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Development of Tough, Moisture Resistant Laminating Resins



R. A. Brand and E. S. Harrison

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SUMMARY

Current high performance epoxy matrix resins employed in commercial aircraft applications are susceptible to small quantities of sorbed environmental moisture. The sorption of moisture has been shown to degrade the elevated temperature, matrix dominated mechanical properties significantly due to plasticization of the resin.

The objective of this program was to develop laminating resins with improved toughness and moisture resistance that exhibit projected cost, handleability, and processing characteristics equivalent to 394 K (250° F) curing expoxies. Previous contractual efforts (Reference 1) indicated that cyanate resins based on bisphenol A dicyanate and monofunctional cyanate resins with hydrophobic substituents sorbed only small quantities (0.5%) of moisture at equilibrium. As a result, the glass transition temperature (T_g) of the wet resin dropped only 36 K. This represented an improvement over epoxies which sorb around 2% moisture at equilibrium.

During this contract, toughening of the previously developed cyanate was accomplished by the precipitation of small $(\sim 1\mu)$ diameter particles of butadiene-nitrile rubber though the resin matrix. The rubber domains act as microcrack termini and energy dissipation sites, allowing increased stress accommodation prior to catastrophic failure. A unique blend of amine terminated butadiene-nitrile elastomer (MW 2,000) and a high nitrile content butadiene-nitrile rubber (Hycar^(R) 1441) yielded the desired resin morphology. Mechanical properties of composites made from unidirectional T-300 graphite and this resin showed 33% lower as-fabricated short beam shear strength than Narmco 5209 due to the impact modifiers incorporated into the resin. Moisture sorption was also quite low (0.3% at equilibrium) and was probably due to the increased hydrocarbon nature of the blended resin. T_{α} depression was only 4 K (8° F) at moisture equilibrium. Neat resin samples show an apparent flexural modulus similar to 2,2-bis(pcyanatophenyl) propane (BPADC) but with an eight-fold increase in ultimate flexural strength. The higher flexural strength is probably due to a higher strain accommodation provided by the precipitated rubber particles.

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INTRODUCTION

The loss of physical properties of graphite reinforced epoxy resin composites at elevated temperatures is a significant problem related directly to the sorption of atmospheric moisture. The sorption of water is characteristic of epoxy resins and results in the plasticization of the matrix. Plastic-ization lowers the glass transition temperature (T_g) with a concomitant lowering of the elevated temperature physical properties. Property loss continues until the matrix becomes saturated.

The successful application of any material system depends primarily on its long-term response to its use environment. Environmental exposures can range from the severe end of the use spectrum, including high temperature spikes and high loading rates, to mild conditions of low temperatures and no loads. The susceptibility of high-performance matrix resin (epoxies) property degradation by the apparent plasticization of the resin by sorbed atmospheric moisture is well documented. The improvement in moisture resistance is critical to the expanded employment of composites in commercial aircraft applications.

Epoxy resins generally exhibit high crosslink densities when cured. The high crosslink density directly relates to the high modulus of the resin, and high modulus is necessary for successful composite property translation. The high modulus of the epoxy resin is also a detriment with regard to impact strength. Materials that have a low strain-to-failure have poor ability to absorb and dissipate energy. As a result, crack propagation is rapid and catastrophic failure occurs at relatively low impact energy levels. A certain degree of success has been achieved by modifying high modulus matrices with "soft" rubber domains to absorb and dissipate energy (References 2, 3). Another approach employing flexibilizers has also led to improvements in impact strength of matrix resins (Reference 4).

1.1 OBJECTIVE

The objective of this program was to develop laminating resins with improved toughness and moisture resistance. The overall objective of this program was to develop cyanates as laminating resins for use with Thornel T-300 graphite reinforcement with cost, handleability (e.g., drape, tack, flowlife, etc.) processability, and mechanical properties equivalent to state-of-the-art 394 K (250° F) curing epoxy systems (e.g., Narmco 5209 resin) but with improved moisture resistance and toughness.

1.2 RESIN REQUIREMENTS

To develop a moisture resistant laminating resin with improved impact strength, a program was planned which first optimized the moisture resistance of the proposed resin system and then was modified to maximize the impact resistance. The B-staged modified cyanate resin, which impregnates the graphite fibers, must possess the following characteristics to be adaptable to current commercial prepregging and curing methods.

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- a. Be resinous at room temperature to allow drape and tack characteristics in the prepreg form.
- b. Cure by an addition or ring opening mechanism with no volatiles evolved during cure.
- c. Have a reasonable shelf life.
- d. Not require an extended high temperature post-cure for complete resin cure.

The cured resin must also possess satisfactory physical properties in addition to superior moisture resistance and increased impact strength. The cured resin properties include:

- a. A glass transition temperature somewhat excess of the cure temperature resulting from sufficient crosslink density and segmental rigidity.
- b. A balance of polar and nonpolar molecular substructures to ensure adequate cohesive energy density levels and yet minimize resin/moisture interaction.
- c. Inclusion of bulky, hydrophobic substituents to lower the microvoid content.
- d. A relatively high flexural modulus.
- e. A higher strain accommodation relative to state-of-the-art epoxies which results in increased resin toughness.

The results of a previous NASA contract (Reference 1) indicated that cyanate resins can be formulated to meet these requirements. The resins are based on 2,2-bis(p-cyanatophenyl)propane (BPADC). BPADC cures to a high crosslink density and shows substantial internal strain when the neat resin is viewed through crossed polaroids. The BPADC resin never cures completely at the defined cure temperatures. The addition of a hydrophobic monofunctional cyanate allowed adjustment of the crosslink density, a more complete resin cure (based on residual unreacted cyanates after cure) and increased moisture resistance. Strain accommodation was increased as evidenced by a decrease in the brittleness of the cured resin and an increase in the impact strength.

1.3 CYANATE RESIN CHEMISTRY

Cyanate resins were selected for this investigation because of their ease of preparation, synthetic latitude in resin modification, and well-known chemistry (Reference 5). A crosslinked system is formed through a thermally activated addition (cyclotrimerization of the cyanates to a cyanurate) cure mechanism. The physical properties of the cured resin are modified by the appropriate choice of a substituted monofunctional cyanate and a difunctional cyanate in proper ratio. A 50:50 mixture of a monofunctional and difunctional cyanate upon cure would, theoretically, lead to a highly branched but uncrosslinked polymer. Therefore, the crosslink density can easily be adjusted to maximize the physical properties of the cured polymer by adjusting the monofunctional to difunctional cyanate ratio. A balance of the physical properties and moisture resistance was achieved in this manner.

Cyanate resins are derived from monofunctional and difunctional aromatic phenols. The phenols are converted to the aromatic cyanates by treatment with a cyanogen halide and triethylamine in a suitable solvent (Figure 1).

The cyanates are purified by recrystalization or distillation and B-staged to the appropriate degree. B-staging allows the prereaction of the cyanate monomers to build up the molecular weight, lose the crystallization characteristic of the unreacted cyanates, and dissipate a large fraction of the heat of reaction associated with the trimerization of the cyanate to the cyanaurate linkage. B-staging occurs at elevated temperatures (425 K, 306° F). Catalysts or catalytic materials that have not been sufficiently removed from the starting materials can cause a runaway degradative exotherm. Catalysts can be mixed in with the resin after B-staging to facilitate cure. The most efficient catalyst found in these studies has been zinc stearate. The zinc catalyzes the trimerization of the residual cyanate moieties and the stearate moiety allows excellent solubility of the catalyst in the resin. A catalyst loading of around 0.5% by weight seemed to yield the best cure times with sufficient prepreg out-time. The catalyst lowers the reaction exotherm temperature of the trimerization reaction by lowering the amount of energy required for trimerization. This produces lower curing temperatures and faster curing times but increases the room temperature advancement of the resin (decreases out-time).

The B-staged cyanate resin is fluid at room temperature, exhibiting a controllable viscosity related to the degree of advancement allowed during Bstaging. The cyanate resin is thus amenable to current hot melt prepregging technology. The resin is also soluble in a wide range of low-boiling organic solvents that can be employed for fiber impregnation.

Moisture resistance in cyanate resins was optimized by the incorporation of monofunctional cyanates with large, flexible aliphatic (hydrophobic) substituents into the polymer structure. Only aromatic cyanates were employed as resins since aliphatic cyanates rearrange easily to the corresponding isocyanate. The cyanate functional group is susceptible to nucleophilic attack by alcohols, amines, carboxylates, and so on, producing an addition product that will not undergo a cyclotrimerization reaction upon thermal cure. Care must be taken not to add any potential nucleophile to the resin mixture inadvertently as a solvent. The reactivity of the cyanate was utilized to chemically bind the butadiene-nitrile rubber impact modifiers to the cyanate matrix. This technique is discussed in the technical discussion section.

1.4 IMPACT MODIFICATION

The enhancement of impact and toughness properties of epoxies are well-known and are generally based on the reduction of brittleness (modulus) of the resin. Usually, however, a reduction in brittleness occurs with a corresponding reduction in physical strength. Flexibilizing additives often cause severe lossess in the thermal/mechanical properties of the resin. Increases in the impact strength of epoxies, or toughening, has occurred when a soft or rubber phase separates out on cure forming a two-phase system. Low molecular weight elastomers with terminal functional groups that are capable of chemically reacting with epoxy groups have been used to modify or toughen epoxy resins. The soft elastomer phase acts as a microcrack terminus capable of dissipating impact energy. This approach was employed to toughen the existing moisture resistant cyanate resins. This program developed a successful method of precipitating butadiene-nitrile elastomer domains of about 1 micron in diameter in the cyanate resin matrix.



Preparation







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TECHNICAL DISCUSSION

Program Approach

Work performed under previous NASA contract (Reference 1) indicated that modified cyanate resins are comparable in performance to $394 \text{ K} (250^{\circ} \text{ F})$ epoxy resins (e.g., Narmco 5209) at room and elevated temperature (355 K, 180° F). The most significant result was in the retention of the original properties after humid aging. Flexural properties were virtually unchanged, while short beam shear strengths showed a nominal decrease of between 15 and 30 percent.

To optimize moisture resistance and maximize cured resin toughness, the following program (Figure 2) was proposed. An iterative loop sequence



Figure 2, Program Task Breakdown

wherein alternative monomer synthesis or formulation changes are suggested by the results of both bulk polymer and laminate test results were followed. The toughness improvement task was based on the feed back of results from bulk resin fracture toughness test results. Optimization of the resin toughness then led to prepreg development and laminate fabrication and testing.

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Previous results inferred that a base resin of BPADC containing 20 to 30 mole percent of nonylphenylcyanate (NPC) exhibited improved moisture resistance over state-of-the-art (394 K, 250° F) epoxy resins.

Additional monofunctional cyanate blending and testing was performed to optimize moisture resistance and increase toughness. Phenylphenylcyanate and nonylphenylcyanate mixtures with bisphenol A dicyanate were evaluated only to show that the best moisture resistance/apparent strength properties were with the 70% BPADC/30% NPC system. The optimized moisture resistant resin was subsequently toughened through the use of flexibilizers and phaseseparated rubber in the matrix resin.

2.1 MONOMER SYNTHESIS

Two monofunctional and one difunctional cyanate monomers listed in Table 1 were synthesized according to the procedure of Grigat, et al. (Reference 5). Cyanogen chloride was employed in the synthesis, producing the products in high yield. A typical synthesis consisted of charging a three-necked, 1 liter round bottomed flask with a solution of 65 g (1.05 moles) of cyanogen chloride in 300 ml of anhydrous acetone and maintaining the temperature of the mixture at 263 K (14° F). The flask was equipped with a mechanical stirrer, thermometer, and an addition funnel. A slow stream of nitrogen swept through the apparatus terminating in a sodium hydroxide/water/isopropanol solution gas trap. A solution of the appropriate phenol (1.0 mole based on the hydroxy group) in 250 ml of anhydrous acetone was also added to the reaction vessel. The solution was stirred and 101 g (110 mole) of triethylamine added dropwise slowly maintaining the temperature below 273 K (32°F). The solution was stirred for an additional 30 minutes upon completion of the triethylamine addition. The reaction slurry was poured into 3 liters of stirred water and the crude product was collected by filtration or separation (if liquid). The solid products were air dried after water washing and recrystallized from the listed solvents. The liquid product was washed thoroughly, dried over anhydrous sodium sulfate, filtered and distilled under reduced pressure. The synthetic reactions should be carried out under a hood in a well-ventilated area. Appropriate handling and safety precautions are necessary when working with cyanogen chloride.

The 2,2-bis(4-cyanatophenyl)propane was recrystallized from carbon disulfide in very good yield. The carbon disulfide is extremely flammable and was heated with warm water with no flames or hot metal present in a hood. All filtrations and drying steps were also done in a hood. The crystals of the product were vacuum dried to remove the last traces of solvent.

2.2 CATALYST STUDY

Although a wide variety of transition metal salt catalysts (including stearates and acetylacetonates) have been investigated for lowering the initiation temperature of cyanate resin polymerization (Reference 1), a latent catalyst system was proposed in this contractual effort to increase the shelf-life or out-time of the resin. As the catalyst (e.g., zinc stearate) concentration increased, the more the reaction exotherm maxima (determined by DSC) decreased. The out-time was correspondingly shorter as Table 1. Monomer Properties

Cyanate Monomer	Melting Point K(F) or Boiling Point K(F) at mm Hg	Literature * Melting or Boiling Point, K(F), at mm Hg	DSC Trimerization Exotherm, K(F) Maximum	Recrystal- lizing Solvent and Yield
2,2-Bis(4-cyanatophenyl)- propane (BPADC)	356-357 (181-183)	354-355 (178-180)	548 (527)	Carbon Disulfide (90%)
4-Nonylphenylcyanate	404 (268) at 0.75 mm	407-409 (273-279) at 0.8 mm	496 (433)	
4-Phenylphenylcyanate	335-336 (144-146)	335 (144)	490 (423)	Ligroin (48%)

*Grigat, E. and Putter, R., <u>Angew</u>. <u>Chem</u>. <u>Int</u>. <u>Ed</u>., <u>6</u>, (1967) No. 3.

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the catalyst concentration increased. A latent catalyst system would allow longer out-times, the catalyst being much less efficient at lower temperatures. The latent catalyst approach employed was based on the solubility of the catalyst in the resin. The zinc ion is an active catalytic agent for cyanate resins, but its activity is dependent on the effective concentration in the cyanate resin. By varying the molecular weight of the zinc counter ion, it was hypothesized that the activity of the catalyst could be controlled by varying the temperature dependent solubility.

Three zinc salts were investigated to determine whether a latent zinc catalyst could be found for the B-staged cyanate resins. The most effective catalyst for lowering the cure temperature of cyanate resins found in this program has been zinc stearate. Zinc stearate has good solubility in the cyanate resins and the cure proceeds relatively rapidly even at room temperatures and out-time of the prepreg was expected to be somewhat low (days instead of weeks). The employment of a latent catalyst would allow increased out-time at ambient conditions and a more rapid cure capability than the uncatalyzed resin. To accomplish this, the cure of a 64/18/18 (BPADC/ NPC/PPC, mole ratio) B-staged resin mixture was monitored with 0.051% (by weight) of zinc in the form of zinc acetate, zinc benzoate and zinc stearate. As the molecular weight of the counterion increases, the solubility of the salt in hydrophobic solvents (cyanates) increased and in hydrophilic solvents decreased. The gel times of the three samples are listed below with the corresponding reaction exotherm maxima as determined by the Du Pont 990 DSC at a heat-up rate of 10 K/minute.

Catalyst	Gel Time at 430 K (Min.	.) Reaction Exotherm Maxima, K
Zinc Steara	te 34	446
Zinc Benzoat	te 40	481
Zinc Acetate	e 43	486

The gel times and reaction exotherm maxima are inversely related to the molecular weight of the counterion and proportional to the apparent solubility of the catalyst in the B-staged resin (the lower the molecular weight, the longer the gel time).

Out-time measurements indicated that the 64/18/18 (BPADC/NPC/PPC) B-staged resin was still "tacky", although more viscous, after 10 days at ambient conditions.

The zinc stearate catalyzed cyanate advanced fastest becoming tack-free and glassy in 4 days; the zinc benzoate catalyzed resin became tack-free in 7 days. The zinc acetate catalyzed resin became glassy after 8 days. Dispersions of inorganic zinc salts may prove to be good latent catalyst systems, but they were not investigated in this program. Ambient moisture does not appear to accelerate or retard the cyanate polymerization. Catalyzed cyanate resins were placed in a desiccator and the advancement rate proved to be identical to resins left in ambient moisture conditions (~50% rel-ative humidity).

The three-week shelf life expectancy of B-staged cyanate resins can be met if the resin is carefully B-staged to a "green" state. Care must be taken to advance the resin far enough so that crystallization of unreacted monomers does not occur but not too far to prematurely age the resin. Addition of the catalyst (0.5%) lowers the shelf life to about one week. Impact modifiers (which are described in more detail in the resin toughening section) are expected to act as a diluent and would be expected to retard the polymerization of the cyanate resin. Unfortunately, the modifiers employed, butadiene-nitrile elastomers, are also somewhat catalytic to the polymerization. The effect is not as dramatic as the zinc salts, but some low temperature exotherm is observed in the DSC. It appears the rubber modified system exhibits the best shelf life without the addition of a zinc catalyst. Its shelf life has exceeded three weeks at ambient conditions with minimal advancement.

2.3 RESIN FORMULATION

Trade-off studies of cyanate resins have indicated that as the moisture resistance increased (i.e., the mole fraction of NPC to BPADC increased), the glass transition temperature (T_g) decreased. This was undoubtedly due to the increased chain flexibility caused by the lower crosslink density. At a 30-mole percent loading of NPC, the T_g was about 433 K (312° F). This temperature reflects the maximum cure temperature of the system, 422 K (300° F). Higher proportions of BPADC would result in an undercured resin with the cure schedule constraints of this program. As a result, a fraction of unreacted cyanate groups would remain in the resin and the physical properties would not be maximized. Therefore, the resin system proposed would have a minimum of 20-mole percent and a maximum of 30-mole percent NPC to maximize reactivity, physical properties and moisture resistance.

2.4 BULK RESIN PROPERTIES

Resin castings for fracture toughness specimens were submitted to NASA Langley for machining and testing. The bulk resin screening program was intended to describe the differences in resin "toughness" brought about by formulation changes in both copolymer components and composition. Fracture toughness values of the bulk resin were employed as a screen for impact resistance development in composite applications. The following series of resin compositions was synthesized and submitted for evaluation.

	Resin	Composi	tion (Mo	le %)
Component	A	В	<u> </u>	<u>D</u>
BPADC	100	80	70	64
NPC	0	20	30	18
PPC	0	0	0	18

A commercial epoxy resin control (Narmco 5209) was also submitted for comparison purposes.

All cyanate resins used in this study were cured at $394 \text{ K} (250^{\circ} \text{ F})$ with a postcure of $422 \text{ K} (300^{\circ} \text{ F})$. A stepwise increase in temperature was employed to avoid destructive exotherms. Cyanate resins which are catalyzed with zinc stearate are particularly sensitive to a runaway reaction. They are gelled about 10 K below the exotherm takeoff point (377-383 K). The temperature is then slowly increased to the 394 K maximum. "Green" resins are more susceptible to degradative exotherms than more advanced resins. However, too much advancement makes the mixing, degassing, and general handling more difficult.

The fracture toughness data received from NASA Langley is presented in Table 2.

Table 2. Fracture Toughness as a Function of Cyanate Resin Composition

Resin System		Fracture Toughness <u>G</u> lc, <u>J/M²</u>
BPADC		108
BPADC/NPC	(80/20)	92
BPADC/NPC	(70/30)	379
BPADC/PPC/NPC	(64/18/18)	320
5209		256

The BPADC (70/30) mixture shows about 250% improvement over BPADC resin. The addition of the monofunctional cyanate (NPC) decreases the crosslink density giving the cured polymer more linear character and, hence, a higher fracture toughness. Inclusion of the pendant nonyl groups probably imparts some flexibility. Considerable improvement (100% to 360%) over the various commercial systems is apparent.

The fracture toughness of the BPADC/NPC (80/20) composition is inconsistent, probably due to improper cure conditions, (and therefore the fracture toughness value suspect) with the trend of adding a monofunctional cyanate to the BPADC to increase toughness and increase moisture resistance. The 70/30 mixture of BPADC/PPC exhibits a fracture toughness 48% higher than the 5209. This is a slight improvement over the state-of-the-art (250° F) cure epoxy. Additional steps were taken to increase the fracture toughness of the cyanate resins; these are described in detail in the "Toughness Improvement" section.

The water sorption curves of BPADC modified with NPC and PPC are shown in Figure 3 as a function of composition. These results were obtained under a previous contractual effort (Reference 1). Composition with 20 and 30 mole percent of the monofunctional cyanate in BPADC result in a weight gain of 0.4 to 0.6 percent water.



Figure 3. Water Sorption of Copolymers

2.5 TOUGHNESS IMPROVEMENT

Fracture toughness of crosslinked resin has been improved by the dispersion of rubber particles of appropriate size throughout the resin matrix. The rubbers are usually chemically bound to the matrix resin and at sufficient degrees of reaction, they coalesce (phase separate) to discontinuous regions. These regions tend to serve as termini for crack propagation and usually increase the fracture toughness of the host thermoset resin.

Four approaches have been investigated to attain the phase separation or precipitation of a "soft" elastomer phase in a high modulus cyanate matrix. The first approach was to blend a low molecular weight (about 2,000g/mole) elastomer with reactive end groups in a cyanate matrix. On cure, the elastomer would react with the cyanate resin theoretically providing a good bond interface between the discontinuous phases. The second approach was to disperse a high molecular weight elastomer in solution into the cyanate resin, remove the solvent, and cure the resulting material. The dispersed high molecular weight rubber could precipitate as discrete particles in the cyanate matrix on cure of the resin. The third approach was to employ a low molecular weight flexibilizer as an additive to the cyanate resin with no reactive end groups. This procedure would decrease the modulus by plasticization of the matrix and may produce phase-separated soft regions. The fourth and final approach taken to toughen the matrix was to utilize a hybrid system consisting of a low molecular weight nitrile rubber with reactive end groups blended with a high molecular weight elastomer. The low molecular weight elastomer could "solubilize" the high molecular rubber until resin advancement was sufficient to precipitate the high molecular weight rubber.

Low molecular weight $(\1,000 - 2,000 \text{ g/mole})$ rubbers terminated with hydroxy, amine, and carboxy groups would be expected to react chemically with the base cyanate resin and improve the fracture toughness characteristics of the base resin. Aromatic cyanates are known to react with alcohols in the following manner forming alky1 aryl iminocarbonates, which can rearrange under acid conditions to form carbamates.

$$Ar - OCN + HO - R \longrightarrow Ar - O - C - O - R$$

$$Ar - O - C - N - R \longrightarrow Acid$$

The reaction of a primary amine could lead to a 2:1 adduct as follows:

$$2 \text{ Ar} - \text{OCN} + \text{R} - \text{NH}_2 \longrightarrow \text{Ar} - \text{O} - \begin{array}{c} \text{NH} & \text{NH} \\ \text{II} \\ \text{C} - \text{N} - \begin{array}{c} \text{C} \\ \text{C} \end{array} - \text{O} - \text{Ar} \\ \text{R} \end{array}$$

Carboxylic acids do not form stable products with cyanates, but do form transient mixed acid anhydride linkages. This reaction would result in an overall decrease in the cyanate density of the resin and the lack of a chemical bond between the cyanate and the rubber modifier.

$$Ar - OCN + R - COOH \longrightarrow \{Ar - 0 - C - 0 - C - R\} \longrightarrow RCOOH$$

$$Ar - 0 - C - NH_2 + R(CO)_2 0 \longleftarrow RCOOH$$

Approach 1

A variety of elastomeric materials ranging in molecular weight and composition were blended with the B-staged 64/18/18 (BPADC/NPC/PPC) resin system in various quantities to ascertain the effect of the rubber toughening agent on fracture toughness and glass transition temperature (T_g). Three amounts (3%, 6%, and 9%) of the rubber toughening agent were chosen for screening purposes. Initial results indicated that 3% or less of the rubber toughening agent is required in this cyanate system to retain a reasonable T_g (>393 K, >248 F).

Table 3 summarizes the results. The liquid, high acrylonitrile (50%) amineterminated butadiene (1300 x 16) reacted with the cyanate resin on mixing, forming a crosslinked, two-phase system. Further heating with zinc stearate cured the remainder of the cyanate resin. This particular system exhibited poor strength and low T_g due to phase separation.

The carboxy-terminated butadiene-nitrile modifiers exhibited satisfactory T_g 's at low loadings (about 3% or less). The apparent decrease in physical and mechanical properties makes these modifiers unsuitable for use as impact modifiers.

No hydroxy-terminated 1,4-poly(butadiene-acrylonitrile) was immediately available, so an alternate hydroxy-terminated 1,2-polybutadiene was substituted. Mixtures of 3%, 6%, and 9% hydroxy-terminated 1,2-polybutadiene in 64/18/18 (BPADC/NPC/PPC) resins were accomplished in benzene solution. After the solvent was removed, the mixture was cured at 394 K (250° F) for eight hours and post-cured 422 K at (300° F) for 20 hours. The 1,2-polybutadiene-modified cyanate resin exhibited some interesting differences from the 1,4-poly(butadiene-acrylonitrile) rubber-modified resin. The hazing, or incompatibility, normally associated with the 1,4-poly(butadieneacrylonitrile), was absent in the 1,2-polybutadiene modified cyanate resin. Thermo-oxidative stability also appears to be somewhat higher since discoloring does not occur on post-cure. The T_g's of the samples, however, are all less than 373 K (212° F). The fracture toughness shows drastic qualitative decreases as in the other PBD modified resins.

Precipitous strength and T_{g} decreases which occurred in the 3% to 9% modifier loading of the cyanate resin (64/18/18: BPADC/NPC/PPC) led to the consideration of lower concentration of impact modifiers (0.5% - 1.5%) in the resin. Instead of a cyanate resin blend, neat BPADC was employed as the baseline resin to better ascertain the effect of the modifier. Cure of BPADC mixed with 0.5%, 1.0%, and 1.5% of amine-terminated 1,4-poly(butadiene-acrylonitrile) (ATBN), carboxy-terminated 1,4-poly(butadiene-acrylonitrile)(CTBN) and hydroxy-terminated 1,2-polybutadiene (HTBD) were accomplished. The cyanate and the rubber modifier were dissolved in benzene and the solvent removed. Cure occurred in two stages. The temperature was raised to 423 K (302° F) and held 20 hours (no zinc stearate was used as a catalyst). The T_{g} 's and subjective toughness were evaluated. Further cure to 473 K (392° F) over 12 hours was accomplished and the evaluation repeated. The T_{g} results are summarized in Table 4) and the summary of the macroscopic examination of the fracture planes is given in Table 5. The glass transition temperatures generally follow the cure conditions and are lowered by the addition of the rubber modifiers. The T_{g} depression appears to be proportional to the amount of modifier added to the base resin.

The rubber modified cyanates discolored during cure from yellow-brown to brown. Again, the greatest discoloration occurred in the poly (butadieneacrylonitrile) rubbers. The 1,2-polybutadiene appeared more stable under thermoxidative conditions than the acrylonitrile-butadiene rubber-modified cyanate resin.

Table 3. Glass Transition Temperatures and Apparent Strength of Modified Cyanate Resin (BPADC/RPC/PPC 64/18/18)

	3%	6%	9%
	T _g /Apparent Strength	T _g /Apparent Strength	T _g Apparent Strength
Amine Terminated 1,4-Poly (butadiene-acrylonitrile) (Hycar 1300 x 16)		Inhomogeneous -	
Carboxy Terminated 1,4-Poly (butadiene-acrylonitrile) (Hycar 1300 x 13)	407 K/Lower	358 K/Lower	358 K/Lower
Carboxy Terminated 1,4-Poly (butadiene-acrylonitrile) (Hycar 1300 x 8)	435 K/Lower	327 K/Lower	300 K/Lower
Hydroxy Terminated 1,2-Polybutadiene (H 1000)	348 K/Lower	308 K/Lower	329 K/Lower

Table 4.	Glass Transition	Temperatures	of	Elastomer
	Modified BPADC Re	esin		

Resin	System	T _g , K (F (423 K, 3	') 802 ⁰ F Cure	т _g , к (р (473 к.3	') 92 ⁰ F Cure
BPADC + 1.5%	ATBN	427	(309)	483	(410)
BPADC + 1.0%	ATBN	420	(297)	473	(392)
BPADC + 1.5%	ATBN	413	(284)	473	(392)
BPADC + 0.5%	CTBN	422	(300)	468	(383)
BPADC + 1.0%	CTBN	415	(288)	463	(374)
BPADC + 1.5%	CTBN	411	(138)	458	(365)
BPADC + 0.5%	HPBD	413	(284)	458	(365)
BPADC + 1.0%	HPBD	409	(277)	465	(378)
BPADC + 1.5%	HPBD	437	(327)	460	(369)
BPADC		422	(300)	485	(414)

Table 5. Microscopic Examination of Fracture Planes

Sample

Description

1.	0.5% ATBN + 99.5% BPADC	Smooth Glass Edge
2.	1.0% ATBN + 99.5% BPADC	Micro Cracks, Orthogonal to Fracture Plane
3.	1.5% ATBN + 99.5% BPADC	Pronounced Stress Cracks Orthogonal to Fracture Plane
4.	0.5% CTBN + 99.5% BPADC	Smooth Edge with Microporous Surface
5.	1.0% CTBN + 99.5% BPADC	Smooth Edge, A Few Stress Lines, Phase Separation
6.	1.5% CTBN + 99.5% BPADC	Smooth Edge, Phase Separation
7.	0.5% HPBD + 99.5% BPADC	Striations Orthogonal to Fracture Plane
8.	1.0% HPBD + 99.5% BPADC	Very Rough Fracture Surface, Two Phase Surface
9.	1.5% HPBD + 99.5% BPADC	Rough Fracture Surface, Two Phase Surface
10.	BPADC	Glass Smooth, Surface (Top) Bumpy from Shrinkage (other Samples Much Less So)

The flexibility of the BPADC resin was increased as evidenced by a greater bending tendency prior to fracture. The best toughener appears to be the amine-terminated 1,4-poly(butadiene-acrylonitrile). The worst was the carboxy-terminated 1,4-poly(butadiene-acrylonitrile) at the 1.5% loading. The CTBN also showed evidence of phase separation of the rubber and cyanate resin. This perhaps accounts for the lower fracture toughness. The resin containing ATBN and the HPBD do not show any macroscopic evidence of phase separation and are presumably uniformly dispersed and reacted with the cyanate resin.

A microscopic examination of the fracture planes (Table 5) was conducted to discern any changes in fracture mechanisms. The cured BPADC fractures produce a smooth apparently homogeneous surface. The addition of rubber modifiers results in the formation of striations and rough fracture surfaces. The "classic" rubber-modified epoxy will show a microscopic "haze" upon fracture. The haze is an accumulation of microcracks, cracks that have been terminated by microscopic rubber domains along the main fracture path.

The T_g's of all the samples tested indicated that higher concentrations of modifier can be added to the BPADC before T_g is depressed too much (T_g < 318 K, 257^o F). This implies a loading of 6% to 10%.

The amine-terminated butadiene-nitrile (ATBN) oligomer (Hycar $^{(R)}$ 1300 x 16), on the other hand, was shown to undergo a continuous macroscopic phase separation in BPADC resin mixtures. Very rapid reaction and local gellation occurred upon introducing the amine-terminated material into staged BPADC/NPC/PPC mistures. A successful approach to homogeneously introducing the ATBN into a BPADC resin matrix was developed. The ATBN was prereacted with a three-fold excess of BPADC in a dilute (5%) benzene solution. Refluxing the solution allowed the terminal amine groups to react with the BPADC presumably forming iso-urea groups with terminal cyanate functionality. The solution was cooled and the clear liquid mixed with BPADC to produce blends of 5%, 10% and 15% ATBN. Cure was accomplished by slow heat up to 423 K (300° F) and was usually complete in several hours. The resin castings were clear with no evidence of phase separation. Very small amounts of a surface oil (source unknown) were noted.

The glass transition temperatures $(T_g's)$ of the ATBN/BPADC mixtures were also in the vicinity of 443 K (337° $_{\rm F}$) (Table 7). A pattern of decreasing T_g with increasing ATBN loading. The clarity of the specimens indicated that the ATBN reacted with the BPADC matrix and did not precipitate upon cure. Unmodified BPADC cured at the same temperature exhibits a similar T_g (447 K) (Table 7). The mechanical properties of BPADC are considerably less than the BPADC/ATBN mixture, undoubtedly due to the undercured condition of the BPADC system.

Approach 2

The second approach employed the dispersion of high molecular weight butadiene-acrylonitrile polymer in solution into a B-staged BPADC resin, removal of the solvent by vacuum treatment, followed by cure of the resin. A high nitrile content rubber was selected to affect a similarity in polarities between polymers, in an effort to obtain a better interfacial adhesion between the cyanate and rubber phases (despite the lack of a permanent chemical bond).

A high nitrile (41%) rubber (Hycar (R) 1441) dissolved in methyl ethyl ketone was dispersed at 3%, 6%, and 9% loadings in B-staged BPADC/NPC/PPC (64/18/18) resin. The solvent was removed by evaporation and the resin cured at 422 K (300° F). The results are given in Table 6. The T_g measurements showed considerable range indicating gross phase separation of the 1441 from the cyanate matrix. Strength precipitously decreases in all of the samples relative to the neat resin.

Approach 3

The third method to increase the resin toughness was through the use of non-reactive, low-molecular weight flexibilizers.

Jefferson Chemical Co., Inc., (a subsidiary of Texaco, Inc.) produces a material designated Jeffamine (R) BuD-2000. It is a urea-terminated polyoxypropylene synthesized from the reaction of their amine-terminated polyoxypropylene (D-2000) with a carbamate yielding the bis(urea). The clear viscous liquid is low molecular weight (~2,000 MW) and is used as a flexibilizer and toughener for certain epoxy systems (Reference 6). The BuD-2000 was therefore selected as a candidate toughening modified for BPADC cyanate resin based on the previous success in epoxy systems and preliminary work performed at NASA Langley with cyanate resin.

The BuD-2000 does not seem to react with the epoxy resin (Reference 6) and remains compatible as long as the material is uncured. During cure, BuD-2000 precipitates into ~1 micron spheres (Figure 4). The matrix surrounding the sphere is mainly cured epoxy which is probably somewhat flexibilized closed to the surface of BuD-2000. These "soft" regions act as microcrack termination sites and impart enhanced fracture toughness. The toughness enhancement is apparently due to the phase separation of the two components (rubber and resin) into domains of optimum dimensions.

During cure, BuD-2000 was found to react with the cyanate functional group, unlike the inert behavior observed with epoxy systems. Differential scanning calorimetry indicated that as soon as a 1:1 mixture of BPADC and urea were melted (423 K) an immediate exotherm occurred. Isolation of an insoluble fraction from this reaction followed by infrared analysis confirmed that urea did react in some manner with cyanate. The BuD-2000 was then refluxed with an excess of BPADC in methyl ethyl ketone and the solution mixed with BPADC in proper properties to obtain mixtures containing 5%, 10%, and 15% BuD-2000. The solvent was removed and the resulting resin cured at 423 K for 6 hours. Clear, homogeneous castings were obtained whose appearance was unlike the epoxy systems which are opaque. The castings were cut into approximately 0.040 x 0.015 x 0.005 m specimen sizes. Flexural strength and modulus, glass transition temperature, and Barcol hardness values were obtained. Table 6. Glass Transition Temperatures (Tg's) of BPADC/NPC/PPC (64/18/18) Cyanate Resin Toughened with Hycar^(R) 1441 Rubber

Cured Mixture	T _g (TMA)
3% Hycar ^(R) 1441 97% Cyanate Resin	409 K (277 ⁰ F)
6% Hycar ^(R) 1441 94% Cyanate Resin	397 К (255 ⁰ F)
9% Hycar ^(R) 1441 91% Cyanate Resin	319 K (115 [°] F)
Neat Resin	435 K (324 ⁰ F)



Figure 4. Photomicrograph of the Fracture Surface of a Cured Epoxy Containing 10 PHR BuD-2000 ("Voids" are Approximately 1 μ m in diameter). 88X

Table 7. Physical and Mechanical Properties of Modified BPADC

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Apparent Flexural Modulus, GPa (msi) 3.57(0.518) 3.57(0.518) 3.25(0.471) 3.57(0.518) 3.66(0.531) 3.71(0.538) 3.71(0.538) 3.71(0.538) 3.87(0.517) 1.12(0.162) 3.87(0.562) 3.87(0.562) bber - 41%	
Apparent Flex- ural Strength, Span= 0.03175m MPa (ksi) 136 (19.74) 108 (15.7) 146 (21.12) 82 (11.93) 74 (10.68) 49 (7.14) 118 (17.1) 18 (2.67) 18 (2.57) 18 (2.57) 19 (2.57) 11 (2.57) 11 (2.57) 12 (2.57) 13 (2.57) 13 (2.57) 14 (2.57) 15 (2.57) 15 (2.57) 16 (2.57) 17 (2.57) 18 (2.57) 18 (2.57) 18 (2.57) 18 (2.57) 18 (2.57) 19 (2.57) 18 (2.57) 19 (2.57) 18 (2.57) 19 (2.57) 18 (2.57) 18 (2.57) 19 (2.57) 19 (2.57) 10 (2.57) 11 (2.57) 11 (2.57) 12 (2.57) 12 (2.57) 13 (2.57) 14 (2.57) 15 (2.57) 15 (2.57) 16 (2.57) 17 (2.57) 18 (2.57) 18 (2.57) 18 (2.57) 19 (2.57) 19 (2.57) 10 (2.57) 10 (2.57) 11	
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sition Hrs Cure Hrs Cure 33 0 x 16) 44 00 x 16) 44 Hycar 1441 41 /5% 44 /5% 44 henol A Dicy ne Terminated (urea) Termi	
Cured Resin Compo 423 K (302 ^o F), 6 BPADC/5% BuD-2000 BPADC/10% BuD-2000 BPADC/10% BuD-2000 BPADC/10% ATBN (13 BPADC/10% ATBN (13 BPADC/10% ATBN (13 BPADC/10% ATBN (13 BPADC/10% BuD-2000 Hycaf R 1441 BPADC/10% BuD-2000 Hycaf R 1441 BPADC (Undercured) BPADC (Undercured) BPADC (Undercured) BPADC = Bis ATBN = Ami BPADC = Bis Hycaf R 1441 = Hig	

* Differences are probably due to the oxidation of the exposed top surface during cure ** Shore "D" hardness

1

It should be noted that the values obtained for apparent flexural strength and modulus cannot be compared to ASTM flexure specimens, since the test specimen dimensions are nonstandard. All comparisons in this report are made with the same test configuration, hence numerical comparisons are valid.

The physical properties are listed in Table 7. The flexural strength is almost eight times that of the deliberately undercured BPADC. The modulus with the BuD-2000 additive was about the same as the BPADC but seemed to 'decrease regularly with increasing BuD-2000 content. The T_g 's were difficult to precisely measure by TMA. since sample expansion was not linear with temperature but rather displayed a curvilinear shape. The T_g 's reported for BuD-2000 materials are probably not an accurate value for the true thermal expansion. This behavior is consistent with plasticized resin matrices. The T_g data indicate that the high-temperature strength may be considerably less (due to plasticization) than desired.

A prereact of ATBN and BPADC in concentrations of 5%, 10%, and 15% in BPADC were also evaluated as elastomeric flexibilizers. The results are presented in Table 7. The apparent flexural modulus was quite close to BPADC and the flexural strength higher by a factor of 3 to 4 times. The implication was that the flexibilizing of the BPADC by ATBN allows for more strain accommodation and therefore a higher apparent flexural strength. A decrease in $T_{\rm g}$ of 3 K was observed at a 15% loading.

Approach 4

The next step was to attempt to blend a low molecular weight rubber with a high molecular weight elastomer. Rubber would precipitate out on cure of the resin and yet be bonded to the cyanate matrix. Since Hycar(R) 1441 was employed earlier in the study and is chemically very similar to the ATBN, a mixture of 10% ATBN terminated with BPADC and 5% 1441 was investigated first. The ATBN terminated with BPADC was thought to provide (a) a route to maintaining the 1441 elastomer in solution since they are chemically similar, (b) provide a flexibilized matrix, and (c) perhaps keep the size of the precipitated rubber particles down to an optimum range for shock absorption and dissipation.

The ATBN was prereacted with a three-molar excess of BPADC in benzene at five-percent by weight of solids (a higher loading encourages crosslinking and gellation of the ATBN, as described earlier). The 1441 was dissolved in methyl ethyl ketone and the two solutions (ATBN and 1441) combined. This served to provide good mixing of the polymers. The prereacted solution then was added to more BPADC to produce a mixture with a total of 15% rubber additives. The solvent was removed and the resin cured at 423 K (302° F). An opaque tan casting was obtained with a brownish skin. The discoloration was probably from the oxidation of the rubber adduct. Hardness readings confirmed this since the exposed surface was consistently harder than the unexposed surface. Apparently a uniform phase separation of the 1441 occurred in the BPADC/ATBN matrix. The ATBN/BPADC adduct served to solubilize the rubber phase in the uncured cyanate resin. Upon cure, discontinuous phase separation occurred with rubber particles in the optimum size region.

The mechanical properties (Table 7) were very similar to the BuD-2000/BPADC mixture. The flexural strength was about 70% stronger than the ATBN-modified BPADC. The flexural modulus was less than that of BPADC and the T_g, 413 K (284° F), was slightly less than that in BPADC. Additional post cure at 473 K (392° F) under N₂ lowered the T_g to 403 K (266° F) probably due to flexibilizer decomposition.

A similar ternary mixture of BPADC (85%), BuD-2000 (10%, and Hycar^(R) (5%) was prepared and cured as before. The BuD-2000 and Hycar^(R) 1441 were incompatible during the cure and phase separated into macroscopic domains. The physical properties (Table 7) were quite low. The fracture took place at the interface between the two phases.

Scanning electron microscope (SEM) examinations of the fracture surfaces revealed that the unmodified BPADC is crazed with cracks and microcracks and that the fracture surface between fibrils is relatively smooth (Figures 5 and 6). Addition of 15% ATBN produces a surface whose cracks are smaller than those in BPADC and whose microcracks under 480 power magnification are less numerous than those in the BPADC. The surface of the 15% ATBN-modified BPADC appeared to be more "fibrous" (Figures 7 and 8). The 15% BuD-2000 modified BPADC surface (Figures 9 and 10) showed rough multiplanar fracture with microcracks progressing in directions dependent on the fracture plane observed. Again, the microcracking was more extensive than with the BPADC (at 480 X magnification). The most interesting SEM photographs occurred with the BPADC modified with 10% ATBN and 5% Hycar^(R) 1441. The fracture surface (Figures 11 and 12) show a very rough surface (88 X magnification) and a dispersion of spherical rubber domains of approximately 0.5 to 2.0 microns in diameter. Microcracks can be seen terminating in the softer rubber domains. This dispersion is very similar to a photo micrograph of BuD-2000 in an epoxy matrix (Figure 4). The BuD-2000 increases the flexural strength of the epoxy (increases accommodation of strain) about 2.6% (68.0-73.0 MPa nominal) and lowers the modulus 22% (0.33 to 0.261 GPa). The modifications of BPADC by ATBN, BuD-2000 and ATBN/1441 all increase flexural strength of the BPADC while maintaining approximately the same flexural modulus. This means that resistance to thermal shock, impact loading and probably fracture toughness may also be improved without a dramatic loss of modulus.

2.6 PREPREG PREPARATION

The resin was applied in a solvent for ease of impregnation of the graphite fiber. Cyanate resins are usually hot melt impregnated but with the addition of cyanate-terminated ATBN and Hycar^(R) 1441 high nitrile elastomer, the neat resin viscoelastic behavior changed dramatically. Solvent impregnation facilitated the wetting of the fibers and the distribution of the resin.

The prepreg was prepared by hand laying the collimated T-300 graphite fibers (390 tows per meter - 6,000 filaments per tow) between double-backed tape and impregnating the fibers with a 30% resin solution [85% cyanate resin (80% BPADC and 20% NPC), 10% ATBN prerated with BPADC, and 5% Hycar^(R) 1441]



Figure 5. Photomicrograph of the Fracture Surface of Cured BPADC 88X



Figure 6. Photomicrograph of the Fracture Surface of Cured BPADC 440X



Figure 7. Photomicrograph of the Fracture Surface of Cured BPADC Containing 15% ATBN (1300 x 16) 88X



Figure 8. Photomicrograph of the Fracture Surface of Cured BPADC Containing 15% ATBN (1300 x 16) 440X



Figure 9. Photomicrograph of the Fracture Surface of Cured BPADC Containing 15% BuD-2000 88X



Figure 10. Photomicrograph of the Fracture Surface of Cured BPADC Containing 15% BuD-2000 480X



Figure 11. Photomicrograph of the Fracture Surface of Cured BPADC Containing 10% ATBN and 5% Hycar 1441 88X



Figure 12.Photomicrograph of the Fracture Surface of Cured BPADC
Containing 10% ATBN and 5% Hycar 14412200X

in methyl ethyl ketone. The solvent was evaporated and the prepreg vacuum bagged and warmed to 344 K (160° F). The resin was then worked into the graphite fibers to thoroughly wet them. The prepreg was inverted and the process repeated. The finished prepreg was sealed in polyethylene bags and stored at 255 K (0° F).

After vacuum/heat processing, the prepreg contained approximately 3% volatiles. These could be removed by further vacuum treatment if desired. The prepreg was cured without special effort to remove the residual solvent. The laminates were weighted after cure and after post-cure and results indicated a solvent residue of about 0.7%. The calculated void content was 2.1%. This is slightly higher than the void content of T-300/80% BPADC + 20% NPC (1.6%) and is undoubtedly due to when the residual solvent, the net resin approach to fabricating the laminates, and/or the late pressure application during cure.

The resin was not catalyzed with zinc stearate because the rubber modifiers themselves appear to catalyze the cure. Differential scanning calorometry (DSC) studies of the modified cyanate resin showed the exotherm (Figure 13) beginning at 303 K (86° F) with the peak maxima located at 468 K (383° F). The peak shape was quite broad which is atypical of cyanates and cyanate mixtures. The modified cyanate resin cured adequately after three hours of post-cure at 422 K (300° F). Fourier-transform infrared spectroscopy was used to follow the cure. Figure 14 and 15 shows the spectra of the uncured and the cured resins. Note the disappearance of the cyanate band at 2,265 cm⁻¹. The cured resin indicates a small nitrile stretch at the same location resulting from the elastomer (butadiene-nitrile) modifiers in the resin.

2.7 LAMINATE FABRICATION

To maximize prepreg quantity, a net resin prepreg was prepared containing about 33% resin by weight. The laminates were fabricated for a net resin layup which is depicted in Figure 16. The edges of the graphite layup were taped to prevent excessive edge bleed.

The following cure cycle was followed:

- a. Pull vacuum on bag
- b. Heat-up at 1-2 K (2-3° F) per minute to 394 K (250° F)
- c. Apply 6.21MPa (90 psi) pressure at 394 K (250° F)
- d. Hold at 394 K (250° F) for three hours
- e. Cool down slowly, release pressure below 339 K (150 $^{
 m o}$ F)
- f. Post-cure unrestrained at 422 K (300° F) for three hours.

By mounting random laminate specimen and polishing, it was observed that occasional resin rich areas between plies were evident (Figure 17). SEM



FIGURE 13. DSC Trace of Modified Cyanate Resin. (85% cyanate resin (80% BPADC and 20% NPC), 10% of a prereact of ATBN with BPADC, and 5% Hycar^(R) 1441).

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Figure 16. Layup Sequence



Figure 17. Modified BPADC [10% CT-ATBN, 5% Hycar 1441, and 85% BPADC/NPC (75/25)] /T-300 Unidirectional Laminate Edge View 50x examination of the polished laminate end surfaces at about 1150x (Figure 18) and 4000x (Figure 19) revealed domains of precipitated rubber that appear as voids. The polishing procedure apparently removed the soft precipitated rubber from the composite surface. The average size of the particles is around 1 micron. The shape, instead of spherical as observed in neat resin, tended to be ovoid, probably due to the application of pressure and the subsequent low flow of the advanced resin. The slight flow of the resin would deform the spheres in the direction of the flow. It is recommended for future studies that since the resin did not bleed excessively (which seems to be characteristic of high-molecular weight elastomer-modified resins), pressure can be applied at the start of the heat-up cycle. The unrestrained post-cure had a tendency to slightly warp the unidirectional laminates and it is recommended that in future work a restrained post-cure be employed. Two 0.127 m by 0.203 m laminates, one 0.254 m by 0.228 m laminate and three 4-inch by 4-inch laminates were prepared in this manner. The laminate properties are listed in Table 8.

2.8 LAMINATE TESTING

The laminate properties of the modified BPADC [85% cyanate resin (80% BPADC and 20% NPC, 10% of a prereact of ATBN with BPADC, and 5% Hycar^(R) 1441] listed in Table 8 have been compared to unidirectional T-300/5209 data (Table 9) obtained as unpublished results from Narmco. Although the initial short beam shear strength of the cyanate resin was less than that of the 5209 by 39%, the retention of strength after humidity exposure of the cyanate resin was superior, actually increasing several percent. This increase in strength was still within the standard deviation of the test and probably represents no significant change in the short beam shear strength of the cyanate resin.

Heat aging increased both the short beam shear and the flexural strength/ modulus values. This was undoubtedly due to embrittlement or oxidation of the impact modifiers and the cyanate resin. Similar results were obtained with BPADC/NPC (80/20 mole ratio) after heat aging only the percent change was smaller.

The humidity-aged test specimens (500 hours at 344 K (160° F) demonstrated excellent moisture resistance. The average sample sorbed only 0.3% at equilibrium. The T_g change was also correspondingly low, only 4 K (8° F). The short beam shear and flexural strength values were essentially unchanged by moisture exposure.

Transverse tensile strength, which is mainly a resin dominated property, drops about 33% from the ambient value of 35.7 MPa (5.1 ksi) after humidity aging. Transverse tensile strength of 5209 was not obtained.

It should be realized that the successful implementation of improving moisture resistance and impact toughness necessitates trade-offs in physical and mechanical properties. The addition of impact modifiers/flexibilizers and the decrease of crosslink density due to the incorporation of monofunctional cyanates in the resin mixture lowers the modulus, T_g and mechanical strength of the resin. These trade-offs must be considered for the ultimate use and potential benefit of the new modified resin system. Specimens were exposed to heat aging at $366 \text{ K} (200^{\circ} \text{ F})$ for 500 hours in circulating air. Except for a very slight initial weight loss (<0.05%) which can be attributed to absorbed moisture, there was no change in specimen weights throughout the entire aging period. Humid aging at greater than 95% relative humidity (RH) and 344 K (160° F) for 500 hours resulted in a very low weight gain of 0.3% (average) at equilibrium for the short beam shear specimens. The weight gains are presented in Figure 20 as a function of the square root of time. A linear plot indicates adherence to Fickian diffusion until equilibrium is attained after about 16 days.



Figure 18. Scanning Electron Microscope Photograph of the Laminate Edge 1150X



Figure 19. Scanning Electron Microscope Photograph of the Resin Between the Fibers 4000X

Table 8. Unidirectional T-300/Modified BPADC Laminate Data

	Resin Content, Notent,	Glass	Short B Strengtl	eam Shear h, MPa (ksi)	Flexural St MPa/GPa (ks	:rength/Modulus ii/msi)
Aging Conditions	Percent	Temperature	RT	355 К (180 ⁰ F)	RT	355 K (180 ⁰ F)
As Fabricated	29.5	413 K	55.3 (7.9)	42.7 (6.1)	1169/123.9 (167/17.7)	784/113.4 (112/16.2)
Heat Aged ³	I	i	63.7 (9.1)	36.4 (5.2)	1197/128.8 (171/18.4)	854/123.2 (122/17.6)
Percent Retention	I		+15.2	-14.8	+2.4 (+4.0)	8.9 (+8.6)
Humidity Aged ⁴	1	409 K	58.1 (8.3)	44.1 (6.3)	1127/119.7 (161/17.1)	672/107.1 (96/15.3)
Percent Retention	1	J	+5.1	+3.3	3.6 (-3.4)	-14.3 (-5.6)
 1 - T-300 graphite fi 2 - 85% Cyanate res 3 - 500 hours at 36 4 - 500 hours at 34 	L ber is a t in (80% BF 6K (200 ⁰ F 4 K(160 [°] F)	trademark of Union Carbic ADC and 20% NPC), 10% CT ?)→(0,1% weight loss '95% + RH - SBS speciment	de Corporation L-ATBN, and 5% Hyc. s showed an averag	ar 1441 e 0.30% weight gain :	it equilibrium	

Table 9. Unidirectional T-300/5209 (Narmco) Laminate Data

% Retention	I	84	68	54	
Beam Strength KSI)	(12.9)	(10.8)	(8.9)	(1.0)	
Short Shear MPa (88.9	75.1	61.3	48.2	
Condition	Dry	Wet	Wet	Wet	
erature, F)			(120)	(160)	
Test Temp ⁶ Deg K (⁰]	RT	RT	324	344	

Specimens. (85% Cyanate Resin (80% BPADC and 20% NPC), 10% of a prereact of ATBN with BPADC, and 5% $\rm Hycar^{(R)}$ 1441) of Time of the Modified Cyanate Resin/T-300 SBS + Humidity as a Function of the Square Root Moisture Sorption at 344 K (160⁰ F) and 95% Figure 20.



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CONCLUSIONS

3

Toughness measurements on bulk cyanate resins indicated that 2,2-bis(pcyanatophenyl) propane containing 30% nonylphenylcyanate exhibited superior toughness to Narmco 5209 by a factor of 50%. This resin was successfully modified further by addition of butadiene-nitrile elastomer. The flexural strength of neat specimens of the modified cyanate showed a significant increase over those made from unmodified 2,2-bis(p-cyanatophenyl) propane. Laminates made with this rubber-modified cyanate exhibited very low water sorption (~0.3%) with little or no apparent change in physical or mechanical properties after humidity aging. The as-fabricated mechanical property values of these laminates were approximately 33% less than those made with Narmco 5209, indicating some trade-offs were necessary to achieve improved toughness and moisture resistance. The goal of this program, i.e., the development of a tough, moisture resistant laminating resin, has been successfully achieved.

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16. Abstract						
A study was conducted to a employment with graphite f handleability and processi The laminating resins were cyanates with hydrophobic small quantities of moistur transition temperature (T sorb around 2% moisture at precipitation of small (~1 the resin matrix. The rub sites, allowing increased A unique blend of amine te nitrile content butadiene- Mechanical properties of u as-fabricated interlaminar modifiers incorporated int equilibrium) and was proba resin. Neat resin samples (p-cyanatophenyl) propane flexural strength. The hi strain accommodation provi	develop tough, mo fibers. The new f ing characteristic e based on bispher substituents. The are at equilibrium and equilibrium. To be domains act a stress accommodate erminated butadier nitrile rubber y inidirectional T-3 shear than a type to the resin. Most ably due to the in s show an apparent (BPADC) but with tigher flexural stre and by the precip	laminatin cs equiva nol A dic nese resi m (0.5% o represen bughening ticles of as microc tion prio ne-nitril ielded th 300 graph bical 250 isture so ncreased t flexura an eight cength is pitated r	sistant g resins lent to yanate (ns have r less) t an imp was acc butadie rack ter r to cat e elasto e desire ite and °F cure rption w hydrocar 1 modulu -fold in probabl ubber pa	lamina exhib 394K (BPADC) been s with m roveme omplis ne-nit mini a astrop mer (M d resi this r epoxy as als bon na s simi crease y due rticle	<pre>iting resins for ited cost, 250°F) curing epoxies. and monofunctional hown to sorb only inimal glass nt over epoxies which hed by the rile rubber throughout nd energy dissipation hic failure. W 2,000) and a high n morphology. esin showed lower due to the impact o quite low (0.3% at ture of the blended lar to 2,2-bis in ultimate to a higher s.</pre>	
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