High Temperature Organic/Inorganic Addition Cure Polyimide Composites, Part 1: Matrix Thermal Properties

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Received 15 January 2007; accepted 6 April 2007
DOI 10.1002/app.27463
Published online 5 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Structure-thermal property interrelationships are characterized and reported for organic/inorganic addition cure polyimide composite matrices based on 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, the reactive terminal group 4-phenylethynyl phthalic anhydride, and stoichiometric controlled diamine ratios of 1,3-phenylenediamine, 1,4-phenylenediamine, or 4,4′-(1,3-phenylenediisopropylidene) bisaniline, combined with bis(*p*-aminophenoxy) dimethyl silane or an α, ω-bis(3-aminopropyl) polydimethylsiloxane oligomer. Polymerization of monomer reactants resin solutions, carbon fiber prepregs and composites, and imidized oligomers are characterized to relate molecular chemical structure and morphology to glass transition temperature, processing characteristics, thermodynamic properties, and thermal stability. Glass transition temperature, thermal decomposition temperature, and char yield were found to increase with increasing siloxane block length in the imide backbone. As the concentration of inorganic component in the imide oligomer backbone increased, the cured glass transition temperature decreased. Char yield and thermal decomposition temperature were observed to decrease as the inorganic component concentration increased. Incorporation of bis(*p*-aminophenoxy) dimethyl silane into the imide oligomer structure did not provide any significant advantages over traditional polyimides relative to thermal properties or composite processing, but aminosiloxanes improved composite toughness, prepreg tack, and composite processability. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3557–3567, 2008

Key words: composites; high temperature materials; polyimides; polysiloxanes

INTRODUCTION

Polymer matrix composites (PMCs) can provide a significant advantage over metals in a multitude of commercial and aerospace structural components as a result of dramatic weight savings, strength improvements, part count reductions, high specific mechanical properties, design flexibility due to tailorable anisotropy, dielectric properties, and lower manufacturing costs. In the aerospace industry, advanced PMCs are classified by their maximum use temperature (based on hot-wet mechanical performance), and can be divided into four temperature regimes, displayed in Table I.

Structural polyimide matrices (predominantly thermosetting addition polyimides) yield the best balance of processability, mechanical properties, and thermo-oxidative stability of known organic materials.[1,2] Many commercial addition polyimides possess a balance of properties suitable for aerospace applications. NASA, DoD laboratories, academia, and industry have been active in developing this technology over the past 30 years in response to the ever increasing need for light weight structural materials with excellent environmental durability. For PMCs, the higher the service temperature capability the more enabling is the technology.

The NASA Lewis Research Center (now Glenn Research Center) developed PMR-15 in the 1970s as a processable addition polyimide comprised of a mixture of monomers in an alcohol solvent that are subsequently used to impregnate reinforcing fibers. The resin is cured through a two-step oligomeric condensation reaction and a final addition reaction for chain extension and crosslinking. PMR-15 was a breakthrough in polyimide matrix polymers as it allowed for volatile free final curing and crosslinking, enabling fabrication of fully densified components at relatively benign pressures. PMR-15 and its polymerization of monomer reactants (PMR) approach are still used today, but new resins are preferred where possible due to the carcinogenic 4,4′-methylene dianiline component in PMR-15.

Second generation systems, such as NASA PMR II-50, the Air Force AFR700B, DuPont Avimid® N, and many others were developed to improve the temperature capability over PMR-15 and reduce the toxicity.[2,3]

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Contract grant sponsor: National Science Foundation; contract grant number: OII-0548639.

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TABLE I
Hot/Wet Thermal Performance Regimes for Aerospace Grade PMCs

Continuous maximum hot/wet service temperature	Characteristic matrix polymers
121°C (250°F)	Epoxies, vinyl esters, phenolics
177°C (350°F)	Advanced epoxies, bismaleimides, cyanate esters
232°C (450°F)	Advanced cyanate esters, polyimides, phthalonitrile
288°C (550°F)	Advanced polyimides

These systems are, however, difficult to process into thick components, some have poor toughness and are susceptible to microcracking, and all suffer from irreversible damage due to hydrolytic degradation.

Scientists and engineers at NASA Langley Research Center recently developed a variety of polyimides based on technology invented by National Starch and Chemical Company.[4] This addition polyimide technology utilized a new oligomer end-cap, 4-phenylethynyl phthalic anhydride (4PEPA), to yield substantial improvements in toughness, processing window (i.e. allows for complete imidization prior to cure), melt viscosity, and hydrolytic stability as compared to norbornene, amine, or anhydride terminated polyimides.[3,5] 4PEPA terminated polyimides cure via a free radical crosslinking mechanism at temperatures above ~ 300°C. Since the development of diaryl substituted acetylene technology by National Starch and Chemical Company, NASA has commercialized a number of composite matrix systems based on this chemistry, including PETI-5, PETI-298, and PETI-330 (Fig. 1).

In recent years there has been a strong research interest in hybrid organic/inorganic polymers in an attempt to incorporate properties of siloxanes, silica, and other inorganics into polymers through sol–gel routes.[6–36] This has been especially true for poly (imide siloxanes) in the microelectronics industry. Incorporation of flexible siloxane segments significantly enhances flexibility in the polyimide backbone, can improve thermo-oxidative stability and mechanical performance, improves transparency, reduces the dielectric constant, improves adhesion, provides for molecular design flexibility, and improves melt flow characteristics. Fundamentally, these improvements stem from the chemistry of silicon, summarized in Table II.

In general, two approaches are taken to form either hybrid poly(imide siloxanes) or ceramers, each yielding different morphologies and material properties. The first technique incorporates an aminopropyl terminated siloxane into the polyimide backbone, yielding a thermoplastic poly(imide siloxane). Synthesis is performed using standard procedures for polyimides.[2] A second approach utilizes polyimide or poly(imide siloxane) oligomers end-capped with

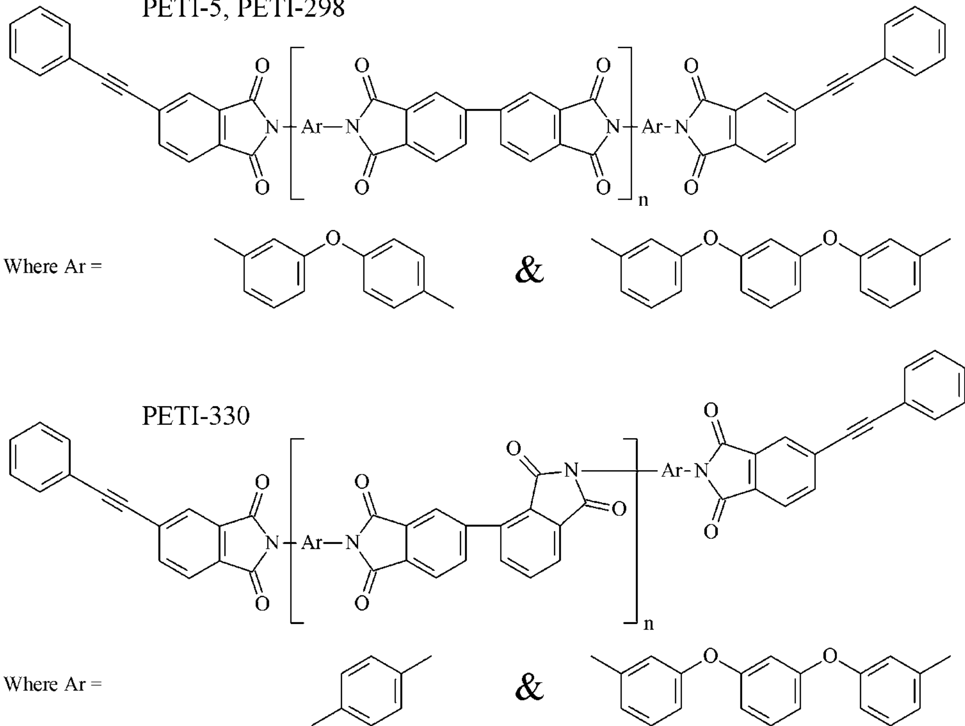


Figure 1 Imide oligomer structures of NASA commercialized polyimide matrix resins PETI-5, PETI-298, and PETI-330.

TABLE II
Comparison of Silicon and Carbon Bonding[6–9]

Chemical bond	Bond length (Å)	Bond angle (°)	Bond strength (kcal/mol)
C—C—C	1.54	112	~ 75
C—O—C	1.42	111	~ 80
Si—O—Si	1.63	130	~ 130
Si—Si	–	–	~ 75
Si—F	–	–	~ 155
C—F	–	–	~ 110
Si—C	–	–	~ 90

methoxy- or ethyoxysilanes that are first hydrolyzed and then crosslinked via condensation. The final cured polymer contains silica domains interconnected by polyimide and/or poly(imide siloxane) segments. Properties of the final polymer hybrid system can be tailored to specific physical, thermal, and mechanical properties and depend on domain size, phase separation, backbone chemistry, coupling agents, sol–gel parameters, and other variables.[6–36]

Cornelius and Marand[26] characterized such a poly (imide siloxane) hybrid ceramer as a function of oligomer molecular weight and found that lower molecular weights exhibited a lesser tendency to phase separate. Also, properties were strongly dependent on the adhesion between the polyimide and silica phases. For materials with good domain adhesion, silica incorporation resulted in improved modulus and mechanical strength at elevated temperatures. The moisture uptake was significantly reduced and the T_g increased with silica concentration until, at high levels, no T_g was observed. In a similar effort, Srinivasan et al.[19] characterized polyimides end-capped with trimethoxy silyl groups and obtained thermal decomposition temperatures (based on mass loss onset) of 538°C in air and T_g values in excess of 480°C for number average molecular weights of 10,000–20,000 g/mol. These materials exhibited lower modulus but higher failure strain and similar strength compared to neat polyimides at room temperature. Furukawa et al.[16] investigated polysiloxane-*block*-polyimides having silicate in the polysiloxane segments, and demonstrated improved creep performance, lower moisture gain, and higher gas diffusion rates. Properties of these hybrid materials and the morphology were found to depend primarily on the composition and chain length of the polysiloxane segments.

The majority of the aforementioned and other published siloxane-containing polyimide research was performed in response to microelectronic chip adhesives, elastomer development, and membrane applications, which do not have the temperature, processing, and performance requirements of structural aerospace materials and thus were engineered according to their specific uses. In the case of alkoxy terminated polyimides and poly(imide siloxanes), complete imidization is often difficult to achieve and the condensation cure reaction is not amenable to the fabrication of thick, void-free composite components.

Our objective in this research is to characterize the structure-property-processing interrelationships for a new class of thermosetting organic/inorganic composite matrix materials formed from combining the latest in addition cure polyimide chemistry and the benefits of telechelic siloxane oligomers and other inorganic monomers/oligomers to achieve novel materials with improved performance and processing characteristics. Thermosetting materials can be processed into thick, void free composite components, unlike condensation cure materials. Understanding the relationships between structure (inorganic amine chemistry, amine ratios, amine chain length, morphology, oligomer molecular weight, and dianhydride), properties, and processing will allow engineering of material systems with previously unobtainable combinations of properties.

EXPERIMENTAL

Raw materials

T650-35/8HS carbon fiber textile (Fabric Development, Quakertown, PA), anhydrous ethanol (200 proof) (AAPER Alcohol Co., Shelbyville, KY), *N*-methylpyrrolidinone (NMP) (AAPER Alcohol Co., Shelbyville, KY) 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) (Chriskev Inc., Lenexa, KS), bis(*p*-aminophenoxy) dimethyl silane (*p*-APDS) (Gelest Inc., Morrisville, PA), 4,4′-(1,3-phenylenediisopropylidene) bisaniline (*m*-BIS), 1,3-phenylenediamine (*m*-PDA) (Dupont, various distributors), and 1,4-phenylenediamine (*p*-PDA) (Dupont, various distributors) were obtained certified from commercial sources and used without additional purification. 4-phenylethynyl phthalic anhydride (4PEPA) was synthesized by the palladium catalyzed cross coupling reaction between phenylacetylene and 4-bromophthalic anhydride in the presence of copper and purified by washing and recrystallization. Table III summarizes the chemical structures and molecular weights of these raw materials. Octamethylcyclotetrasiloxane (D_4), 1,3-bis(3-aminopropyl)-tetramethylsiloxane (MM), and tetramethylammonium siloxanolate (TMAS) catalyst were purchased from Gelest and used to synthesize the telechelic oligomers.

Synthesis of α, ω-bis(3-aminopropyl) polydimethylsiloxane oligomers

Telechelic siloxane oligomers with aminopropyl functionality (APS) were synthesized by the base

TABLE III
Reactive Monomers and Oligomers Used for Organic/Inorganic Polyimide Synthesis

Designation	Chemical name	Structure	Molecular weight (g/mol)
m-PDA	*m*-Phenylenediamine		108.14
p-PDA	*p*-Phenylenediamine		108.14
m-BIS	4,4′-(1,3-Phenylenediiso-propylidene) bisaniline		344.49
BTDA	3,3′,4,4′-Benzophenone tetracarboxylic dianhydride		322.23
4PEPA	4-Phenylethynyl phthalic anhydride		248.23
APS-15, APS-30	Aminopropyl terminated polydimethylsiloxane		1622, 3019
p-APDS	Bis(*p*-aminophenoxy) dimethylsilane		274.39

(TMAS) catalyzed ring opening polymerization reaction between D_4 and MM at 80°C under a nitrogen atmosphere for 48 h. The ratio of D_4/MM was varied to control the oligomeric molecular weight. After reacting, the inorganic diamine product was heated to 160°C to decompose the catalyst, and then cooled and vacuum stripped at 105°C to remove residual cyclic reaction byproducts. Two different functional oligomers were prepared and molecular weights measured via nonaqueous end-group titration. Molecular weights of 1622 g/mol (APS-15) and 3019 g/mol (APS-30) were synthesized and used in subsequent polyimide resin formulations.

Polyimide monomer reactant resin solution formulations

Three-neck round-bottom flasks equipped with magnetic stir bars, condensers, and nitrogen purge were charged with ethanol, NMP, 4PEPA, and BTDA. Molar fractions of 4PEPA and BTDA were 0.4 and 0.2, respectively, and the ratio of ethanol/NMP was 9. The solution was refluxed for 2 h to convert the acid anhydrides into acid ethyl esters, and then cooled to room temperature. Organic and inorganic diamines were added (total diamine mole fraction of 0.4) and the solution mixed for an additional 1 h at

2 + 1

ethanol/NMP reflux

A

one inorganic diamine

B

one organic diamine

$A + B = 2$

Monomer Reactants Solution

260°C

316-400°C

Crosslinked Organic/Inorganic Polyimide

Scheme 1 Synthesis of organic/inorganic addition cure imide oligomers.

room temperature after all solids had dissolved. Each phenylethynyl terminated organic/inorganic imide oligomer contained one type of organic diamine and one type of inorganic diamine. Resins were formulated with inorganic diamine ratios (mass of diamine/mass of oligomer) of 5, 10, 20, 25, 30, 35, 40, and 80%. Stoichiometry was controlled during synthesis to achieve these values. All resin solutions were prepared at 55% by weight theoretical imidized solids, providing an adequate viscosity for textile impregnation. The overall synthesis approach is described in Scheme 1. APS containing resin solutions were generally transparent and *p*-APDS solutions were opaque. Monomer resin solutions were stored in a freezer before use.

Resin imidization

A portion of the resin solutions were poured into aluminum boats and step-heated to perform solvent removal, amide formation, and subsequent imidization at 240°C/4 h + 260°C/1 h. Under these time-

temperature condition, no reaction of the phenylethynyl group occurs, but >98% imidization is achieved based on thermogravimetric analysis results.

Composite laminate fabrication

T650-35/8HS carbon textiles were impregnated with the resin solutions using standard laboratory practices for composite prepregging. Eight-ply, warp aligned prepreg laminates (10 cm × 10 cm) were prepared by wet lay-up then imidized at 240°C/4 h + 260°C/1 h. After imidization, the laminates were compression molded at 1.4 MPa using the following cure cycle: 280°C/1 h + 327°C/1 h + 371°C/3 h. No postcure was used. Prepregs were made at 38% imidized solids to achieve laminate fiber volume fractions of (55 ± 3)%.

Thermal characterization

Differential scanning calorimetry (DSC) was performed on a TA Instruments® Q100 instrument with a nitrogen flow rate of 50 mL/min. Imidized resins were scanned at 10°C/min to 450°C to determine oligomer glass transition temperature (T_g), melt behavior, and reaction exotherm. Thermal decomposition, char yield, and mass loss behavior of imidized resins was performed using a TA Instruments® 2950 Hi-Res TGA thermal gravimetric analyzer at heating rates of 10°C/min to 900°C under a 50 mL/min nitrogen purge. Composite laminate glass transition temperature was measured using a TA Instruments® 2980 dynamic mechanical analyzer (DMA) at a heating rate of 5°C/min, 1 Hz frequency, and single cantilever deformation mode.

RESULTS AND DISCUSSION

Polyimide morphology

Thermoset poly(imide siloxane) physical, thermal, and mechanical behavior are dependent on the physical as well as chemical structure. Figure 2 displays the effects of APS incorporation into the phenylethynyl terminated oligomer backbone on the oligomeric molecular weight. In effect, these curves demonstrate that as the amount of inorganic (siloxane) component is increased, the theoretical distance between crosslinks increases. Also, as the siloxane concentration increases to extremely high values (>40%) the cured material behaves more as a crosslinked siloxane elastomer than a structural polyimide matrix. APS-30 introduces longer inorganic blocks between organic (i.e. backbone imide) segments than APS-15, and the formulated imide oligomer molecular weights used in this study were

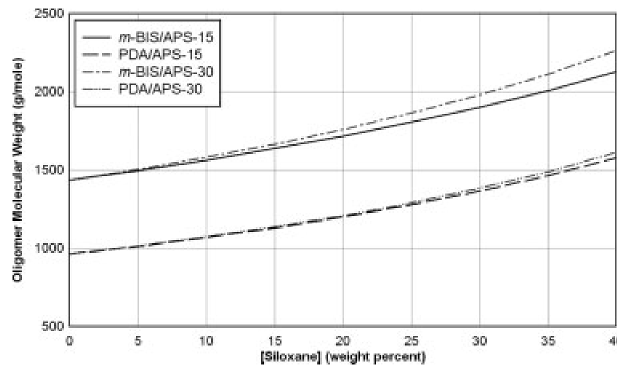


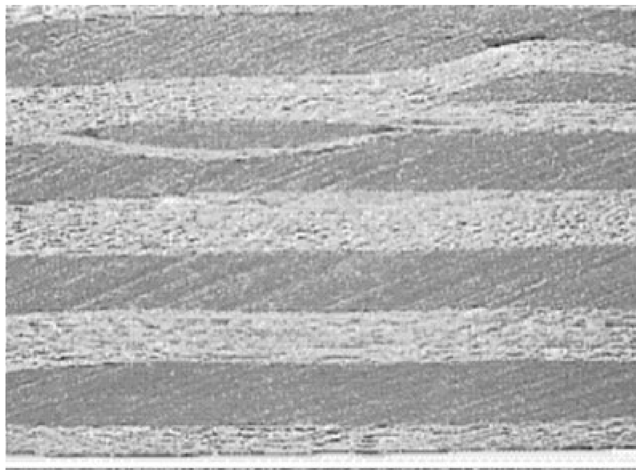
Figure 2 Relationship between siloxane concentration and imide oligomer molecular weight.

roughly the same for both APS inorganic diamine oligomers.

Siloxane incorporation leads to a number of physical differences that were observed during resin fabrication and composite processing. Siloxane containing prepregs exhibited much better tack characteristics at much lower volatile levels than purely organic polyimide prepregs. Also, the monomer solution solubility of the organic/inorganic imides was superior to the traditional polyimide monomer solutions. In the imidized state, obvious phase separation occurred in some of the APS-30 based oligomers, but no visible phase separation was observed for the polyimides containing the siloxane APS-15 moiety. These results are consistent with those of Cornelius and Marand,[26] who characterized poly(imide siloxane) hybrid ceramers as a function of oligomer molecular weight and found that lower molecular weights exhibited a lesser tendency to phase separate. Contrary to the APS based resin solutions, *p*-APDS was found to have much lower solubility in the ethanol/NMP monomer solutions. Much longer mixing times were required to completely dissolve the monomer and significant phase separation was observed after imidization.

Composite laminate quality

T650-35/8HS composite laminates were evaluated by optical microscopy. All composite formulations containing *m*-PDA and *m*-BIS and at least 10% APS were found to be of low (<2%) void content. Matrix formulations containing *p*-PDA or *m*-PDA and less than 10% APS showed some microcracking after cure and poor consolidation, whereas formulations with ≥ 10% APS and either meta substituted organic diamine did not display evidence of microcracking via optical microscopy (Fig. 3). These results indicate an improvement in matrix toughness and melt flow through siloxane incorporation. None of the composites formulated with *m*-BIS as the organic diamine



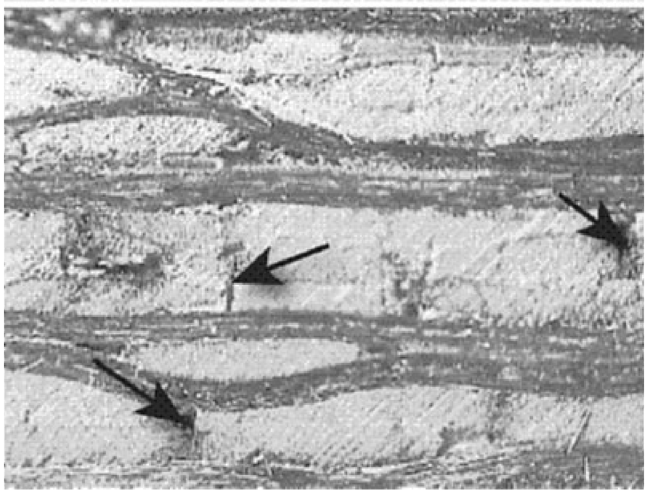


Figure 3 650-35/8HS composite laminate cross section optical micrograph for a 10% siloxane/*m*-BIS polyimide (top) and 5% siloxane/*p*-PDA polyimide (bottom). Arrows point to microcracks.

displayed evidence of microcracking, most likely due to the higher flexibility of *m*-BIS compared to the phenylenediamines. Laminates made using matrix resins containing phenylenediamines and *p*-APDS were generally of poor quality, regardless of the *p*-APDS concentration. The toughening effects and processing improvements imparted by the aminosiloxane oligomers were found to be far superior to any toughness that may be imparted by the *p*-APDS monomer.

Organic/inorganic imide thermodynamic properties

Typical dynamic DSC scans of imidized oligomers are shown in Figure 4, demonstrating the oligomer glass transition temperature (T_g^{oligomer}), "liquid region," and reaction exotherm. The "processing window" for polyimides used as matrix resins in composites can be qualitatively defined as the difference between the cure reaction onset and T_g^{oligomer}. Table IV summarizes the average processing window for the organic/inorganic imide oligomers studied here. Note that the largest processing window is achieved with the meta substituted organic diamines, *m*-PDA and *m*-BIS, as these monomers provide more of a kinked molecular structure compared to the rigid para diamines. All of the imide oligomers containing *p*-PDA exhibited T_g^{oligomer} values of 250–260°C and therefore very narrow processing windows. It should be noted, that although the *m*-PDA and *m*-BIS based imides displayed similar processing windows of 224–235°C, the *m*-BIS had significantly higher melt flow as evidenced from melting of the samples used in the DSC experiments and flash during composite processing.

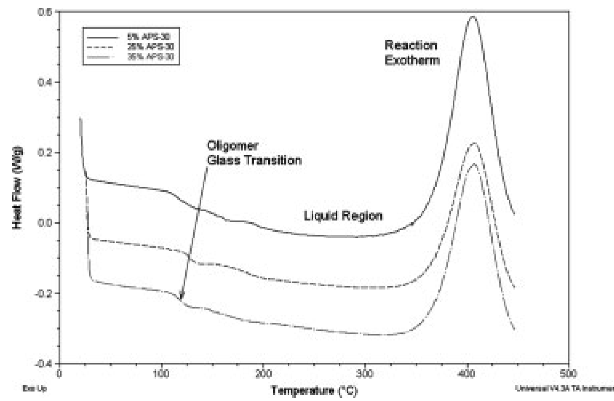


Figure 4 Dynamic DSC scans of APS-30/*m*-BIS imidized oligomers displaying oligomer T_g, liquid processing region, and reaction exotherm. Curves shifted vertically.

Comparison of the inorganic diamine effects revealed that as the concentration of siloxane increased, the processing window also increased. This effect is illustrated in Figure 5, where T_g^{oligomer} is plotted against siloxane concentration. Imides containing APS-30 demonstrated a slightly higher (~ 10°C) processing window than those containing APS-15, indicating that the longer inorganic block

TABLE IV
Average Processing Window for Organic/Inorganic Imide Oligomers

Organic/inorganic imide matrix system		
Organic diamine	Inorganic diamine	Average processing window (°C)
m-BIS	APS-15	234
	APS-30	225
	p-APDS	221
m-PDA	APS-15	235
	APS-30	224
	p-APDS	227
p-PDA	APS-15	92
	APS-30	89
	p-APDS	95

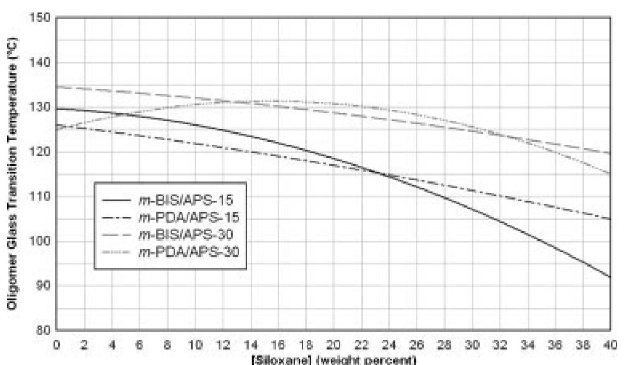


Figure 5 Oligomer glass transition temperature as a function of siloxane concentration, second order curve fit to raw data.

segments provide lower imidized glass transition temperatures than shorter segments, even at the same siloxane concentrations. No significant effects relative to processing window and oligomer glass transition temperature were observed in imides containing the aminosilane *p*-APDS as compared to the purely organic systems. As the concentration of *p*-APDS was increased, no trends in processing window or T_g^{oligomer} were observed.

The interrelationships between organic/inorganic imide oligomer chemical structure, rheological properties, thermodynamics, and molecular physical state can also be qualitatively evaluated by examining the cure reaction enthalpy, ΔH_{rxn}. For example, Figure 6 displays the heat of reaction as a function of the concentration of 4PEPA for the imides containing APS-30. Consistent trends were also observed for the APS-15 and *p*-APDS imides. Highly mobile imide oligomers (e.g. those containing meta substituted organic diamines) displayed higher heats of reaction, since the increased molecular mobility enables the network to achieve a higher degree of conversion. Figure 6 displays three tiers of reaction enthalpies based on the three organic amines used. No obvious relationships between siloxane concentration could be drawn. The increased molecular mobility as a function of imide structure is also manifested in composite processing, as the more molecularly mobile materials exhibited lower melt viscosities and subsequently more easily processable composite laminates. In total, the heats of reaction covered the range of 50–300 kJ/mol for all of the organic/inorganic imide oligomers.

Organic/inorganic imide thermal stability

Dynamic TGA scans of imidized oligomers were evaluated under nitrogen atmosphere to determine mass loss behavior, thermal decomposition temperature, T_d, and char yield, as a function of chemical structure. T_d was determined from the slope intersection method (onset point) of the mass versus temperature curve. Figure 7 displays typical mass loss behavior for the organic/inorganic imide oligomers. Mass loss in the 300–400°C temperature regime is primarily due to degradation of the imide carbonyls, cleavage of Si—CH_3 bonds, and mass loss resulting from residual imidization.[2,19] Notably, the APS-30 containing imides exhibited less mass loss in the 300–400°C range than imides containing APS-15 or *p*-APDS.

Similarly, organic/inorganic imides containing APS-30 exhibited higher thermal decomposition temperatures than their APS-15 counterparts for each system. Figure 8 displays thermal decomposition temperature plotted as a function of siloxane concentration for each of the aminosiloxane/organic amine imide oligomers. As shown by example using shading in Figure 8, the thermal decomposition temperature is generally bounded on the upper end by APS-30 and lower end by APS-15. This remains true for each of the organic/inorganic amine combinations, indicating that longer siloxane block segments in the imide backbone led to a higher thermal decomposition temperature.

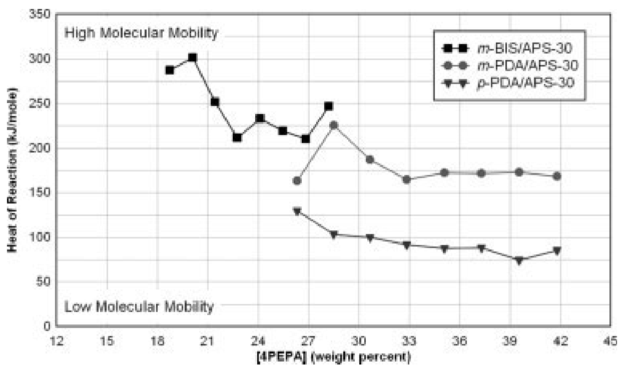


Figure 6 Heat of reaction as a function of 4PEPA concentration and inorganic component for organic/inorganic imide oligomers containing *m*-BIS as the organic diamine.

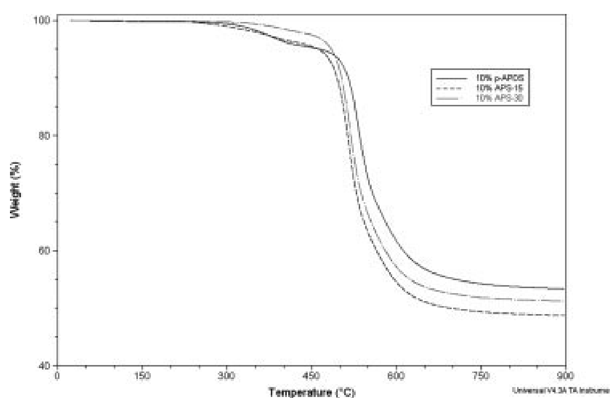


Figure 7 Dynamic TGA scans of organic/inorganic imides containing *m*-BIS as the organic diamine.

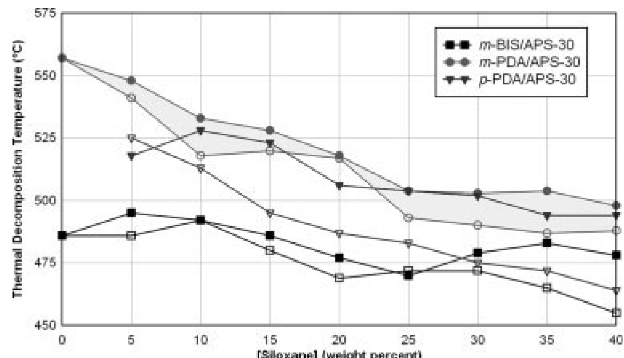


Figure 8 Thermal decomposition temperature as a function of siloxane concentration and organic diamine. Closed points are APS-30 and open points are APS-15 imides.

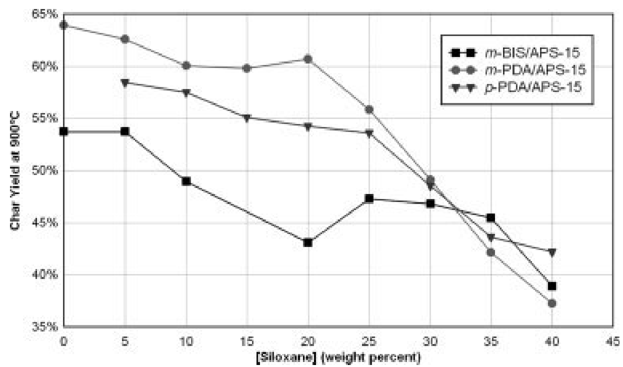


Figure 10 Char yield (900°C/N_2) for APS-15 based imides.

Of the three organic amines evaluated, T_d followed the general trend *m*-PDA > *p*-PDA > *m*-BIS, which was anticipated since *m*-BIS contains aliphatic moieties. Higher thermal stability exhibited by *m*-PDA compared to *p*-PDA was significant (>25°C in some instances) and somewhat surprising. This difference may be related to the reactivates of the amines on the 1,3 versus the 1,4 position of the benzene ring and the network formation during the TGA experiment. After imidization and cure, which occur quickly during the TGA experiment, the final network morphologies between the *m*-PDA and *p*-PDA materials are different. The enhanced mobility provided by the 1,3 substitution may provide for faster cure and/or higher degree of conversion, producing a more stable network. Another contribution may be that the 1,3 substituted phenyl group is simply more thermally stable than 1,4.

Imides containing the *p*-APDS exhibited higher thermal decomposition temperatures, as expected, which were less affected by inorganic diamine concentration (Fig. 9). In this case, however, the *m*-PDA/*p*-PDA trend was reversed; *p*-PDA based imides showed better thermal stability than those based on *m*-PDA, although the difference was small (<5°C). Inclusion of *p*-APDS relative to *m*-BIS actually improved the thermal stability significantly (>20°C) compared to the purely organic polyimide system.

Char yield generally displayed the same behavior as observed for T_d, with *m*-PDA > *p*-PDA > *m*-BIS, a trend which held true for both the siloxane and the *p*-APDS containing imides. Longer siloxane block materials (those containing APS-30) exhibited slightly higher char yield values (3–8%) than the imides containing shorter siloxane blocks (APS-15). Figure 10 displays the char yield plotted as a function of siloxane concentration for the APS-15 containing materials.

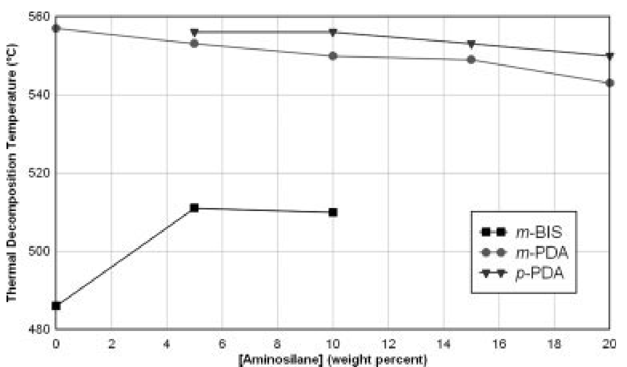


Figure 9 Thermal decomposition temperature as a function of *p*-APTS concentration.

Organic/inorganic polyimide glass transition temperature

A representative DMA scan for the T650-35/8HS organic/inorganic thermoset polyimides is shown in Figure 11, displaying storage modulus (E′), loss modulus (E″), and damping factor (tan δ). Here, we report the temperature at the peak maximum in the

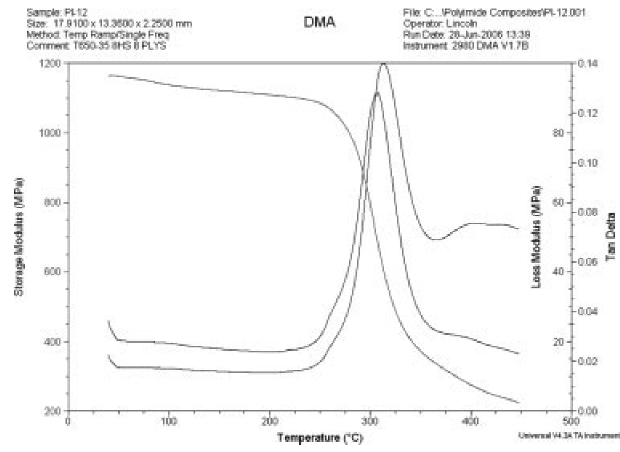


Figure 11 Dynamic DMA scan of a 10% APS-15/*m*-BIS T650-35/poly(imide siloxane) composite.

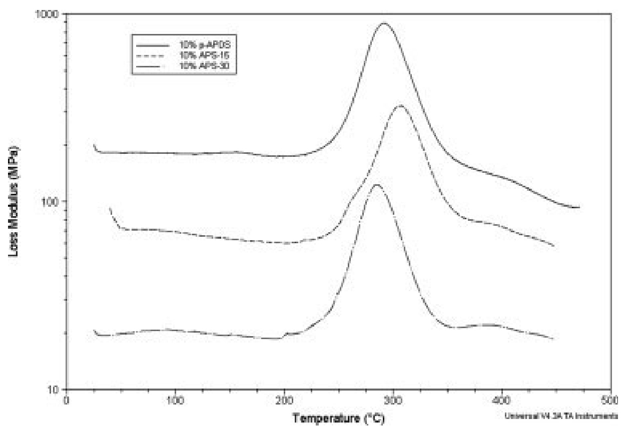


Figure 12 Loss modulus spectra at 10% concentration of inorganic diamine for *m*-BIS based polyimide composites.

E″ versus temperature curve to represent the glass transition temperature for the purposes of measurement consistency (Fig. 12).

Cured polyimide glass transition temperature as a function of organic/inorganic oligomeric chemistry varied over a broad temperature range of ~ 300–450°C. With the exception of a few anomalies, the glass transition temperature (T_g), generally decreased as the inorganic concentration in the imide oligomer increased. This generalized inverse relationship between T_g and inorganic concentration is illustrated in Figure 13 for the aminosiloxane containing polyimides. As a function of organic diamine component, the trend for T_g was found to be *p*-PDA > *m*-PDA > *m*-BIS; the less rigid and geometrically constrained organic diamines yielded lower values for T_g, which was anticipated based on polyimide structure-property relationships.

Comparison of the long (APS-30) and shorter (APS-15) siloxane blocks in the polyimide backbone revealed that longer block segments yielded slightly higher glass transition temperatures than the shorter block segments. This result is consistent with traditional thermoplastic polymer and polysiloxane chemistry, where one would expect a higher molecular weight to yield a higher glass transition temperature up to some critical molecular weight.

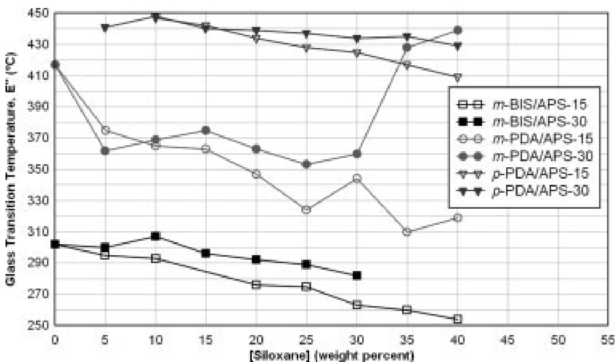


Figure 13 Glass transition temperature of poly(imide siloxanes) as a function of siloxane concentration and imide chemistry.

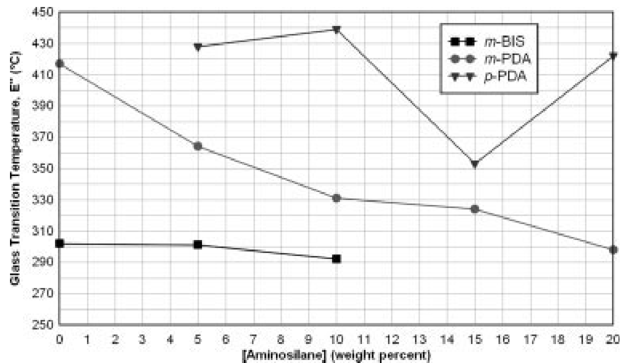


Figure 14 Glass transition temperature of organic/inorganic polyimides as a function of aminosilane concentration and organic diamine.

Figure 14 displays the T_g-structure relationships for the *p*-APDS containing imide chemistries. Again, the general decreasing T_g trend as a function of aminosilane concentration is observed, as is the organic amine relationship for T_g: *p*-PDA > *m*-PDA > *m*-BIS. Numerically, the magnitude of glass transition temperature reduction as a function of inorganic concentration is higher for the *p*-APDS systems than for the siloxane containing systems. This may be, in part, due to morphological differences caused by the varying extent of phase separation observed between the different inorganic diamine types.

CONCLUSIONS

Structure-thermal property relationships for a new class of addition cure organic/inorganic polyimide composite matrices were presented. Relationships between oligomeric chemistry (molecular weight, inorganic diamine, organic diamine, and inorganic component concentration), oligomer glass transition temperature, processing window, reaction enthalpy, composite laminate processing behavior, cured glass transition temperature, char yield, and thermal decomposition temperature were determined. Glass transition temperature (both oligomer and cured polyimide), thermal decomposition temperature, and char yield were found to increase with increasing siloxane block length in the imide backbone. As the concentration of inorganic component (either silane or siloxane) in the imide oligomer backbone increased, the cured glass transition temperature decreased. Char yield and thermal decomposition temperature were observed to decrease as the inorganic component concentration increased.

Aminosiloxanes incorporated into the imide oligomer backbone provided alcohol based prepregging resin solutions with improved tack properties at lower volatile levels than traditional polyimide monomer resin solutions, improved processability (lower melt viscosity), and improved toughness of the as-cured T650-35/8HS carbon fiber composite laminates, evidenced by reduced microcracking. Incorporation of bis(*p*-aminophenoxy) dimethyl silane into the imide oligomer structure did not provide any significant advantages (compared to traditional polyimides) relative to thermal properties or composite processing.

Any opinions, findings, and conclusions or recommendations expressed in this manuscript are those of the authors and do not necessarily reflect the views of the National Science Foundation.

References

1. Cassidy, P. Thermally Stable Polymers: Synthesis and Properties; Marcel Dekker: New York, 1980.
2. Ghosh, M.; Mittal, K., ed. Polyimides: Fundamentals and Applications; Marcel Dekker: New York, 1996.
3. Lincoln, J. PhD Dissertation, Michigan State University, 2001.
4. Paul, C.; Schultz, R.; Fenelli, S. U.S. Pat. 5,138,028 (1992).
5. Curliss, D.; Thorp, K.; Lincoln, J.; Price, W. High Temple XXII Workshop, Clear Water, FL, 2002.
6. Zeldin, M.; Wynne, K.; Allcock, H., Ed. Inorganic and Organometallic Polymers; American Chemical Society: Washington, DC, 1988.
7. Archer, R. Inorganic and Organometallic Polymers; Wiley: New York, 2001.
8. Stevens, M. Polymer Chemistry: An Introduction, 2nd ed.; Oxford University Press: New York, 1990.
9. Brook, M. Silicon in Organic, Organometallic, and Polymer Chemistry; Wiley: New York, 2000.
10. Breiner, J.; Mark, J. Polymer 1998, 39, 5483.
11. Avadhani, C.; Chujo, Y. Appl Organomet Chem 1997, 11, 153.
12. Itoh, M.; Inoue, K.; Hirayama, N.; Sugimoto, M.; Seguchi, T. J Mater Sci 2002, 37, 3795.
13. Ahmad, Z.; Sarwar, M.; Wang, S.; Mark, J. Polymer 1997, 38, 4523.
14. Ahmad, Z.; Mark, J. Chem Mater 2001, 13, 3320.
15. Mascia, L.; Zhang, Z.; Shaw, J. Compos A 1996, 27, 1211.
16. Furukawa, N.; Yuasa, M.; Kimura, Y. Polymer 1999, 40, 1853.
17. Park, C.; Lowther, S.; St. Clair, L. U.S. Pat. 6,521,052 (2003).
18. Park, C.; Lowther, S.; Smith, J., Jr.; Connell, J.; Hergenrother, P.; St. Clair, T. Int J Adhesion Adhesive 2000, 20, 457.
19. Srinivasan, S.; Hedrick, J.; Miller, R.; Di Pietro, R. Polymer 1997, 38, 3129.
20. Tsai, M.; Whang, W. J Polym Res 2001, 8, 77.
21. Kioul, A.; Mascia, L. J Non-Cryst Solids 1994, 175, 169.
22. Kang, D.; Kim, Y. J Inorg Organomet Polym 2002, 12, 79.
23. Chang, T.; Wu, K. Polym Degrad Stab 1998, 60, 161.
24. Yamada, Y. High Perform Polym 1998, 10, 69.
25. Iyoku, Y.; Kakimoto, M.; Imai, Y. High Perform Polym 1994, 6, 95.
26. Cornelius, C.; Marand, E. Polymer 2002, 43, 2385.
27. Mascia, L.; Kioul, A. Polymer 1995, 36, 3649.
28. Furukawa, N.; Yuasa, M.; Yamada, Y.; Kimura, Y. Polymer 1998, 39, 2941.
29. Sysel, P.; Pulec, R.; Maryska, M. Polym J 1997, 29, 607.
30. Nagase, Y.; Takamura, Y.; Akiyama, E. High Perform Polym 1995, 7, 255.
31. Mahoney, C.; Gardella, J., Jr.; Rosenfeld, J. Macromolecules 2002, 35, 5256.
32. Jwo, S.; Whang, W.; Liaw, W. J Appl Polym Sci 1999, 74, 2832.
33. Smith, J., Jr.; Connell, J.; Hergenrother, P.; Lowther, S.; Park, C. U.S Pat. US2003/0,158,351 A1 (2003).
34. Andre, S.; Guida-Pietrasanta, F.; Rousseau, A.; Boutevin, B. J Polym Sci Part A: Polym Chem 2001, 39, 2414.
35. Yoon, T.; McGrath, J. High Perform Polym 1992, 4, 203.
36. Park, H.; Kim, J.; Kim, J.; Lee, Y. Macromol Rapid Commun 2002, 23, 544.