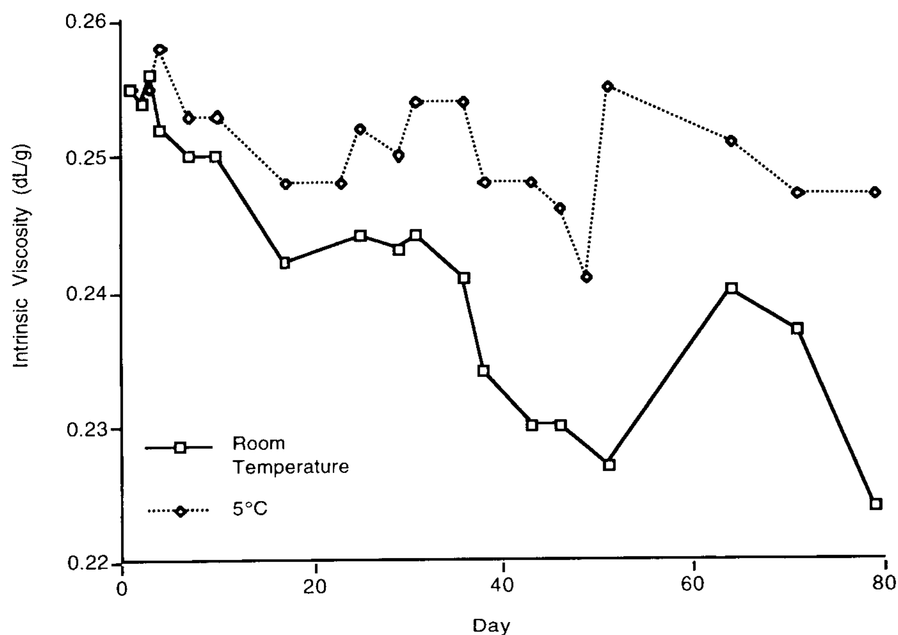


Figure 3 Effect of aging on intrinsic viscosity of PTPEAA-1

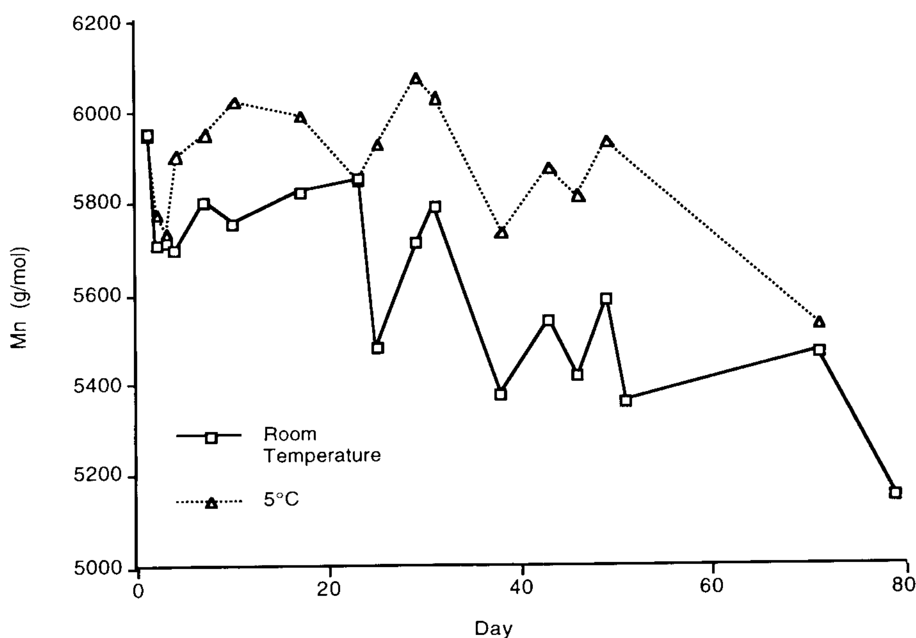


Figure 4 Effect of aging on $\overline{M}_n$ of PTPEAA-1

from 5900 to 5600 g mol^{-1}. This study indicates that short term storage of PTPEAA solutions under ambient conditions is acceptable, but long term storage will require refrigeration. The effects of the changes in intrinsic viscosity and $\overline{M}_n$ on laminate properties has not been determined.

SUMMARY

Amide acid and imide oligomers containing pendent and terminal phenylethynyl groups were prepared at calculated $\overline{M}_n$s of 5000 g mol^{-1}, characterized and preliminary neat resin, adhesive and carbon fibre reinforced laminate properties were determined. The cured oligomers exhibited high T_gs and high unoriented thin film tensile properties. Adhesive panels and carbon fibre laminates were readily fabricated under 1.4 MPa. Titanium tensile shear specimens fabricated from one composition exhibited excellent retention of room temperature properties when tested at 232°C. Preliminary composite properties of one system exhibited high open hole compressive strengths with excellent retention of strength when tested at 177°C wet.

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