

Lessons Learned in the Processing of Polycyanurate Resin Composites

15 February 2002

Prepared by

R. J. ZALDIVAR
Space Materials Laboratory
Laboratory Operations

Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE SPACE COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

20020422 243

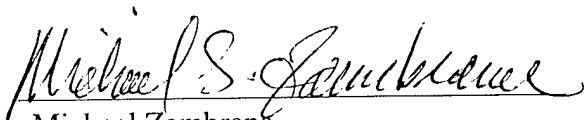
Engineering and Technology Group

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-00-C-0009 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by P. D. Fleischauer, Principal Director, Space Materials Laboratory. Michael Zambrana was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

A handwritten signature in cursive script that reads "Michael P. S. Zambrana". The signature is written in dark ink and is positioned above the printed name.

Michael Zambrana
SMC/AXE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 15-02-02			2. REPORT TYPE			3. DATES COVERED (From - To)			
4. TITLE AND SUBTITLE Lessons Learned in the Processing of Polycyanurate Resin Composites						5a. CONTRACT NUMBER F04701-00-C-0009			
						5b. GRANT NUMBER			
						5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S) R. J. Zaldivar						5d. PROJECT NUMBER			
						5e. TASK NUMBER			
						5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Laboratory Operations El Segundo, CA 90245-4691						8. PERFORMING ORGANIZATION REPORT NUMBER TR-98(8565)-8			
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Space Command 2430 E. El Segundo Blvd. Los Angeles Air Force Base, CA 90245						10. SPONSOR/MONITOR'S ACRONYM(S) SMC			
						11. SPONSOR/MONITOR'S REPORT NUMBER(S) SMC-TR-02-16			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.									
13. SUPPLEMENTARY NOTES									
14. ABSTRACT Polycyanurate resins are a class of thermosetting polymers that have replaced epoxies as the matrix material of choice for structural composites used in space applications. Composites using a polycyanurate matrix are superior to those with epoxy matrices due to their increased toughness and dimensional stability, lower moisture absorption, reduced outgassing, and higher glass-transition temperatures. However, many of these superior properties are not always achieved due to difficulties that are commonly encountered during processing. This report discusses several cyanate ester monomers and resin blends commercially available, their polymerization behavior, and their properties. In addition, we focus on a number of issues encountered during the processing of these materials and how they were identified and resolved. The most notable problem with this resin system is the inherent sensitivity of the monomer to moisture during processing. This affects the thermal and mechanical behavior of the resin and its resultant composites. In addition, the effects of cure schedule sensitivity are discussed.									
15. SUBJECT TERMS Cyanate ester, Polycyanurate, Siloxane, Composites, Fibers, Processing, Polymers									
16. SECURITY CLASSIFICATION OF:				17. LIMITATION OF ABSTRACT		18. NUMBER OF PAGES		19a. NAME OF RESPONSIBLE PERSON Rafael Zaldivar	
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED				23		19b. TELEPHONE NUMBER (include area code) (310)336-1999	

Contents

1.	Introduction	1
2.	Background.....	3
3.	Composite Processing Difficulties Encountered During Processing	7
3.1	Viscosity.....	7
3.2	Moisture-Induced Reactions.....	7
3.3	Moisture Effects.....	9
3.4	Oxidative Degradation.....	15
3.5	Fracture Toughness.....	17
4.	Summary.....	21
	References.....	23

Figures

1.	Schematic showing the primary polymerization (cyclotrimerization) reaction of three cyanate ester monomers	3
2.	Schematic showing the different backbone structure for available cyanate ester monomers	4
3.	Schematic showing the hydrolysis reaction of cyanate ester monomers leading to carbamate formation.	8
4.	Schematic showing how carbamate formation during polymerization of cyanate esters will prevent cyclotrimerization reaction.	8
5.	Fourier Transform Infrared spectroscopy scan (FTIR) of cyanate ester monomer and hydrolyzed cyanate ester monomer.	9
6.	Photograph showing typical blister formed in polycyanurate composite parts during post cure	10

7. Weight loss versus temperature plot of a cured polycyanurate polymer and a polycyanurate polymer that was pre-exposed to moisture during processing.	11
8. Distribution and identification of volatiles produced during heat-treatment of cured polycyanurate polymer and polycyanurate sample that was pre-exposed to moisture during processing.	11
9. Ply separation and microcracking of a polycyanurate composite that has indications of carbamate formation on the outer plies as verified by FTIR.	12
10. Overhead view showing blistered aluminized Kapton film on the surface of a polycyanurate composite facesheet.	13
11. Optical micrograph showing cross-section of polycyanurate composite facesheet bonded to Kapton film	14
12. Fracture surface of typical polycyanurate resin dogbone sample	14
13. Fracture surface of typical polycyanurate resin dogbone sample that has been pre-exposed to moisture during processing and has carbamate formation as verified by FTIR.....	15
14. Differential scanning calorimetry of polycyanurate resin samples	16
15. Fracture surface of typical polycyanurate resin dogbone sample that has been pre-exposed to moisture during processing and has carbamate formation as verified by FTIR.....	17
16. The interlaminar fracture toughness for both an unmodified and a siloxane-modified polycyanurate system with their corresponding composites.	18
17. Micrographs of M40J/996 composite HT to 175°C showing silicon-rich phase preferentially wetting fibers.....	19
18. Interlaminar fracture toughness vs delamination growth for M40J/996 effect of cure temperature.	20

Tables

1. Resin Properties of Commercially Available Cyanate Resin Systems.....	6
2. Interlaminar Toughness of Carbon Fiber Reinforced Polymer Matrix Composite Systems	18

1. Introduction

Polycyanurates are a class of thermosetting resins that over the last 10 years have become the material of choice over epoxies in the fabrication of high-performance, resin-based, fiber-reinforced composites. Polycyanurate resins are primarily used as the matrix material in structural composites used for space applications. The manufacturing processes, as well as the mechanical properties of these composite systems, are quite similar to those of graphite/epoxy systems. However, they possess additional benefits. They have considerably lower moisture absorption, on the order of 0.6% or less in comparison to over 2.0% for epoxies. This translates into reduced outgassing and thus greater dimensional stability. They have increased fracture toughness relative to both unfilled and elastomeric-filled epoxies, which also contributes to a decrease in composite microcracking. They have glass-transition temperatures in excess of 250°C in comparison to less than 200°C for the highest temperature-tolerant epoxy systems. However, even though this material system appears to satisfy the requirements necessary for most space applications, there are a number of factors that must be carefully monitored and controlled to achieve such high performance. Over the last ten years, some space programs have encountered problems resulting in composites with extremely low mechanical and thermal performance.

This report outlines several cyanate ester monomers and resin blends commercially available and their polymerization behavior and properties. In addition, we will focus on a number of issues encountered during the processing of these materials and how they were identified and resolved. The most notable problem with this resin system is its inherent sensitivity to moisture during processing that may affect the chemical structure of the polymer. The effect of cure schedule effects will also be discussed.

2. Background

Polycyanurate resins are typically synthesized by the polymerization of cyanate ester monomers. A number of authors have discussed and studied these primary reactions.^{1,2,3} By the addition of heat and/or a metal catalyst, three of these difunctional monomers come together by a cyclotrimerization reaction, forming an intermediate molecular weight prepolymer. This cyclotrimerization reaction occurs by the reaction of three cyanate groups opening up and forming a symmetrically substituted triazine ring as shown in Figure 1. This polymerization has been shown to dominate over any other type of reaction within this system, accounting for over 98% of polymerization. The prepolymer further reacts with other prepolymers or monomers within the system to fully polymerize, resulting in a fully cross-linked polymer. The trimerization of cyanate groups is strongly subject to catalysis by a variety of materials. Lewis acids and bases, salts, proton acids, and heavy-metal organic salts have also been found suitable.⁴ The rate of trimerization depends on the chemical nature of the cyanate ester monomer, the temperature, the purity of the monomer, and the catalyst type and concentration. Cobalt carboxylates are primarily chosen as the catalyst of choice, usually in the 40 to 200 ppm range; however, a number of other materials are also available and have been shown to accelerate the crosslinking reaction. The type of catalyst may increase hydrolysis sensitivity. Zinc octoate promotes hydrolysis 10 times as fast as resins catalyzed with Mn^{+2} , Co^{+2} , and Cu^{+2} carboxylates. The implications of hydrolysis of these resins during cure are discussed in a later section. The addition of catalyst to cyanate ester resins greatly accelerates the rate of reaction as expected; yet the end-cured product is identical in properties to that of uncatalyzed systems.

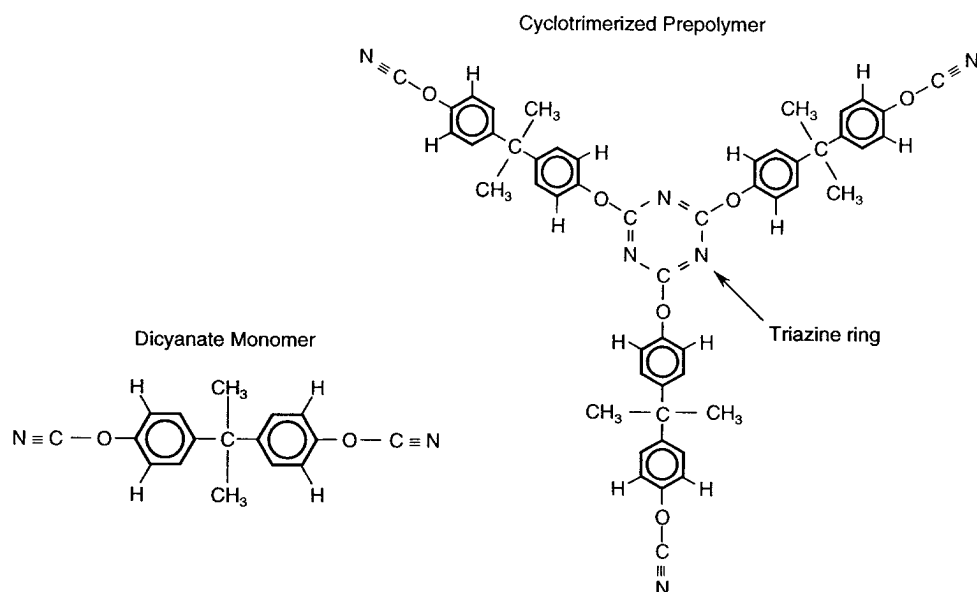
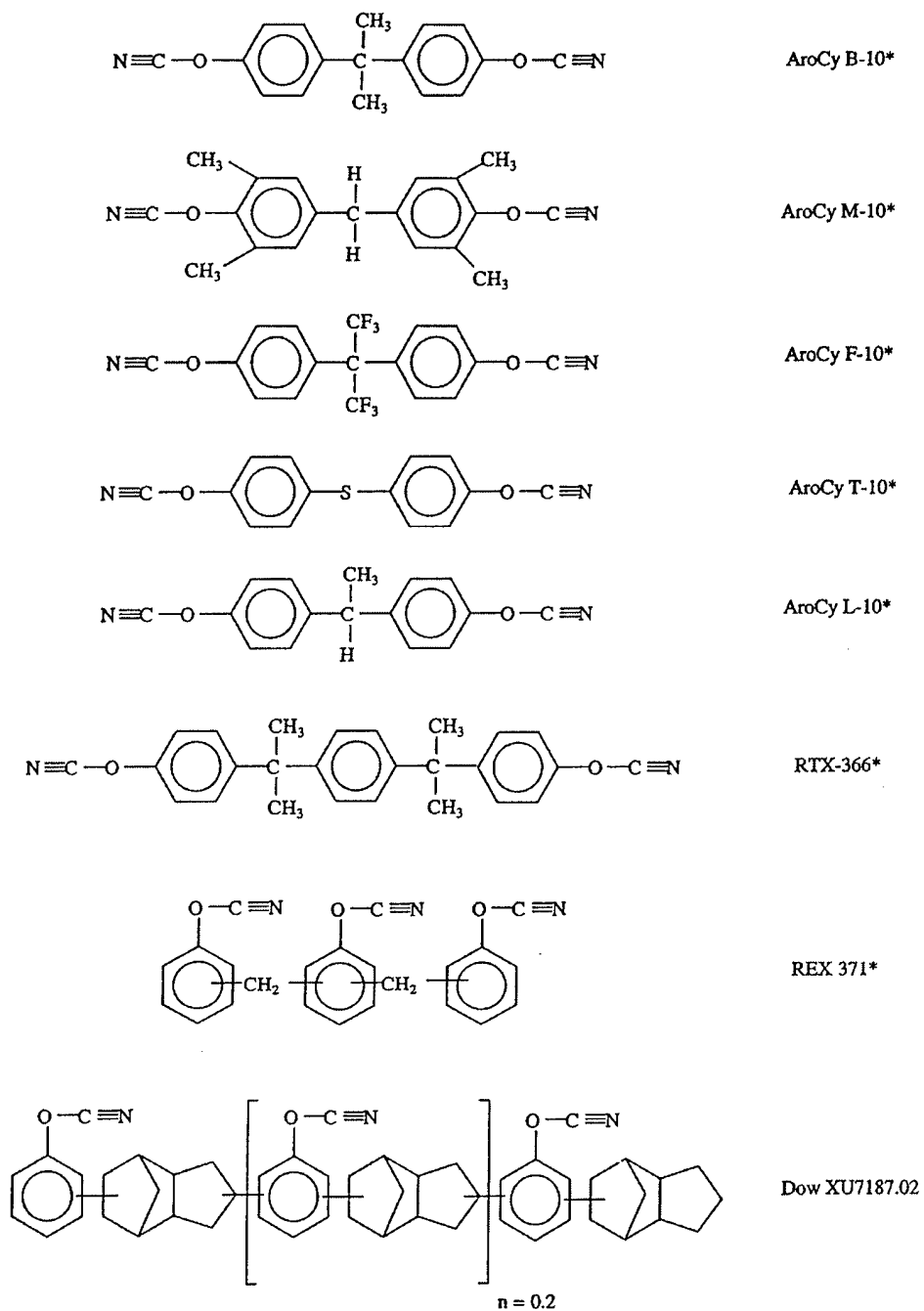


Figure 1. Schematic showing the primary polymerization (cyclotrimerization) reaction of three cyanate ester monomers.

A large number of cyanate ester monomers are available that differ primarily by the linkage group between the cyanate, as described by Shimp et. al.⁵ Figure 2 shows a schematic of some of the different backbone structures available in cyanate ester formulations. These structural variants have a



* Ciba Geigy monomers

Figure 2. Schematic showing the different backbone structure for available cyanate ester monomers.

direct effect on the resins' physical and mechanical performance. By changing the chain length or composition of the cyanate linkage, these systems are optimized to take advantage of certain properties. Some of these monomers are formulated to produce resins with very low dielectric constants, while others are synthesized to take advantage of increased flexibility or a higher temperature capability. The vast majority of prepreg vendors (Hexcel, YLA, Inc., Bryte, etc.) utilizing polycyanurate resins blend a mixture of different cyanate ester monomers. The properties are adjusted by varying combinations of these cyanate ester monomers. Depending on the processing route, the amount and type of catalyst, and blend ratios, monomers can be adjusted to maximize processability and optimize final properties.^{6,7}

In addition, a number of formulations currently available incorporate thermoplastic and rubber fillers, usually in the 5–10% level when used in composites. Millard and Pucket have shown that by the addition of discrete submicron rubber particulates to their dicyclopentadiene cyanate ester monomer (DOW XU7187.02) they were able to achieve a wide range of properties without significantly lowering the glass-transition temperature (T_g) of the resin or affecting the rheological behavior of the resin during processing. A 10% addition has been shown to substantially increase the degree of fracture toughness of the resultant bulk resin from 0.4 to 2.8 in-lb/in², increase the strain-to-failure from 4.0 to 7.5%, and decrease the modulus from 3309 to 2344 MPa. Though many of these properties appear beneficial, a decrease in resin modulus may lead to higher creep rates for higher temperature applications, and therefore, the resin must be tailored to its final use. The addition of insoluble submicron core-shell rubber particulates, as used in both Hexcel 954-3 and YLA, Inc. RS14 resins, is one of several toughening mechanisms. The modification of cyanate networks by the incorporation of co-reacted modifiers such as siloxanes, elastomeric rubbers, and engineering thermoplastics have also been used to enhance fracture toughness of these relatively brittle materials. These toughening mechanisms have been extensively used in the past on epoxies and other thermosetting resins. The phase-separated rubber domains are presumed to act as stress-concentration sites that initiate energy absorbing "toughening" processes such as crazing and shear banding

Table 1 shows values for many of the key material properties reported for a number of commercially available polycyanurate resins in comparison to a high-performance epoxy. Each of the resins shown represents a select family of cyanate ester formulations or blends that have been optimized for selected uses. YLA's RS14 is a high- T_g cyanate ester formulation with excellent mechanical properties and a rheological profile that has been tailored for resin transfer molding and filament winding applications. Hexcel's 954-3 is a comparable system, but is more tailored for prepreg uses. The Bryte 1515 system can be processed and cured at lower temperatures, which should translate into lower residual stresses in composite hardware. Hexcel's 954-2a is also a high- T_g system that has been modified with a thermoplastic to sharply increase the fracture toughness of the resin over unmodified systems. Hexcel's 996 is a lower T_g modified system with a siloxane additive that has the benefits of increased fracture toughness, further reduced moisture uptake, and greatly enhanced oxygen stability. As shown, similar to epoxies, the cyanate ester resins available can vary in properties (glass-transition temperature, toughness, moisture uptake, etc.) over a wide range, depending on the monomer and/or blend chosen.

Table 1. Resin Properties of Commercially Available Cyanate Resin Systems

PROPERTY	RESIN					
	YLA RS14	Bryte 1515*	Hexcel 954-3*	Hexcel 954-2a*	Hexcel 996*	Hexcel 934*
Description	cyanate ester	cyanate ester	cyanate ester	thermoplastic modified cyanate ester	siloxane modified cyanate ester	epoxy
Cure condition (°C)	250	121	177	177	177	177
T _g (°C)	284	128	258	249	150-163	194
G _{IC} (J/m ²)	190	n/a	175	333	367-400	90
Moisture uptake (%)#	0.5	0.4	0.46	0.85	0.21	1.6
TML (%)	0.20	0.18	0.20	0.45	0.17	1.09
CVCM (%)	0.01	0.007	< 0.01	0.004	0.01	0.07
WVR (%)	.05	n/a	0.04	0.19	0.11	0.26
Density (g/cc)	1.19	1.16	1.19	1.24	1.14	1.30
cte , ppm/°C (>22°C)	50	64	45	n/a	58	61
Oxygen Stability [^] (µg/cm ² hr)	550	n/a	580	580-600	299	701
Tensile strength (MPa)	89.6	n/a	56.5	68.9	47.6–54.5	68.9–75.8
Strain/failure	5.8 %	n/a	2.4 %	2.6 %	1.7 %	0.7%
Tensile Modulus (GPa)	2.75	3.37	2.75	3.03	2.96	4.14
Flexural strength (MPa)	125	132	119	116	76	n/a

* Data provided by Hexcel Satellite Products
 + Data provided by Bryte Technologies, Inc.
 # Tested for 220 days at 50% RH

TML = total mass loss
 CVCM = collected volatile condensed matter
 WVR = water vapor recovered

3. Composite Processing Difficulties Encountered During Processing

Most of the cyanate ester composite hardware built over the last several years for the space industry has been fabricated using hand lay-up of prepreg. Solar panels, optical benches, antenna reflectors and arrays, struts, and truss structures have been assembled and manufactured by this standard method by numerous contractors. Therefore, the vast majority of problems associated with the manufacturing of these composite parts is usually related to a prepreg-manufacturing route. However, fabrication difficulties have also been experienced during filament winding and RTM processing, which will also be discussed.

3.1 Viscosity

Most cyanate ester resin formulations have a rheological profile quite similar to that of epoxies. However, the minimum viscosity is on average an order of magnitude lower than that of epoxies. Initially, the lower viscosities of cyanate resins led to the fabrication of composite parts that were resin lean and had considerably higher fiber volumes than for the fiber/epoxy composites. This was caused by excessive resin flow out of the part during the consolidation process. This also created excessive wrinkles within the parts and resulted in fiber misalignment. The problem has been solved with the addition of cauls, dams, and molds, which help keep the resin within the part during consolidation and cure. These molds are similar to those that have been used for other low-viscosity resin systems and are usually fabricated of rubber, composites, and aluminum.

3.2 Moisture-Induced Reactions

One of the primary problems in the fabrication of polycyanurate composites is associated with moisture exposure. Even though cured polycyanurate resins were initially proposed to replace epoxies due to their low moisture uptake and their excellent outgassing behavior after they are cured, moisture exposure "during cure" can be even more deleterious than with epoxies. In the past, moisture exposure during processing was not controlled, and a high degree of degradation was found in mechanical and physical performance.

In the case of epoxies, moisture has been shown to affect the properties of uncured resin in a number of ways. It has been shown to: (a) form clusters that may nucleate microvoids; (b) disrupt the strong hydrogen bonds in the network and form weaker water-related hydrogen bonds; and (c) plasticize the network due to moisture uptake. Many of these effects are reversible due to the weak chemical interaction between the water and the epoxide species.

In the case of cyanate esters, exposure to moisture at slightly elevated temperatures causes the cyanate monomer to become hydrolyzed and form a carbamate, as described by Shimp⁸ and shown in Figure 3. This hydrolysis first forms an imidocarbonic acid intermediate that rearranges to the more stable carbamate structure. If the carbamate is formed, the cyclotrimerization reaction cannot occur, and, therefore, the cyclotrimerized "rings" will not be formed that contribute to the excellent

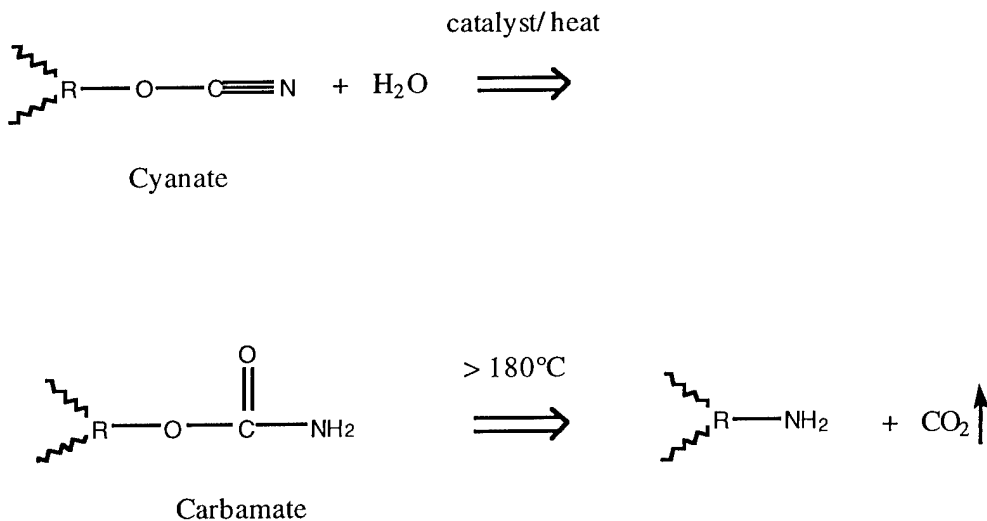


Figure 3. Schematic showing the hydrolysis reaction of cyanate ester monomers leading to carbamate formation.

properties of this resin system, as shown in Figure 4. Carbamate formation is usually dependent on the cyclotrimerization catalyst type and concentration, humidity level, and temperature.⁹ Kaseghan et al. have shown that varnishes containing as little as 1.0 % moisture can have a high degree of carbamate formation, depending on the catalyst used. This carbamate formation has been observed to decrease the glass-transition temperature of the resultant polymer by fragmenting the network. The formation of carbamates prevents the cyanate groups from polymerizing, and, therefore, decreases the resultant polymer network glass-transition temperature.

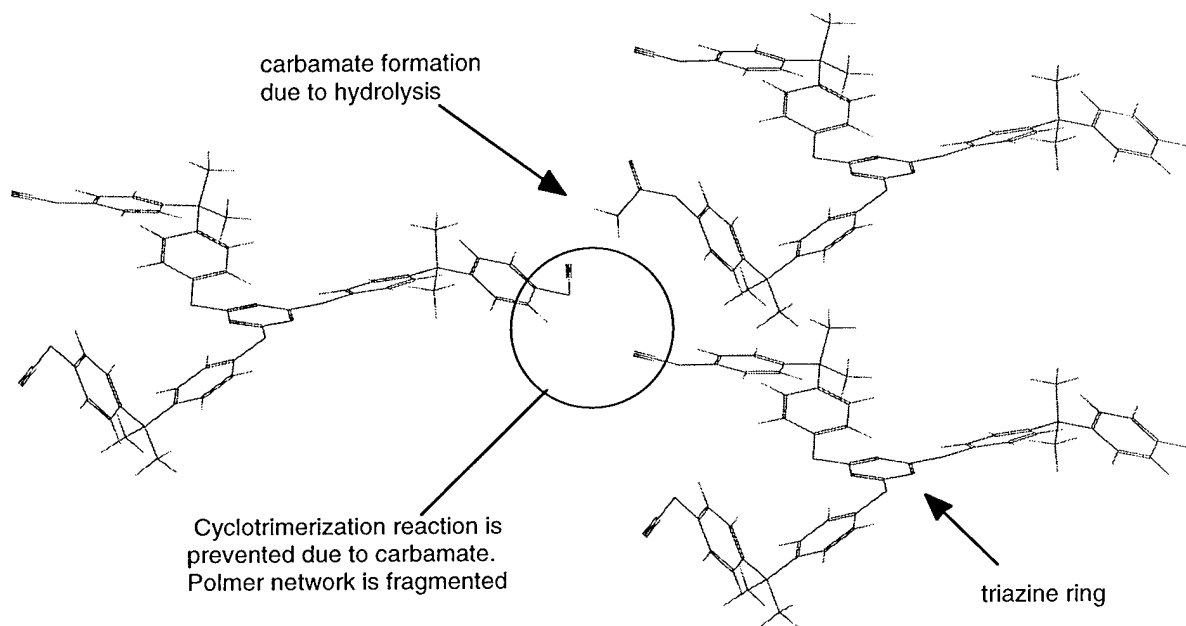


Figure 4. Schematic showing how carbamate formation during polymerization of cyanate esters will prevent cyclotrimerization reaction.

3.3 Moisture Effects

Moisture exposure during the processing of polycyanurates has greatly affected the resultant composite part. In one case, a contractor was fabricating a filament-wound composite rotor. The matrix material was an unmodified cyanate ester resin typically used in the aerospace industry. The resin was chosen over epoxy due to its higher glass-transition temperature as well as for its low moisture absorption capabilities. High dimensional stability and low creep rates during lifetime were necessary to meet system lifetime requirements. However, once the part was fabricated and tested, it exhibited excessively high creep rates and a lower than expected glass-transition temperature.

In our laboratory, we performed Fourier transform infrared spectroscopy (FTIR) in order to verify whether the cyanate ester resin had become hydrolyzed during processing. FTIR results indicated that the polymer was indeed affected by moisture. Figure 5 shows a typical FTIR scan of a cyanate ester resin sample exposed to humidity (>90% R.H., 85°C) and an unexposed control (35% R.H., 85°C) sample. The control sample shows a peak for the unreacted cyanate peak at 2250 cm^{-1} with negligible carbamate formation as evidenced by the carbonyl peak at 1750 cm^{-1} . On the other hand, the exposed sample shows the complete disappearance of the cyanate peak and the formation of the carbamate peak. This indicates that a large fraction of cyanate monomer is hydrolyzed, and the resultant polymer network will be only partially crosslinked with heat treatment. Of course, this exposure limit is much greater than normal, but even exposure to much lower humidity levels was observed to strongly affect carbamate formation. Even in cases where the humidity level was monitored and maintained below 25 R.H.%, carbamate formation was evident in processing, and low T_g composites were produced. Unlike prepreg manufacturing, where samples are bagged and sealed before they experience higher temperatures, the resin is heated in an open environment and wound on an open mandrel during the filament winding procedure. This magnifies the sensitivity to moisture

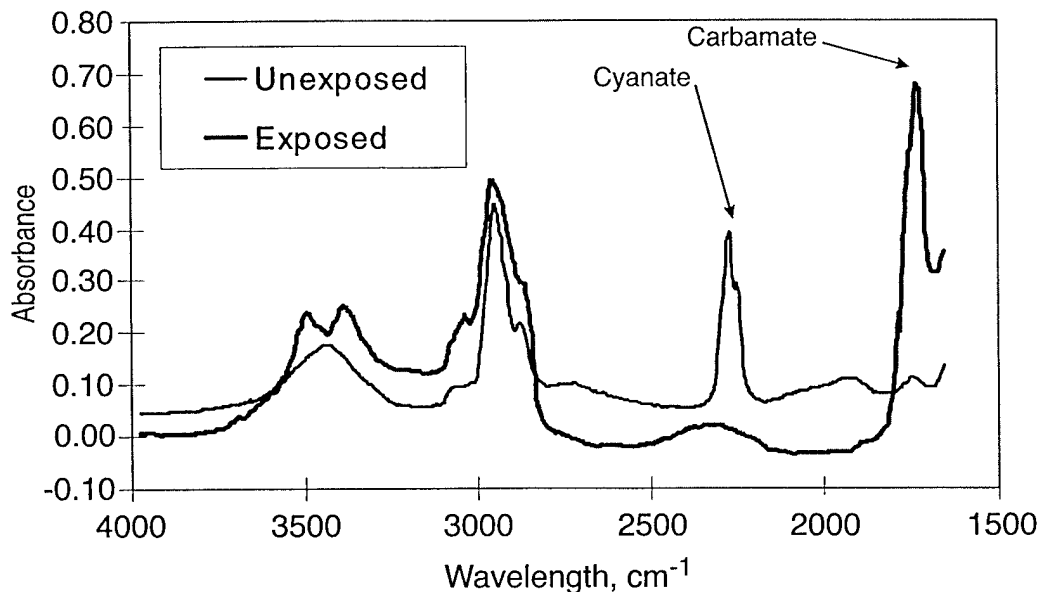


Figure 5. Fourier Transform Infrared spectroscopy scan (FTIR) of cyanate ester monomer and hydrolyzed cyanate ester monomer.

and leads to more elaborate measures necessary to prevent contamination. The contractor was forced to build additional environmentally controlled chambers to prevent further hydrolysis. Subsequent fabricated composite parts exhibited creep rates orders of magnitude lower than previously measured.

Another example was observed when a contractor was fabricating a large number of composite tubes to be used on a satellite array structure. The resin used was an unmodified cyanate ester resin. The tubes were being fabricated using an aluminum mandrel and composite cauls to prevent excessive flow. After cure, a large number of blisters were observed throughout many of the composite tubes, as shown in Figure 6. Upon closer examination, the blisters observed were delaminations within the outer plies. FTIR analysis indicated that the resin was hydrolyzed forming carbamates. The humidity was controlled in the room where the parts were layed up and cured; however, the composite cauls were not placed in a controlled environment. The cauls were also fabricated using a high-temperature epoxy matrix that tends to absorb moisture with time. During fabrication and cure, these cauls were wrapped in proximity to the prepreg. As the samples were heated, the moisture from the cauls diffused into the prepreg and formed carbamates. The blistering was formed due to the decomposition of the carbamates formed. Figure 7 shows the thermal decomposition behavior of a polycyanurate resin sample that has experienced hydrolysis. This figure shows weight loss as a function of temperature for an exposed and unexposed sample. As shown, the unexposed resin remains stable in an inert atmosphere up to 418°C. Upon exposure to this temperature, degradation of the polymer network is observed, as would be expected. By 600°C, there has been a mass loss of over 60%. This figure also shows the thermal profile for the sample pre-exposed to humidity. As shown, the onset of weight loss occurs at approximately 180–200°C, much earlier than the unexposed sample. This would be of much concern in an application where dimensional stability and outgassing are critical. By 600°C, approximately 80% of the polymer's initial weight has been lost.

FTIR was also used to identify the overall distribution of volatiles evolved as a function of temperature for both systems. As shown, the resin is stable up to 400°C, upon which there is a single evolution of gaseous by-products for the unexposed system. There is a negligible amount of carbon dioxide produced prior to degradation at elevated temperature, as shown in Figure 8. By 400°C, some residual unreacted cyanate monomer and/or prepolymer evolution occurs. After 400°C, the largest volume of volatiles produced is associated with the fragmentation and decomposition of the polymer structure.

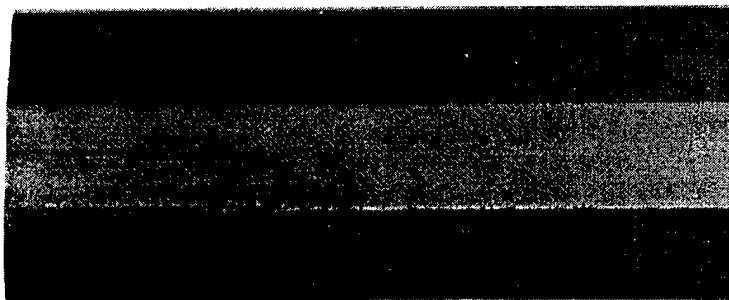


Figure 6. Photograph showing typical blister formed in a polycyanurate composite part during post cure. Blisters were formed due to carbon dioxide evolution from carbamate decomposition.

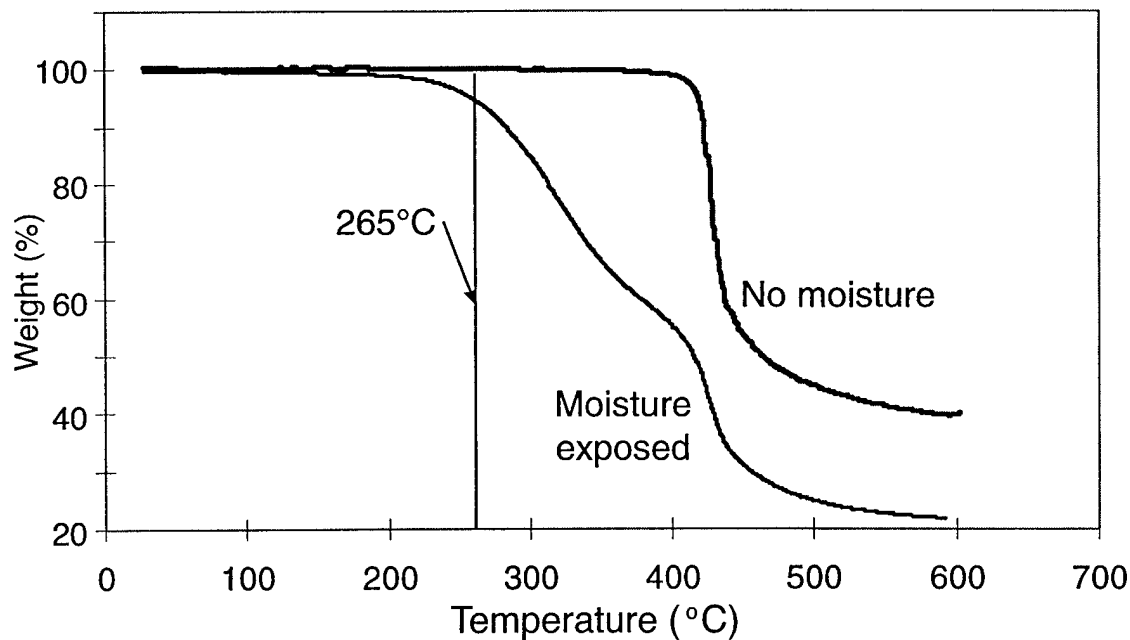


Figure 7. Weight loss versus temperature plot of a cured polycyanurate polymer and a polycyanurate polymer that was pre-exposed to moisture during processing.

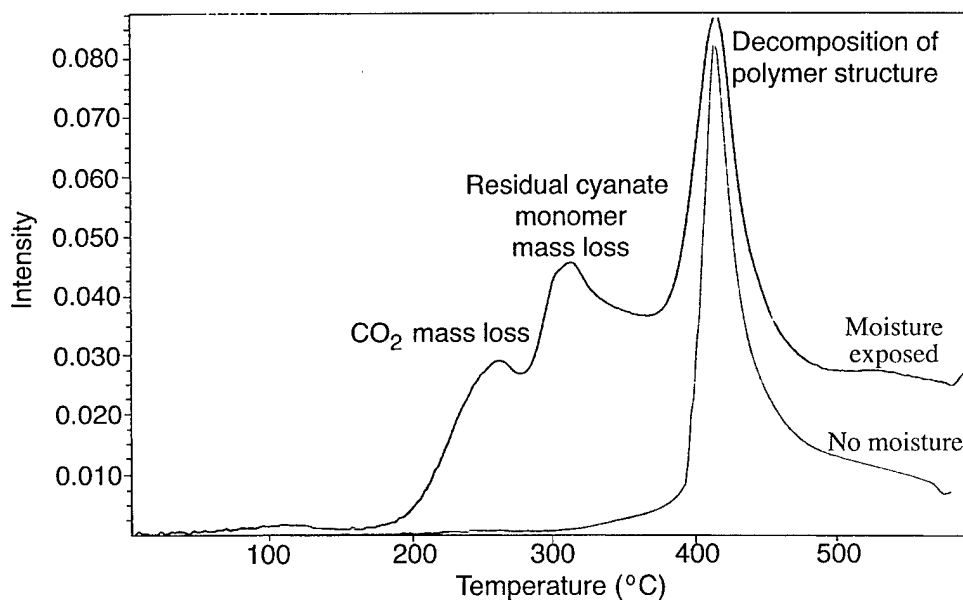


Figure 8. Distribution and identification of volatiles produced during heat-treatment of cured polycyanurate polymer and polycyanurate sample that was pre-exposed to moisture during processing.

Unlike the profile of the unexposed sample, three distinct regions of mass loss are shown for the moisture-exposed sample. The initial peak is representative of carbon dioxide evolution as verified by FTIR. Substantial quantities of carbon dioxide gas (2350 cm^{-1}) are produced as a by-product due to carbamate decomposition as described earlier. The second peak is due to the evolution of unre-

acted residual cyanate monomer and/or lower-molecular-weight oligomeric units. The third peak is again due to the complete thermal decomposition of the polymer structure. There is a substantially greater amount of monomer and oligomeric volatile evolution due to a sharp reduction in the degree of cyclotrimerization caused by moisture. The system is thus less crosslinked, leading to the formation of smaller, less thermally resistant units.

This is especially critical since most polycyanurate composites are post-cured above the decomposition temperature of carbamates. Therefore, if carbamates are formed during the cure process, subsequent decomposition and CO₂ gas evolution will occur during cure. In a laminated composite, this can cause blistering between the prepregs, causing delaminations. The contractor changed the matrix material of the composite cauls to a low moisture absorbing resin, and stored the cauls in an environmentally controlled room. Subsequent parts were fabricated with no delaminations.

A contractor was fabricating fiber-reinforced composite tubes using a siloxane-modified cyanate ester resin system. After processing, the samples appeared well consolidated and cured by visual inspection. However, as part of quality assurance, the contractor usually wiped the surfaces of the tubes with acetone to ensure that the system was well cured. A poorly cured resin system will typically degrade and release a large degree of carbon fiber residue. These samples exhibited residue indicating that the matrix material was not properly cured. Dynamic mechanical analysis and optical microscopy were performed to evaluate the parts. The T_g of the composite tube cross section was only 10°C lower than expected for a fully cured system. Yet, on closer examination it was observed that the outer 2–3 plies were the only parts of the composite that were not cured properly as evidenced by a T_g of over 40°C below the expected value. The soluble matrix material was extracted from the tube with solvent, and FTIR indicated that the reason the resin had not experienced full cure was due to hydrolysis of the monomer during cure. Optical microscopy exhibited porosity and extensive microcracking on the surface of the composite as shown in Figure 9. The origin of the moisture is believed to be due to absorption of water by the prepreg material prior to layup during a

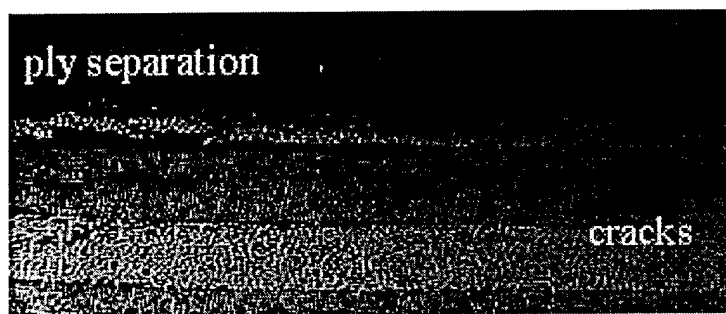


Figure 9. Ply separation and microcracking of a polycyanurate composite that has indications of carbamate formation on the outer plies as verified by FTIR.

prepreg bleeding procedure. During cure, the tubes were not allowed to properly vent and release the trapped moisture within the plies. The moisture was trapped on the outer faces of the tube, causing the formation of carbamates. Proper venting allowed all subsequent tubes to be processed without hydrolysis. This type of hydrolysis on the outer ply layers is typical in fabrication using cyanate ester resins. It is critical to evaluate the outer layers of the samples during quality assurance because weak outer plies can be masked by the well-cured inner plies when using DMA for analysis.

A similar case of carbamate formation was observed in the fabrication of a polycyanurate composite facesheet-aluminum honeycomb sandwich structure. A contractor was fabricating the honeycomb structure in which the outer polycyanurate composite face sheets were co-cured onto the aluminum substructure. In addition, an aluminized Kapton film was cured onto the outer prepreg ply. After cure, the sample was shown to have blisters randomly distributed throughout the Kapton film, as shown in Figure 10. A cross section of the sample once again indicated that blistering had occurred due to carbamate decomposition during cure within the prepreg. This decomposition formed CO_2 gas and formed porosity within the outer plies. Subsequently, the aluminized Kapton film directly above these regions of carbamate decomposition exhibited complete decoupling, as shown in Figure 11. In comparison, areas of good bonding showed no indications of decomposition within the prepreg. The contractor is currently in the process of making subsequent parts and understands the sensitivity of the system to hydrolysis contamination. Extended vacuum debulking and drying of the prepreg for this system is believed to preclude future similar complications.

Another contractor was experiencing high variability in mechanical and thermal (T_g) properties of molded resin samples processed at their facility. The application required high strength and excellent dimensional stability at high temperature. Sample T_g 's that were being processed ranged by as much

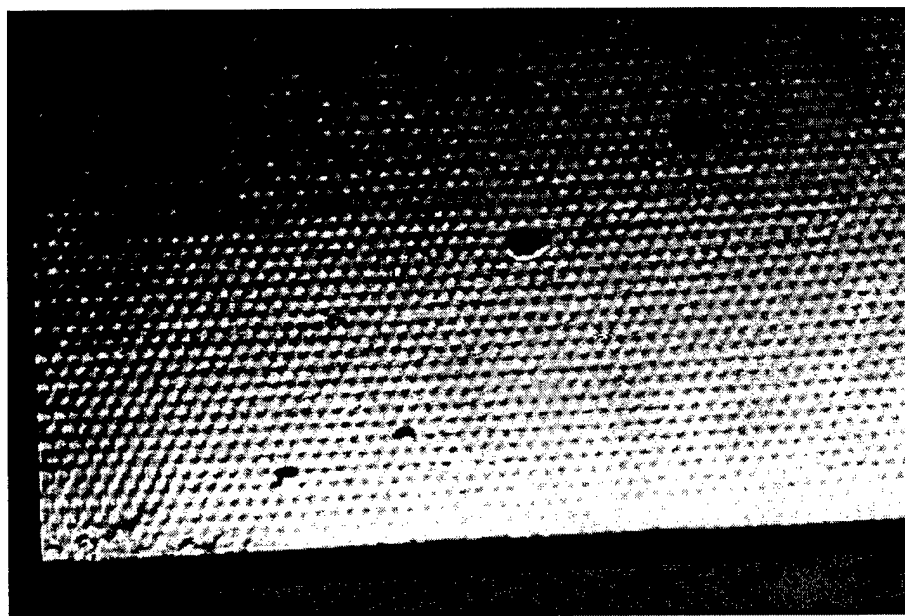


Figure 10. Overhead view showing blistered aluminized Kapton film on the surface of a polycyanurate composite facesheet.

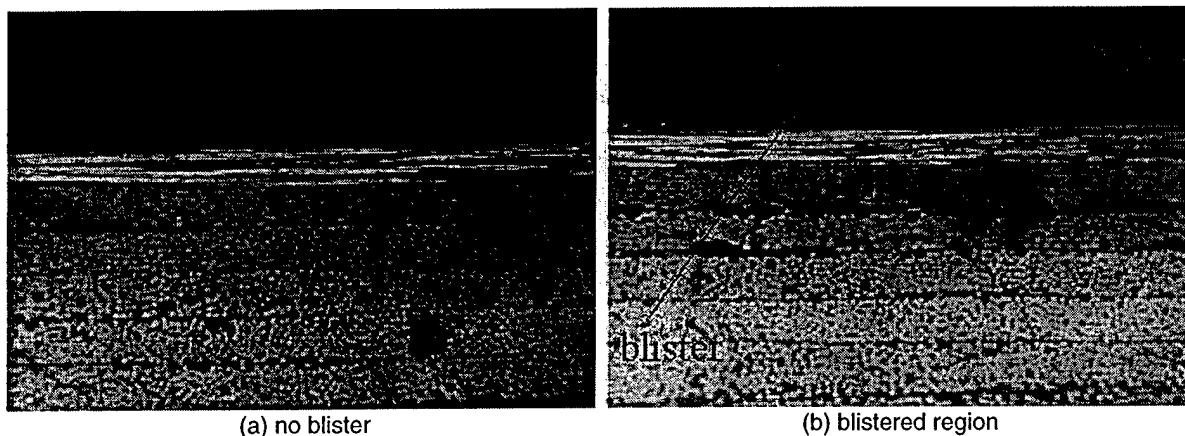


Figure 11. Optical micrograph showing cross-section of polycyanurate composite facesheet bonded to Kapton film. As shown, the areas where decomposition of carbamates occurred within the composite caused a mechanism for carbon dioxide gas decomposition product to blister film.

as 100°C and exhibited a range in strain-to-failure from 1 to 5%. The cure and post-cure temperatures were verified to assure that the samples had been properly heat treated. The samples were all processed in an identical manner for different periods of time. FTIR was used to confirm that all of the samples with poor mechanical properties had some degree of carbamate formation, while those with good mechanical properties exhibited no contamination. Some samples exhibited even greater than expected thermal and mechanical degradation due to additional thermal cycling during cure. The additional thermal exposure caused further degradation of the network with each heat treatment. However, samples that were properly cured in a dry atmosphere and had no carbamate formation exhibited no Tg or mechanical degradation with additional thermal cycling. The fracture surfaces of these polycyanurate resin dogbone samples are shown in Figures 12 and 13. The samples that were

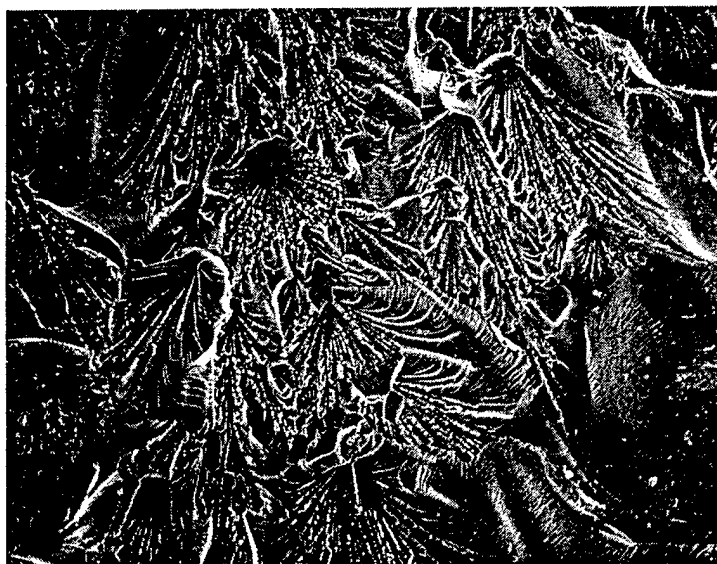


Figure 12. Fracture surface of typical polycyanurate resin dogbone sample. Sample exhibits ductile failure.

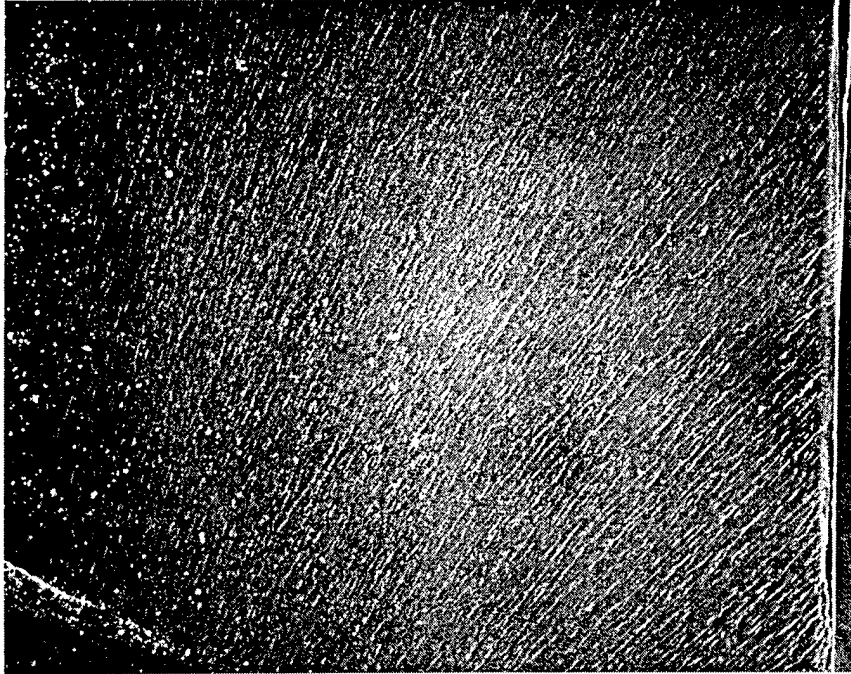


Figure 13. Fracture surface of typical polycyanurate resin dogbone sample that has been pre-exposed to moisture during processing and has carbamate formation as verified by FTIR. Sample exhibits brittle fracture.

properly cured in an inert atmosphere and exhibited no carbamate formation show a ductile failure, as evidenced by the highly yielded and dimpled fracture face shown in Figure 12. The same type of fracture surface is observed for all of the high-strength resin samples. Figure 13 shows the fracture surface of a specimen that has experienced some carbamate formation. This fracture surface indicates a less compliant or yielding failure than that of the previous samples. As verified by the mechanical test data, the strain-to-failure of this sample was considerably lower than the control sample.

Additional problems have also been associated with moisture, not only during processing and cure, but upon exposure after the composites are fabricated. Lee and Holl¹⁰ have reported that a blended cyanate ester formulation (Hexcel 954-2a) that was commonly used in satellite structures exhibited considerable post-cure moisture sensitivity. In their studies, composites (IM7/954-2a) fabricated from this material were exposed to a humid environment (90% R.H., 60°C) and were shown to develop extensive microcracking at the fiber/matrix interface, as well as from delaminations between plies within 50 days. They reported that even though the moisture uptake was very low, this small amount of moisture appeared to selectively attack the fiber-matrix interface of the composite. The in-plane shear strength and the fatigue lifetime (relating to thermal cycle life) were shown to degrade substantially.

3.4 Oxidative Degradation

The variability and low mechanical performance realized by some of the samples analyzed in this study were shown to be attributed to moisture contamination; however, oxidative degradation during processing was also commonly observed with these systems. Polycyanurate resins often demand high

post-cure temperatures in order to achieve a full degree of cure. A typical post-cure schedule is 4 h at 250°C. The type of atmosphere used for curing is often not well specified. However, Zacharia and Simon¹¹ have shown T_g degradations due to thermal aging in both inert and air atmospheres with some cyanate resins. They explained that the degradation is more a factor of the catalyst than the resin. As the copper catalyst concentration increased, more drastic signs of degradation were observed: the time when T_g begins to drop is earlier, and the magnitude of the drop is greater. Uncatalyzed resins exhibited no degradation.

Tests were also performed in our laboratory to develop a better understanding of the thermal aging characteristics of cyanate ester resins in different environments at post-cure temperatures. As shown in Figure 14, we did not observe any T_g degradation whatsoever after exposure in nitrogen for over 24 h at 250°C for a polycyanurate resin with 40 ppm nickel catalyst. T_g degradation was only observed in samples that had been exposed to humidity during processing. However, some T_g degradation was observed in samples aged at these temperatures in air. TGA data exhibited negligible weight loss for properly cured resins exposed in air and inert atmosphere at post-cure treatment temperatures (250°C). However, mechanical tensile tests of the samples exposed to air at these temperatures for prolonged periods of time (24 h) show a sharp decrease in mechanical strength. Scanning electron microscopy indicates a distinct phase within 150–200 μm from the outer surface of the samples, as shown in Figure 15. This may be attributed to oxidative degradation. Oxidation of the outer surface of the sample appears to be the primary cause of failure. The low strain-to-failure associated with this sample was due to premature failure induced by the brittle notch sensitive outer layer of the sample. In most cases, the resin/prepreg suppliers do not stipulate that an inert atmosphere must be used when processing composite parts. Samples exposed to an air atmosphere exhibited a change in color from tan to dark brown. The color variation is usually observed on the outer skin surface of the resin samples. The degree of this darkening effect is usually magnified in samples that have been processed in higher humidity conditions, upon which the material is less tolerant of high-

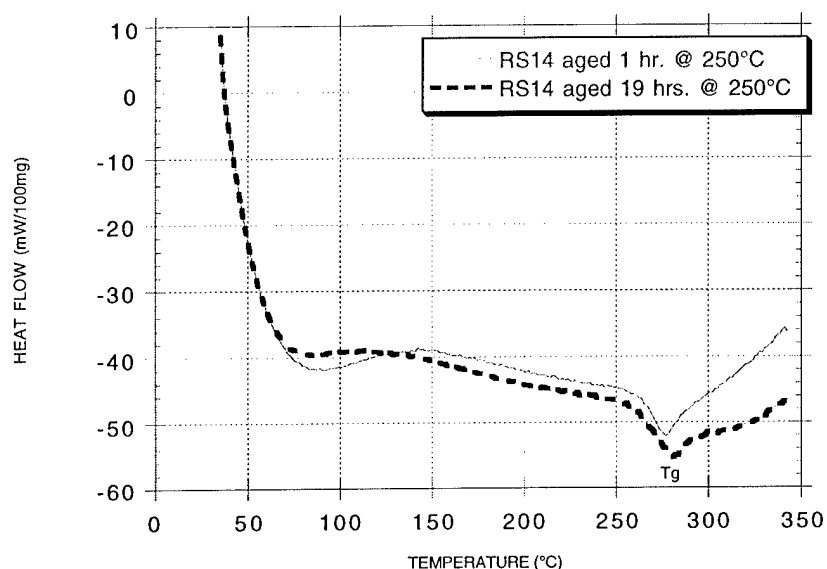


Figure 14. Differential scanning calorimetry of polycyanurate resin samples (a) control 250°C for 1 h, (b) control with isothermal hold @ 250°C in nitrogen for 19 h.

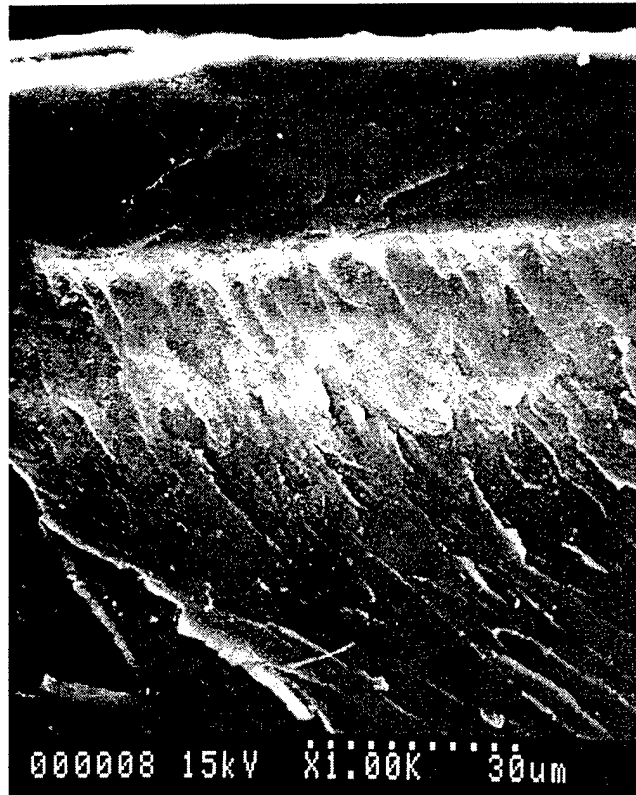


Figure 15. Fracture surface of typical polycyanurate resin dogbone sample that has been pre-exposed to moisture during processing and has carbamate formation as verified by FTIR. Shell-like brittle fracture is formed on outer surface of sample.

temperature exposure. Elevated temperature exposure such as elevated temperature mechanical testing (i.e., creep tests) in air environments is also a critical concern for cyanate ester resins and their composites. In a composite, these color variations are not so easily resolvable and may cause catastrophic failure if undetected. However, variations in the FTIR scans of these air-processed composites can be used to identify degradation.

3.5 Fracture Toughness

Improved fracture toughness and reduced moisture absorption have made resin systems like the siloxane-modified polycyanurate resin a prime candidate for the next generation of satellite composite matrix materials. As shown in Table 1, the 996 resin is considerably more damage tolerant and absorbs considerably less moisture than its predecessors. This translates into higher dimensional stability and delamination resistance in the composite structure. However, processing with these phase-separated systems introduces a number of new challenges. Steckel et al.¹² have shown that the delamination resistance of most cyanate ester composites is superior to those of comparable high-temperature epoxy composites. As shown in Table 2, the higher fracture toughness value for the polycyanurate resin translates to a higher composite G_{IC} value in comparison to the epoxy systems. The type of fiber used controls the magnitude of contribution of the composite fracture toughness. In cases where there is sufficiently strong fiber-matrix bonding, the increased fracture toughness of the

Table 2. Interlaminar Toughness of Carbon Fiber Reinforced Polymer Matrix Composite Systems

Composite System	Process Route	Resin G_{IC} (J/m^2)	Composite G_{IC} (J/m^2)	Composite G_{IIC} (J/m^2)
P100/B30-B50*	prepreg	140	109	180
T300/B30-B50	prepreg	140	202	1070
T300/N5208	prepreg	77	87	900
AS1/3501-6	prepreg	81	130	450
AS4/3502	prepreg	70	88	n/a
T40/Epoxy	filament wound	n/a	312	1160
T1000/Epoxy	filament wound	n/a	140	750

B30-B50 - YLA Inc. formulation of unfilled Ciba Geigy bisphenol A cyanate ester monomer resin.

resin is translated to the composite. In cases where the fiber-matrix interface coupling is poor, the fracture toughness contributions are negligible.

The translation of toughness properties from phase-separated polycyanurate resins may not be so easily realized. The degree of contribution may be more dependent on the fiber-matrix interaction than the bulk resin values. Woo et al.¹³ have shown that even though the fracture toughness of the neat resin was shown to increase sharply with increasing concentration of a co-reacted modifier, the opposite was observed in the composite structure. They believed that the fiber reinforcement in the composite affected the morphology of the phase-separated resin, producing lower G_{IC} values than their corresponding neat resin samples. Zaldivar and Steckel¹⁴ have shown similar results for siloxane-modified polycyanurate matrix systems. Figure 16 shows the interlaminar fracture toughness for both an unmodified and a siloxane modified polycyanurate system with their corresponding composites.

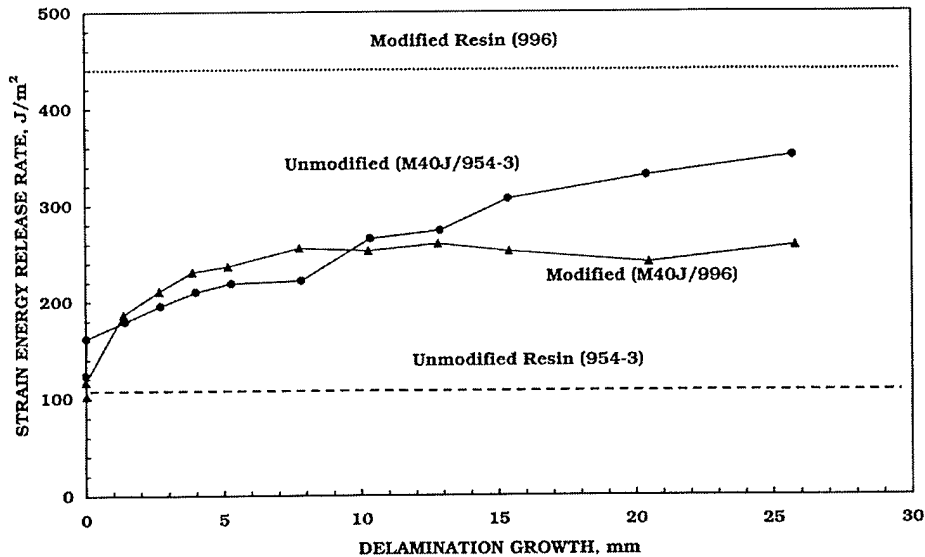


Figure 16. The interlaminar fracture toughness for both an unmodified and a siloxane-modified polycyanurate system with their corresponding composites.

As shown, the siloxane-modified resin is substantially tougher than the unmodified system. However, upon incorporation into a composite, the modified system shows a decrease in delamination resistance while the unmodified system shows an improvement, even though both systems are using the same strongly bonded PAN-based fiber. The unmodified system is surprisingly somewhat more resistant to delaminations than the siloxane-modified system. The reason for this variation can be attributed to the resultant morphology. When processing the neat resin, the second silicon-rich phase is distributed evenly and through fine submicron domains. In the composite, that may not always be the case depending on the processing cure schedule and the type of fiber used. Figure 17 shows the morphology of a fracture surface of a siloxane-modified system that has been fully cured and tested. As shown, the silicon-rich phase appears to agglomerate along the fiber surface. The size of these domains are also considerably larger than those observed in similar neat resins. Both of these factors could contribute to the sharply lower delamination resistance of the composite. In addition, another factor that should be noted is the sensitivity of the siloxane-modified system to final cure temperature variations. Figure 18 shows the delamination resistance curves for an M40J/996 composite system that has been cured to a number of different cure temperatures. As expected, as the cure temperature increases and the degree of cure increases, there is a subsequent increase in fracture toughness. However, a variation of only 10°C in final cure temperature from 175 to 165°C causes a sharp decrease in delamination resistance. This is an area of concern when processing this material. Further work is necessary and ongoing to determine the effect of cure schedule variations on the siloxane-modified composite properties.

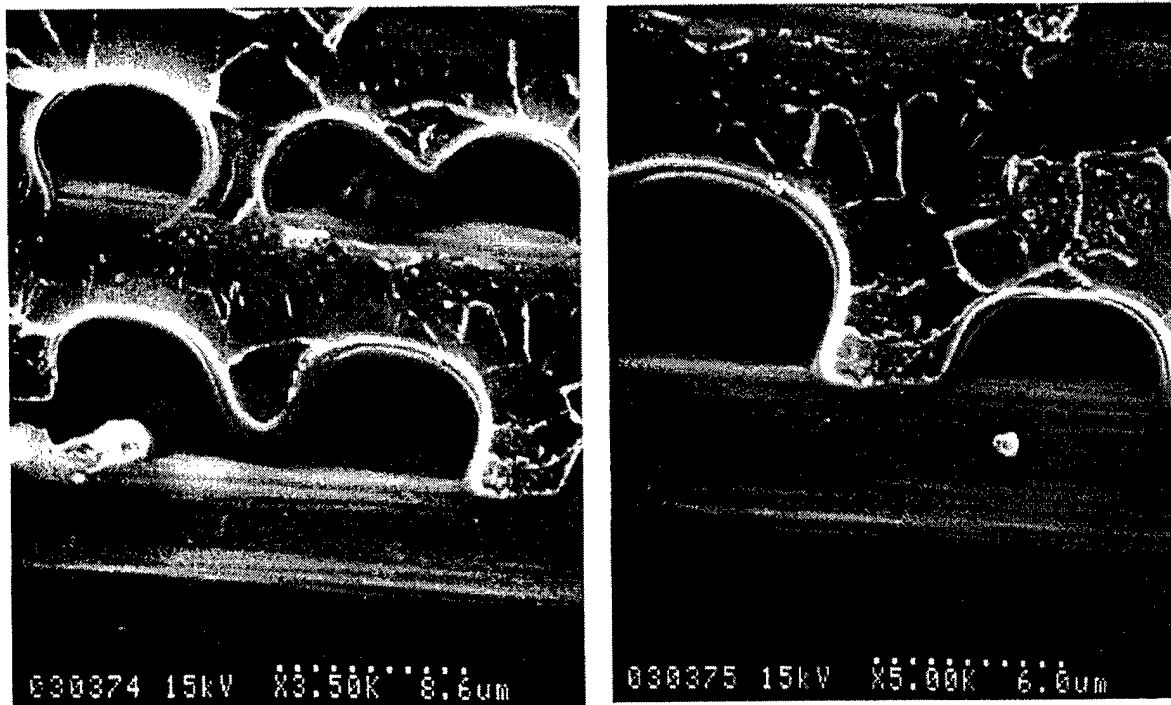


Figure 17. Micrographs of M40J/996 composite HT to 175°C showing silicon-rich phase preferentially wetting fibers.

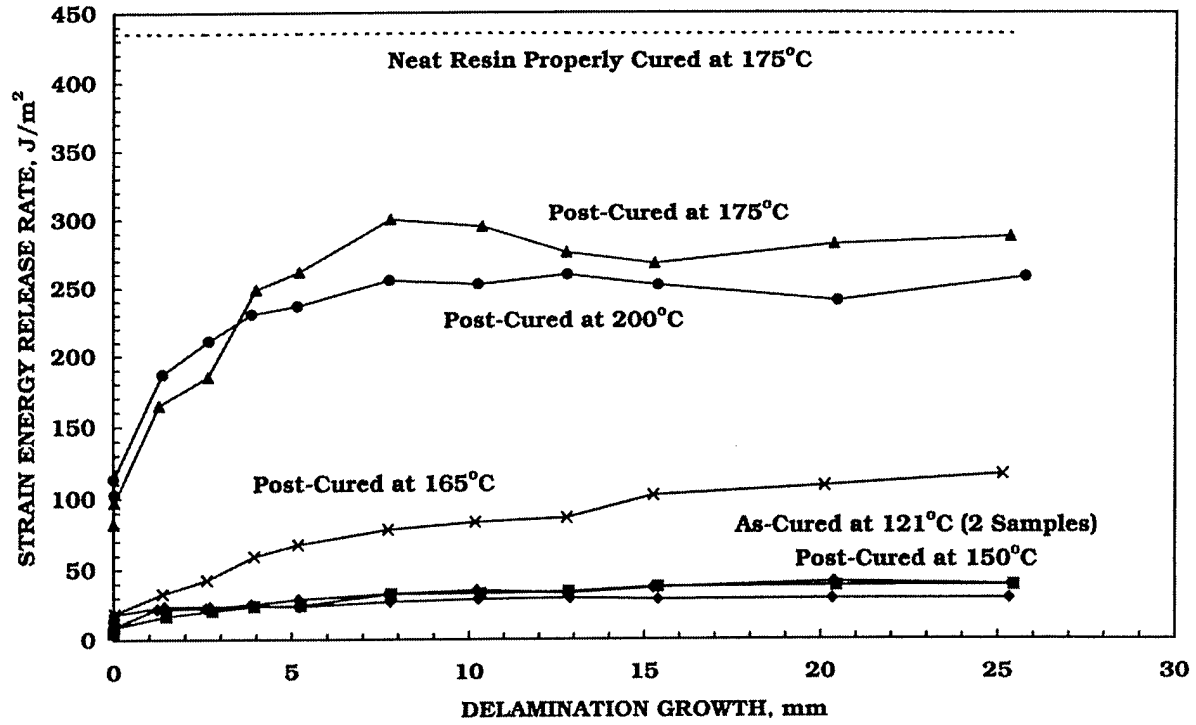


Figure 18. Interlaminar fracture toughness vs delamination growth for M40J/996 effect of cure temperature.

4. Summary

Polycyanurate resins are rapidly replacing epoxies as the new generation of matrix materials used in high-performance composites. The mechanical properties of their composites are comparable to those of graphite/epoxy composites, with the added benefits of higher glass-transition temperatures, reduced outgassing, lower moisture absorption, excellent dimensional stability, and increased toughness. A number of cyanate monomers currently available can be tailored to produce a wide range of desired properties. Polycyanurate composites can be processed using conventional graphite/epoxy manufacturing routes with minor modifications.

The actual cure schedules used have only a minor effect on the final mechanical and thermal behavior of the polycyanurate composites, making them very robust in nature. The highest post-cure temperature has the greatest bearing on most properties. In addition, most unmodified cyanate ester resins have excellent out-time aging characteristics in comparison to epoxies. However, the sensitivity of cyanate esters to moisture during processing is one disadvantage compared to epoxies, especially during filament winding procedures. Moisture contamination at elevated temperature hydrolyzes the monomer, prevents complete cyclotrimerization of the polymer, and lowers T_g . The lowered T_g of the polymer results in an earlier onset of thermal degradation and reduced mechanical properties. This type of moisture contamination does not appear to be reversible. Post-cure treatments, as well as mechanical testing at elevated temperature, should be performed in an inert atmosphere to prevent degradation of the polymer network. Elevated temperature aging of these resins in an inert atmosphere has a negligible effect on thermal and mechanical properties.

Phase-separated polycyanurate systems, on the other hand, may be more susceptible to processing cure schedule variations due to their distinct matrix morphology. The resultant composite properties may not be well translated from bulk resin properties. Future work is necessary to fully evaluate those systems.

References

1. D. Shimp, F. Hudock, and S. Bobo, Proc. of the 18th International SAMPE Technical Conference, pp. 851–861, 1986.
2. J. E. McGrath, P. M. Sormani, and S. Kilie, Makromol. Chem., Macromol. Symp., **6**, p. 67, 1986.
3. R. J. Zaldivar and R. M. Castaneda, ATR-8290-3, The Aerospace Corp. (1996) pp. 1–16
4. J. Pascault, in Chemistry and Technology of Cyanate Ester Resins, I. Hammerton, Ed.; Blackie, London, 1994, Chap. 2.
5. D. Shimp, SAMPE Q. **19** p. 41 (1987), .
6. A. Osei-Owusu and G.C. Martin, Proc. ACS Div., PMS&E **66** pp. 449–450 (1992).
7. T. Fang and F. M. Houlihan, Proc. ASC Polymers Div **35**(1) pp. 535–536 (1994)
8. D. A. Shimp, in Chemistry and Technology of Cyanate Ester Resins, I. Hamerton, Ed., Blackie, London, 1994, Chapter 10.
9. L. Kaseghan, I. Haury, C. Macosko, and D. Shimp, J. Appl. Polymer Sci. **64**, pp.107–113 (1997).
10. B. Lee and M. Holl, Composites Parts **27A**, pp. 1015–1022 (1996).
11. R. Zacharia and S. L. Simon, Proc. ASC Polymers Div., **35** (1) pp. 209–210 (1994).
12. G. Steckel, R. W. Kobayashi, and R. J. Zaldivar, Proc. of the 3rd International Conference on Composites, p.350 (1994).
13. E. Woo, B. Fukai, and J. Seferis, J. Appl. Polymer Sci. **23**, pp.192–203 (1992).
14. G. Steckel and R. Zaldivar, TR-2002(8565)-02, The Aerospace Corporation, in press.

LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Laboratory Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual organizations:

Electronics and Photonics Laboratory: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Space Materials Laboratory: Evaluation and characterizations of new materials and processing techniques: metals, alloys, ceramics, polymers, thin films, and composites; development of advanced deposition processes; nondestructive evaluation, component failure analysis and reliability; structural mechanics, fracture mechanics, and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena.

Space Science Applications Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; infrared surveillance, imaging, remote sensing, and hyperspectral imaging; effects of solar activity, magnetic storms and nuclear explosions on the Earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation, design fabrication and test; environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes.

Center for Microtechnology: Microelectromechanical systems (MEMS) for space applications; assessment of microtechnology space applications; laser micromachining; laser-surface physical and chemical interactions; micropropulsion; micro- and nanosatellite mission analysis; intelligent microinstruments for monitoring space and launch system environments.

Office of Spectral Applications: Multispectral and hyperspectral sensor development; data analysis and algorithm development; applications of multispectral and hyperspectral imagery to defense, civil space, commercial, and environmental missions.