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NITRILE CROSSLINKED POLYPHENYL-QUINOXALINE/GRAPHITE FIBER COMPOSITES

by William B. Alston
Lewis Research Center and
U.S. Army Air Mobility R&D Laboratory
Cleveland, Ohio 44135

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William B. Alston
Lewis Research Center and
U.S. Army Air Mobility R&D Laboratory
Cleveland, Ohio

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Abstract

Studies were performed to reduce the 600° F thermoplasticity of polyphenylquinoxaline (PPQ) matrix resins by introducing crosslinking by the reaction of terminal nitrile groups. Seven solvents and solvent mixtures were studied as the crosslinking catalysts and used to fabricate crosslinked PPQ/HMS graphite fiber composites. The room temperature and 600° F composite mechanical properties after short time and prolonged 600° F air exposure and the 600° F composite weight loss were determined and compared to those properties of high molecular weight, linear PPQ/HMS graphite fiber composites.

1. INTRODUCTION

Polyphenylquinoxalines (PPQ) are considered to have excellent potential for use as high temperature matrix resins in advanced fiber composites.(1, 2) However, because of the composite processability problem when using high viscosity-high molecular weight PPQ solutions and the elevated temperature thermoplasticity of fiber reinforced PPQ composites, the potential of PPQ as a high temperature matrix resin has never been fully achieved. The elimination of the need for high viscosity-high molecular weight PPQ solutions by the application of "polymerization of monomeric reactants" (PMR) technology considerably improved the ease of composite fabrication of high molecular weight, linear PPQ matrix resins.(3) Studies have been conducted to reduce the high temperature thermoplasticity of PPQ resins by various methods such as the incorporation of pendant nonreactive bulky groups on the PPQ polymer chain(4) and the crosslinking of the polymer chain by pendant reactive groups.(2, 4, 5) The use of trifunctional monomers(6) and intramolecular cyclizations(7) have also been studied. These investigations encountered organic synthesis and composites application difficulties. The crosslinking of a PPQ resin in a composite has been studied by use of pendant(2, 6) and terminal reactive groups.(8, 9) However, PPQ composites which are clearly superior to the linear high molecular weight PPQ composites(3) have not been successfully demonstrated at this time.

The purpose of this investigation was to reduce the high temperature thermoplasticity of PPQ matrix resins by crosslinking a low molecular weight processable PMR-PPQ matrix resin in a HMS graphite fiber composite. This was accomplished by the use of a nitrile containing endcapper for molecular weight control and subsequent crosslinking. Seven solvents and solvent mixtures were studied as the nitrile crosslinking catalysts. Crosslinked PMR-PPQ/HMS graphite fiber composites were fabricated and their room temperature and 600° F mechanical properties were determined after short time and prolonged 600° F air exposure. The composite thermo-oxidative stability (TOS) was also determined. The mechanical properties and weight loss characteristics of crosslinked PMR-PPQ/HMS graphite fiber composites are compared to those of composites prepared with high molecular weight linear PMR-PPQ matrix resins.

2. EXPERIMENTAL

2.1 MATERIALS

The monomers and crosslinker-endcapper used in this study are shown in Table I. The Hercules HMS and HTS graphite fiber, the solvents/catalysts, 3, 3', 4, 4'-tetraaminobenzophenone (TABP) and 1, 4-bis (phenylglyoxalyl) benzene (PPGB) were obtained from commercial sources and used in the as received condition. The 3, 4-diaminobenzonitrile (DABN) was prepared in four steps in an overall purified yield of 26.9 percent from commercially obtained p-acetamidobenzaldehyde according to the literature procedure.(10) The synthetic procedure was altered only in that Raney Nickel in methanol was substituted for platinum oxide in ethanol in the catalytic reduction synthesis step and, instead of recrystallization, the DABN was purified by sublimation two times to remove the DABN from a tarry residue.

2.2 PMR SOLUTIONS AND PREPREG PREPARATION

PMR solutions of the PPQ matrix resin were prepared by separately dissolving the amines (TABP plus DABN) and the ketone (PPGB) each at 25 to 30 weight percent solids, in the following solvents: meta-cresol (m-cresol), N, N-dimethylformamide (DMF), 2-pyrrolidone (2-PYR), N-methyl pyrrolidone (NMP) and 10 weight percent m-cresol mixed with 90 weight percent of each of the other three solvents. The molar ratio of the three monomers was n/(n + 1)/2 where n = moles TABP, n + 1 = moles PPGB and 2 = moles DABN. The value of n is determined by the desired formulated molecular weight (FMW) in the following equation: n(molecular weight of TABP) + (n + 1) (molecular weight of PPGB) + 2(molecular weight of DABN) - (n + 1)(4)(molecular weight of water) = FMW. In almost all the PMR solution preparations, gentle heating was required to dissolve the monomers, particularly the PPGB. The solutions were allowed to cool slowly to room temperature or until the solution turned cloudy (a precipitate was about to form) and then the amine and ketone solutions of the same solvent(s) were combined together. The heat of mixing and initial reactions kept the monomers/polymers from precipitating. The solutions were stirred for 30 seconds and immediately applied to drum wound (8 turns/in.) Hercules HMS or (6 turns/in.) HTS fiber. The quantities of fiber and resin were calculated to yield a composite containing 40 weight percent resin (about 45 vol.% resin). The low molecular weight PPQ formed on the graphite fiber surface as the excess solvent was removed by heating the rotating prepreg drum with heat lamps. After drying, the percent volatile content of the prepregs was determined from the average of the weight losses of five samples of prepreg subjected to 30 minutes exposure to 600° F in a circulating air oven.

2.3 COMPOSITE FABRICATION

The prepreg was removed from the drum, cut and unidirectionally stacked into ten 3- by 3-inch plies or twelve 3- by 8-inch plies (with the fiber direction parallel to the 8-in. dimension). The stacked plies were staged at atmospheric pressure for various times and elevated temperature (depending on the solvent/catalyst employed) until a very dry ply stack was obtained. The layup was then placed in a matched metal die which had been treated with mold release agent. The assembled mold (at room temperature) was placed in a 750° F press and contact pressure was applied. After 7 minutes had elapsed, vapor evolution resulted. The composite was then compacted by cycling between 0 psi and 50 psi pressure at least once a minute for the next 8 minutes, after which no further vapor evolution was observed. The pressure was then increased to 400 psi and the temperature was held at 750° F for 2 hours. The press platen heaters were then shut off and the press was allowed to cool slowly to room temperature, after which the pressure was released. The resultant laminates were inspected for structural integrity using an ultrasonic C scan technique(11) and then cut into strips 0.2 inch wide. The strips were postcured in air according to the following schedule: 2 hours each at 392°, 437°, 482°, 572°, 617°, and 662° F and 3 hours at 700° F with an initial 20 minute heat up to 392° F and 10 minutes heat up between each temperature level. The oven heat was then shut off to slowly cool the strips from 700° F to room temperature. The postcure weight losses were determined as the average weight loss of all the 0.2-inch wide strips from each laminate.

2.4 COMPOSITE TESTING

Long term isothermal exposure of the specimens was accomplished in a forced air convection oven at 600° F. The air change rate in the oven was 100 cubic centimeters per minute. Composite weight loss measurements were made throughout the 600° F air exposure period and reported as the average of the percent weight loss of all the specimens still remaining for mechanical testing. Photomicrographs (×50) of the specimen cross sections were prepared and used for qualitative indication of void contents, for comparison to earlier C scans and for observation of any visual effects of aging on the specimens. Room temperature and 600° F flexural strength, flexural modulus and interlaminar shear strength (ILSS) were determined for postcured and unpostcured specimens and for postcured 600° F aged specimens. Flexural strength and flexural modulus were determined using a

3-point loading fixture with a fixed span of 2 inches and a center loading rate of 0.05 inch per minute. The span to depth ratio ranged from 23 to 27 for specimens from the 3- by 3-inch laminates and 16 to 18 for specimens from the 3- by 8-inch laminates. ILSS tests were conducted at a constant span to depth ratio of 5. The 600° F ILSS and flexural tests were performed in an environmental heating chamber after the specimen had been equilibrated for 15 minutes without an applied load. The mechanical strength properties reported are, in almost all cases, the average of three tests at each condition.

3. RESULTS AND DISCUSSION

3.1 PMR-PPQ MATERIALS AND SOLUTIONS

PPGB and TABP were selected as the monomers for the PPQ polymer backbone in this study because a previous study had shown that the TABP/PPGB monomer combination provided the best performance at 600° F in air.(3) Other studies also conducted with PPGB and TABP showed that the use of these monomers provided acceptable composite mechanical properties, TOS,(2, 12, 13) and high glass transition temperature.(2) The HMS and HTS graphite fibers were selected for use in this study because of the availability of comparative PPQ composite data.(3, 12) The HMS fiber was used more extensively because of its superior 600° F TOS.(14)

Although the terminology "PMR" is applied to these nitrile crosslinked resins, it should be pointed out that because the reaction leading to quinoxaline rings proceeds at an appreciable rate at low temperature, that some polymerization does occur as soon as the PMR solution is prepared. Normally, PMR implies that the solution remains a mixture of monomers until after the PMR solution is applied to the fiber. However, the majority of the polymerization probably occurs on the fiber because the PMR-PPQ solutions were applied to the fiber immediately after mixing. The limited solubility of the PPGB, TABP, and DABN and the rapid formation of low molecular weight PPQ polymer required solvents possessing higher solvent power than that normally provided by the methanol solvent employed for PMR polyimides. The viscosity of PMR-PPQ solutions tends to be quite high at low solids content and increases markedly as the solids content is increased. Therefore, in order to obtain adequate fiber wetting, the PMR-PPQ solutions employed in this study had a lower solids content than PMR-polyimide solutions.

3.2 PROCESSING PARAMETERS

Preliminary investigations were performed with m-cresol to determine suitable FMW and processing parameters (staging conditions, process time, temperature, pressure, and postcure requirements). The FMW of the polymer prepared from the reaction of PPGB with TABP and the crosslink density were controlled by adding varying amounts of the nitrile crosslinker-endcapper, DABN. The FMW range investigated ranged from 2000 to 7000. The time, temperature, and pressure processing parameters investigated ranged from 0.5 to 5.0 hours, 660° to 800° F and 400 to 1000 psi, respectively. At FMW's of 2000 and 3000 a suitable balance of resin flow and composite mechanical properties was not found for HTS composites. The excessive resin flow was difficult to control. At a FMW of 4000 for HTS fiber composites fabricated at 750° F, 0.75 hour, and 660 psi a suitable balance of resin flow and mechanical properties was obtained. Cure temperatures of 660° and 700° F were found not to result in a sufficient rate of crosslinking to prevent excessive resin flow. Higher temperature, longer time and higher pressure (790° F, 2.5 hr, and 1000 psi) were not found to have a significant effect on the mechanical properties of FMW 4000 PMR-PPQ/HTS composites. At a higher FMW of 5000, the ILSS was lower, probably due to a decreased crosslink density. However, it is possible that the prolonged 5-hour process time at the higher 790° F processing temperature caused degradation in the FMW 5000 HTS laminate, resulting in the decreased ILSS.

Similar results were obtained for HMS fiber composites. A suitable balance of resin flow and mechanical properties was also found at a FMW of 4000. Below a FMW of 4000, HMS composites exhibited excessive resin flow. At FMW's above 5500 difficulty in removing the solvent or a reduced crosslink density permitted fiber wash to occur prior to composite consolidation. Within the FMW range of 4000 to 5500 the best room temperature and 600° F mechanical properties after postcuring, with the exception of 600° F ILSS, were obtained at a FMW of 4000. These HMS composite results together with the HTS composite results led to the decision to select the FMW of 4000 processed at 750° F for 2 hours at 400 psi for the remainder of the study. Although staging of the HTS laminates in the hot press gave satisfactory results, the HMS laminates which were staged in the press exhibited excessive resin flow. This indicates the need for an oven staging to obtain a very dry prepreg to control the resin flow. The increases in the mechanical properties after postcuring indicated a need for a postcure to attain acceptable 600° F composite mechanical properties.

3.3 SOLVENT/CATALYST STUDY

Using the selected FMW and processing parameters, other solvents were investigated for use as the solvent and crosslinking catalyst. The ability of a solvent to function as the crosslinking catalyst is advantageous because it eliminates the possibility of nonvolatile catalyst residues which might cause decreased composite performance. An acidic solvent/catalyst (m-cresol), a relatively neutral solvent/catalyst (NMP), two basic solvents/catalysts (DMF and 2-PYR) and m-cresol mixtures of the other three solvents/catalysts were selected to investigate their effectiveness in fabricating crosslinked PMR-PPQ composites. The use of 2-PYR has been reported(15) as a solvent/catalyst for model compound studies of aromatic nitriles.

Table II reports the solvents' boiling points, volatile contents before and after staging, staging conditions, laminate thickness, postcure weight loss and the mechanical properties of nitrile crosslinked PMR-PPQ/HMS composites fabricated employing the selected solvent/catalysts. The increasing order of the volatile contents, DMF < NMP < m-cresol < 2-PYR, correlates with the increasing order of the boiling points of the solvents. At the completion of the drying time the prepregs were flexible, but not tacky, except for 2-PYR prepregs. For prepreg preparation using 2-PYR solvent, precipitation of the PPQ resin on the fiber occurred. The excess 2-PYR solvent could not be removed by continued heating of the prepreg drum with heat lamps.

The severity of the staging conditions, reported in Table II, required to obtain a dry stacked ply layup also correlates with the increasing order of boiling points of the solvents/catalysts studied. In the remainder of this study, a staging condition of 400° F for 5 hours was used for prepregs containing m-cresol because these conditions produced the composite layup having the volatile content needed to control the resin flow during fabrication. The 400° F/5-hour m-cresol staging condition is consistent with the staging conditions reported in Table II for the other solvent/catalysts investigated.

The postcure weight losses reported in Table II were less than 1 percent for all the solvent/catalysts investigated. When specimens exhibited a postcure weight loss of greater than 1 percent, the specimens would usually have blistered during postcuring. For all the laminates any shiny appearance or odor, usually m-cresol, present before postcuring would disappear during postcuring. In order to obtain suitable composites after postcuring it is important to have staged a laminate to a dry condition for resin flow control and to use a fabrication cycle which leaves no more than traces of the solvent/catalyst in the laminate.

The room temperature and 600° F mechanical properties of unpostcured and postcured composites fabricated employing four separate solvent/catalysts and three mixed solvents/catalysts are also shown in Table II. The postcured mechanical properties of the composites fabricated using the four separate solvent/catalysts were found to be quite similar. The thermoplastic behavior at 600° F of unpostcured composites fabricated using m-cresol (Table II) strongly emphasizes the need for a postcure. The 2-PYR was eliminated as a solvent/catalyst because it allowed the PPQ resin to precipitate on the fiber during prepreg drying and also because it resulted in a postcured composite with the lowest room temperature and 600° F modulus and the lowest 600° F flexural strength. DMF was eliminated as a solvent/catalyst only because its use resulted in a prepreg which was very dry and difficult to fabricate into a composite. The DMF fabricated composite did exhibit postcured mechanical properties similar to the properties of m-cresol and NMP fabricated composites. The postcured mechanical properties of the m-cresol and NMP fabricated composites were virtually identical except that the room temperature ILSS of the m-cresol fabricated composite was significantly higher. Attempts to effect a cure at lower temperatures (660° F and/or 700° F) with DMF, 2-PYR and NMP were unsuccessful. This agrees with the m-cresol conclusion that a 750° F cure temperature is required. Thus, m-cresol was chosen for further investigation of its utility as a solvent/catalyst in the mixed solvent/catalysts studied. The mechanical properties reported in Table II for the mixed solvents/catalysts showed that when m-cresol was mixed with each of the other three solvent/catalysts, the postcured ILSS were about 10 percent lower and the postcured flexural strength and modulus were generally much lower than when using DMF, 2-PYR, or NMP without m-cresol added. These results eliminated mixed solvents/catalysts from the study. Based on the single and mixed solvents/catalysts results and the increased mechanical properties after postcuring, m-cresol was selected as the solvent/catalyst to be used in the remainder of the study.

3.4 CROSSLINKING MECHANISMS

It may be speculated that m-cresol functions as a solvent/catalyst because the acidic hydroxyl group of m-cresol enters into a reversible reaction with the DABN nitrile group to form an imidate which facilitates the crosslinking reaction. This is analogous to the catalysis of model compound nitrile reactions by the imidate formed from the addition of methanol across the nitrile group of benzonitrile.(16) However, it cannot be unequivocally ruled out that the crosslinking reaction of the nitrile groups proceeds only by thermal initiation and m-cresol provides the necessary resin flow by simply acting as a plasticizer. Thermally propagated reactions of nitrile groups are widely reported.(17, 18) But, if this were true then the use of the mixed solvents/catalysts would be expected to produce composite mechanical properties similar to the composite properties of the m-cresol fabricated composite. The residual m-cresol in the laminates fabricated with mixed solvents/catalysts would provide the necessary plasticization and adequate resin flow for good laminate fabrication. Instead, diluting the m-cresol acidic solvent/catalyst with the more neutral NMP solvent/catalyst or neutralizing the m-cresol with the basic DMF and 2-PYR solvents/catalysts resulted in lower mechanical properties. These findings suggest that m-cresol does act as an acid catalyst for the crosslinking mechanism.

The nitrile crosslinking reaction was studied by infrared spectroscopy of flashings produced during laminate fabrication. It is reported(15) that the use of 2-PYR as a solvent/catalyst for model compound reactions of aromatic nitriles forms triazines below 572° F and forms linear carbimide polymers above 662° F, with a mixture of the two products at intermediate temperatures. However, a decision between triazine ring formation and linear carbimide formation was not possible for the composites fabricated using m-cresol because of the overlapping of aromatic, quinoxaline, triazine, and carbimide infrared absorption bands in the 6 to 8 micron spectrum region. The infrared spectra did show that the nitrile absorption band at 4.5 microns was considerably smaller in the mold flashings than in the DABN or prepreg solution. Using the absorption data, it was estimated that about 80 percent of the nitrile groups were consumed in the composite processing. The presence of unreacted nitrile groups did not appear to have an adverse effect on composite mechanical properties or TOS, as will be shown later.

Further evidence that the nitrile group enters into the crosslinking reaction was obtained by a comparison of the composite mechanical properties in Table III. A nitrile crosslinked laminate, a laminate fabricated with an unreactive non-nitrile endcapper (*o*-phenylenediamine) and two laminates fabricated with unbalanced stoichiometries to produce diketone and diamine endcapping were each prepared employing FMW 4000 formulations in *m*-cresol and the previously selected processing parameters. Table III shows that *o*-phenylenediamine endcapping produced laminates with fair room temperature composite mechanical properties. However, even after postcuring, the laminate exhibited thermoplastic behavior and the 600° F mechanical properties were quite low. The diketone terminated composite, produced with n moles of TABP and n + 1 moles of PPGB, had fairly high room temperature mechanical properties but the 600° F mechanical properties were low, even after postcuring. The diamine terminated composite, produced with n moles of PPGB and n + 1 moles of TABP, formed a staged layup that was considerably thicker than the other laminates and could not be compacted during composite processing. This was probably due to the excess TABP amino groups condensing with the TABP ketone groups during staging. This was not observed in the other laminates in which the total number of moles of diamine groups was equal to or less than the number of moles of diketone groups. The diamine endcapped laminate exhibited the lowest room temperature mechanical properties, with and without postcuring. However, the 600° F unpostcured mechanical properties were the highest of the non-nitrile composites, which might be attributed to some amino-ketone crosslinking. The decreases in the room temperature and 600° F mechanical properties after postcuring could be attributed to the thermo-oxidative instability of amino-ketone crosslinking and unreacted amine groups. These results all indicate that the nitrile group of DABN is definitely involved in the crosslinking reaction.

3.5 COMPOSITE MECHANICAL PROPERTIES

The initial mechanical properties of HMS and HTS/nitrile crosslinked PMR-PPQ 3- by 3-inch composites and the comparable literature data(12) from HMS and HTS/high molecular weight linear PMR-PPQ 3- by 4-inch composites are indicated in Table IV. The nitrile crosslinked composites exhibited higher flexural strengths and lower ILSS when compared to the high molecular weight linear PPQ composites. These differences are due to the higher fiber volume of 60 to 62 percent for the nitrile crosslinked composites compared to 52 to 54 percent for the linear high molecular weight PPQ composites. Some of the difference may be due to an increased brittleness in the postcured nitrile crosslinked composites.

When larger (3- by 8-in.) HMS/nitrile crosslinked PMR-PPQ composites were fabricated an overall decrease in the mechanical properties was observed. A similar observation can be made for high molecular weight linear PMR-PPQ/HMS composites by comparing the mechanical property data in references 3 and 12. The decreases in the mechanical properties of larger PPQ laminates may be due to an increase in the difficulty in the removal during fabrication of the high boiling solvents/catalysts from the larger laminates, resulting in increased void contents. It may be concluded that in order to compare the mechanical properties of different composites, the comparisons should be done with laminates prepared from similar solvents and fabrication sizes, thus representing a similar degree of fabrication difficulty. Therefore, the 600° F weight loss and mechanical property comparisons of the nitrile crosslinked and the high molecular weight linear PPQ composites reported in subsequent figures and tables were from laminates of 3- by 8- and 3- by 10-inch fabrication sizes.

The ultrasonic C-scan of the 3- by 8-inch nitrile crosslinked composite indicated the presence of some internal defects. The photomicrograph of the laminate cross section (shown in fig. 1) of the 3- by 8-inch nitrile crosslinked laminate contained very few voids. It was not as "void free" as the 3- by 3-inch laminate but was still considered to be satisfactory. Also, it is quite similar in appearance to the photomicrograph of the linear high molecular weight PPQ composite shown in reference 3. The minimal amount of intraply voids in figure 1 indicates good fiber wetting. The occasional large interply voids are probably caused by a localized lack of resin flow during processing. This may be the result of dry spots created by the extensive staging of the prepreg. Photomicrographs of specimens before and after postcuring and after prolonged 600° F exposure in air did not indicate that any visual changes occurred in the internal structure of the nitrile crosslinked composite. The composite thermo-oxidative degradation and weight loss occurs only on the surface of the laminate where loose fibers are found after 1000 hours of 600° F air exposure. This observation was also reported for high molecular weight linear PMR-PPQ/Thornel 300 composites.(14)

A second 3- by 8-inch nitrile crosslinked laminate was fabricated by extending the cure time at 750° F from 2 to 5 hours. The physical and mechachanical properties of this laminate were similar to the properties of the first 3- by 8-inch laminate. The thicknesses and fiber volume percents of the first and second laminate were 0.114 inch and 58.2 percent and 0.124 inch and 54.6 percent, respectively. The percent fiber volume of the high molecular weight linear PPQ composite(3) was 55 percent. Thus, mechanical property and weight loss comparisons in the subsequent data for the nitrile crosslinked and high molecular weight linear PPQ composites were made without corrections for the minimal fiber volume percentage differences. Duplicate data points obtained from aged specimens of the two nitrile crosslinked laminates have been averaged in figures 2 to 5 and Table V, making the initial and 1000 hour exposure data points an average of six values.

Figure 2 compares the percent weight loss as a function of 600° F air exposure time of the nitrile crosslinked PMR-PPQ composites to the percent weight loss of the high molecular weight linear PMR-PPQ composite.(3) The two weight loss curves in figure 2 are almost identical.

Figure 3 shows the room temperature and 600° F ILSS of nitrile crosslinked PMR-PPQ/HMS composites after 600° F air aging. Also shown in figure 3 are the initial room temperature and 600° F ILSS of high molecular weight linear PMR-PPQ/HMS composite after 600° F air aging.(3) The initial room temperature ILSS of the nitrile crosslinked composites was less than that of the high molecular weight linear PPQ composite (5600 psi compared to 7600 psi), possibly due to the increased brittleness of the nitrile cross-linked matrix. The room temperature ILSS of the nitrile crosslinked composite remained constant for 500 hours of 600° F air aging. After 500 hours of 600° F air exposure, a continuous decrease in room temperature ILSS was observed. At 1000 hours of 600° F air exposure, the ILSS determined at room temperature decreased to the value of the 600° F ILSS after 1000 hours of 600° F air exposure.

The 600° F ILSS of the nitrile crosslinked and high molecular weight linear PPQ composites which were aged at 600° F in air were identical. Significant decreases in the 600° F ILSS of nitrile crosslinked and high molecular weight linear PPQ composites occur after 500 hours of 600° F air exposure. The decreases in room temperature and 600° F ILSS after 500 hours of 600° F air exposure correspond to the increased rate of thermo-oxidative degradation after 500 hours of 600° F air exposure, as shown by the weight loss data presented in figure 2.

Figure 4 shows the room temperature and 600° F flexural strength of nitrile crosslinked PMR-PPQ/HMS composites after 600° F air aging. Also shown in figure 4 are the initial room temperature and 600° F flexural strength of high molecular weight linear PMR-PPQ/HMS composite after 600° F air aging.(3) The initial room temperature flexural strength of the nitrile crosslinked composites was less than that of the high molecular weight linear PPQ composite (109 000 psi compared to 123 000 psi), possibly due to the increased brittleness of the nitrile crosslinked matrix. The room temperature flexural strength of the nitrile crosslinked composite remained constant for 500 hours of 600° F air aging. After 500 hours of 600° F air exposure, a continuous decrease in room temperature flexural strength was observed. At 1000 hours of 600° F air exposure, the flexural strength determined at room temperature decreased to the value of the 600° F flexural strength after 1000 hours of 600° F air exposure.

The 600° F flexural strength of the nitrile crosslinked composites remained constant until 500 hours of 600° F air exposure, after which a continuous decrease was observed. The nitrile crosslinked and the high molecular weight linear PPQ composites exhibited similar behavior for the 600° F flexural strength except for the time interval between zero and 400 hours during which the high molecular weight linear PPQ composite exhibited an increase and then a decrease in flexural strength. Significant decreases in room temperature and 600° F flexural strength of nitrile crosslinked composites occur after 500 hours of 600° F air exposure. The decreases in room temperature and 600° F flexural strength of nitrile crosslinked composites after 500 hours of 600° F air exposures correspond to the increased rate of thermo-oxidative degradation after 500 hours of 600° F air exposure, as shown by the weight loss data presented in figure 2.

Figure 5 shows the room temperature and 600° F flexural modulus of nitrile crosslinked PMR-PPQ/HMS composites after 600° F air aging. The initial room temperature modulus of the nitrile crosslinked composites was less than that of the linear high molecular weight composite(3) (16.[illegible] msi compared to 20.7 msi) while the initial 600° F modulus was higher (12.3 msi compared to 10.2 msi). The higher 600° F modulus indicates that nitrile crosslinking is a method of controlling the high temperature thermoplasticity of PPQ composites. Both the room temperature and 600° F flexural modulus of nitrile crosslinked PPQ composites remained constant for 500 hours of 600° F air aging. After 500 hours of 600° F air exposure, a continuous decrease in the room temperature and 600° F flexural modulus was observed. At 1000 hours of 600° F air exposure, the modulus determined at room temperature decreased to the value of the 600° F modulus after 1000 hours of 600° F air exposure. The decreases in room temperature and 600° F modulus after 500 hours of 600° F exposure correspond to the increased rate of thermo-oxidative degradation after 500 hours of 600° F air exposure, as shown by the weight loss data presented in figure 2.

Table V summarizes the postcured mechanical properties and weight loss of the nitrile crosslinked and high molecular weight linear PMR-PPQ/HMS composites. The table shows that nitrile crosslinking of PMR-PPQ composites results in slightly lower initial room temperature mechanical properties and a slightly higher initial 600° F modulus when compared to the high molecular weight linear PPQ composites.(3) The table also shows that after 600 hours of 600° F air exposure both the weight loss and the retention of 600° F mechanical properties of nitrile crosslinked and high molecular weight linear PPQ composites are comparable and excellent. Beyond 600 hours of 600° F air exposure, the increased rate of thermo-oxidative degradation of nitrile crosslinked and high molecular weight linear PMR-PPQ composites caused a deterioration in the mechanical properties and a greater weight loss rate. It may be concluded that PPQ matrix resins undergo an accelerated rate of thermo-oxidative degradation once a certain threshold of elevated temperature air exposure is reached. In this case, 500 to 600 hours of 600° F air exposure initiates the rapid deterioration of the nitrile crosslinked PPQ composite.

4. CONCLUDING REMARKS

The use of a solvent as the crosslinking catalyst is a means of crosslinking nitrile terminated PMR-PPQ matrix resins. Nitrile crosslinking allows the fabrication of PMR-PPQ composites that exhibit acceptable nonthermoplastic mechanical properties at 600° F. However, the processing conditions required to achieve the nitrile crosslinking are more difficult to control and more severe than the processing conditions for high molecular weight linear PMR-PPQ composites.

The mechanical properties and thermal stability of nitrile crosslinked PPQ composites are comparable to the properties of high molecular weight linear PPQ composites. However, significant improvements in mechanical properties and thermo-oxidative stability were not attained by the nitrile crosslinking of PMR-PPQ composites. The 600° F service life of nitrile crosslinked PPQ composites is limited to 600 hours. Beyond 600 hours of 600° F exposure the increased rate of thermo-oxidative degradation corresponds closely to decreases in room temperature and 600° F mechanical properties.

REFERENCES

1. Hoggatt, J. T., Hergenrother, P. M., and Shdo, J. G.: "Development of Polyphenylquinoxaline Graphite Composites," The Boeing Company, NASA CR-121109, January 1973.

2. Hoggatt, J. T., Hill, S. G., and Shdo, J. G.: "Development of Polyphenylquinoxaline Graphite Composites," The Boeing Company, NASA CR-134674, July 1974.

3. Serafini, T. T , Delvigs, P., and Vannucci, R. D.: "In Situ Polymerization of Monomers for Polyphenylquinoxaline/Graphite Fiber Composites," NASA TN-7793, October 1974.

4. Port, W. S., and Loszewski, R. C.: "Quinoxaline Polymers and Copolymers Derived from 1,4-Bis (1' - Naphthalenyloxalyl) Benzene," Avco Corporation, NASA CR-134715, November 1974.

5. Wentworth, S. E., and Mulligan, G. D.: Preparation and Preliminary Thermal Evaluation of Poly-p-Tolylquinoxaline, A Cross-Linkable Polyphenylquinoxaline, AMMRC TR 74-12, May 1974.

6. Shdo, J. G.: "Development of Polyphenylquinoxaline/Graphite Composites," The Boeing Company, NASA CR-135041, 1976.

7. Hedberg, F. L., and Arnold, F. E.: "Synthesis of Quinoxaline Polymers Curable by Intramolecular Cyclizations," AFML TR-75-278, 1975.

8. Browning, C. E., et al.: "Initial Development of ATQ Matrix Resin," AFML TR-75-214, 1975.

9. Arnold, F. E., Kovar, R. F., and Eblerf, G. F.: "Acetylene Terminated Quinoxalines, ATQ," AFML TR-76-71, 1976.

10. Stephens, F. F., and Bower, J. D.: J. Chem. Soc., pt. 2, 1722 (1950).

11. "Ultrasonic Immersion Tests," Nondestructive Testing Handbook, Vol. 2, Sec. 46, R. C. Masters, Ed., Ronald Press Co., New York, 1959, pp. 46-1 to 46-27.

12. Serafini, T. T., Delvigs, P., and Vannucci, R. D.: J. Appl. Polymer Science, 17, 3235 (1973).

13. Griffin, R. N.: "Development of High Temperature Resistant Graphite Fiber-Coupling Agents," General Electric Company, NASA CR-134925, November 1975.

14. Griffin, R. N.: "Further Development of High Temperature-Resistant Graphite Fiber Coupling Agents," General Electric Company, NASA CR-134987, March 1976.

15. Gump, K. H.: U.S. Patent 3,678,049, July 18, 1972.

16. Schaefer, F. C., and Peters, G. A.: J. Organic Chem., 26, 2778 and 2784 (1961).

17. Kabanov, V. A., et al.: J. Polymer Sci., pt. C, 1009 (1963).

18. Wöhrle, D.: "Polymers from Nitriles," Advances in Polymer Science, Vol. 10, H. J. Cantow, et al , Eds., Springler-Verlhe, Berlin, 1972, pp. 37-105.

BIOGRAPHY

Dr. William B. Alston is presently a Materials Engineer with the U.S. Army Air Mobility R&D Laboratory, assigned to the Polymer Matrix Composites Section of NASA-Lewis Research Center since 1971. He received his B.S. in Chemistry from the University of Wisconsin, M.S. and Ph.D. in Chemistry from the University of Iowa. His current research is in the area of polymer synthesis and crosslinking, composite fabrication and characterization.

TABLE I. - MONOMERS AND CROSSLINKER USED FOR NITRILE

CROSSLINKED PMR-PPQ SYNTHESIS

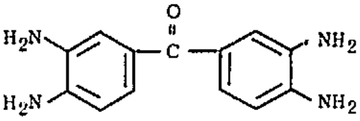
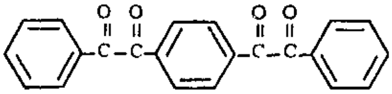
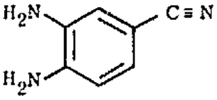
Structure	Name	Abbreviation
	3, 3', 4, 4'-Tetraaminobenzophenone	TABP
	1, 4-Bis(phenylglyoxalyl)benzene	PPGB
	3, 4-Diaminobenzonitrile	DABN

TABLE II. - SOLVENT/CATALYST EFFECT ON LAMINATE FABRICATION CHARACTERISTICS AND INITIAL MECHANICAL PROPERTIES OF FMW 4000 NITRILE CROSSLINKED PMR-PPQ/HMS GRAPHITE FIBER COMPOSITES

Solvent/catalyst	Boiling point, F^{o}	Prepreg volatile content, %	Staging conditions, ^{o}F/hr	Staging volatile content, %	Laminate thickness ×10^{3}, in.	Postcure weight loss, %	Test temper-ature, ^{o}F	Interlaminar shear strength, psi		Flexural strength, ksi		Flexural modulus, msi	
								No postcure	Postcured	No postcure	Postcured	No postcure	Postcured
m-cresol	398	28.2	600/0.25	5.6	73	0.27	70	7961	7340	181	162	24.9	23.8
							600	[a]2177	4747	[a]22	136	[a]1.3	20.6
DMF	308	7.9	200/0.1	3.4	77	0.42	70	5082	4619	135	118	23.2	21.6
							600	5195	5054	120	149	21.5	22.4
DMF/m-cresol	---	12.9	200/0.1 then 400/0.25	2.3	77	0.21	70	4215	4141	134	146	22.7	23.2
							600	3192	4514	89	114	16.3	21.8
2-PYR	475	48.1	400/6 then 450/2.5	5.4	85	0.69	70	5962	5341	137	176	17.3	18.9
							600	5274	5577	112	111	17.6	16.8
2-PYR/m-cresol	---	48.1	400/6 then 450/2.5	5.5	89	0.54	70	5238	4468	81	76	11.7	10.1
							600	4711	4889	60	64	8.1	8.3
NMP	396	20.6	400/2	5.7	77	0.44	70	4635	5073	148	161	24.4	25.1
							600	4759	4796	116	139	21.0	21.8
NMP/m-cresol	---	22.0	400/5	6.3	85	0.59	70	4626	4382	109	119	19.6	20.8
							600	4673	4650	96	101	16.0	18.8

[a] Thermoplastic.

TABLE III. - EFFECT OF NITRILE CROSSLINKING ON INITIAL MECHANICAL PROPERTIES OF FMW 4000 PPGB/TABP PMR-PPQ/GRAPHITE FIBER COMPOSITES

Polymer termination	Test temperature, °F	Interlaminar shear strength, psi		Flexural strength, ksi		Flexural modulus, msi	
		No postcure	Postcured	No postcure	Postcured	No postcure	Postcured
DABN	70	7961	7340	181	162	24.9	23.8
	600	[a]2177	4747	[a]22	136	[a]1.3	20.6
o-Phenylenediamine	70	4429	4229	87	99	23.6	17.4
	600	[a]890	[a]2678	[a]5	42	[a]0.4	5.8
Diketone (excess PPGB)	70	5215	5638	159	169	22.9	23.5
	600	[a]2410	3958	[a]28	75	[a]2.6	10.7
Diamine (excess TABP)	70	3543	2916	50	43	5.6	4.8
	600	3257	2766	46	[a]31	3.7	[a]2.5

[a] Thermoplastic.

TABLE IV. - INITIAL MECHANICAL PROPERTIES OF POSTCURED NITRILE CROSSLINKED AND HIGH MOLECULAR WEIGHT LINEAR PMR-PPQ/GRAPHITE FIBER COMPOSITES

Fiber		HMS		HTS	
Matrix resin		Crosslinked	Linear[a]	Crosslinked	Linear[a]
Fiber volume, %		62	54	60	52
Interlaminar shear strength, psi	Temperature, °F				
	70	7340	8200	9136	15 000
	600	4747	6100	7533	-----
Flexural strength, ksi	70	162	130	243	187
	600	136	114	176	---
Flexural modulus, msi	70	23.8	---	17.4	---
	600	20.6	---	18.8	---

[a] Ref. 12.

TABLE V. - COMPARISON OF POSTCURED NITRILE CROSSLINKED AND HIGH MOLECULAR WEIGHT LINEAR PMR-PPQ/HMS GRAPHITE FIBER COMPOSITE PROPERTIES

Mechanical and thermal properties	Test temperature, °F	Exposure conditions, °F/hr	Matrix resin	
			Crosslinked	Linear[a]
Flexural strength, ksi	70	70/0	109	123
	600	600/0	74	70
	600	600/600	74	73
Flexural modulus, msi	70	70/0	16.3	20.7
	600	600/0	12.3	10.2
	600	600/600	12.2	----
Interlaminar shear strength, ksi	70	70/0	5.6	7.6
	600	600/0	4.2	4.2
	600	600/600	4.3	4.0
Composite weight loss, %	70	600/600	3.5	4.5

[a] Ref. 3.

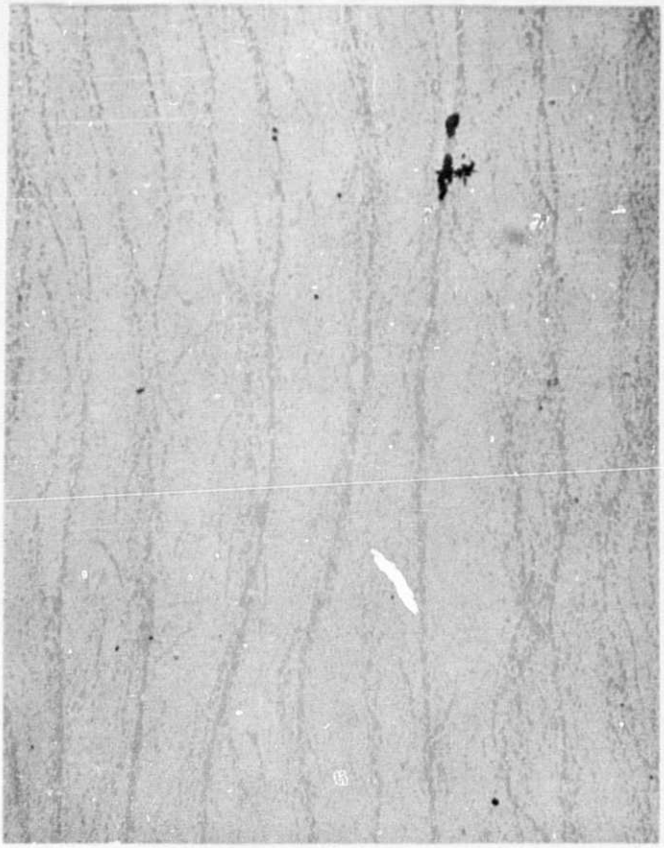


Figure 1. - Photomicrograph of 3-by 8-inch FMW 4000 *m*-cresol fabricated nitrile crosslinked PMR-PPQ/HMS graphite fiber composite, X50.

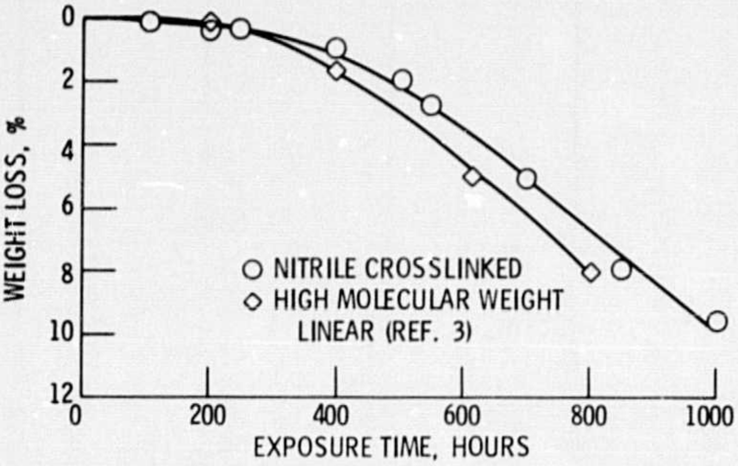


Figure 2. - Weight loss of nitrile crosslinked and high molecular weight linear PMR-PPQ/HMS graphite fiber composites, exposed in air at 600° F.

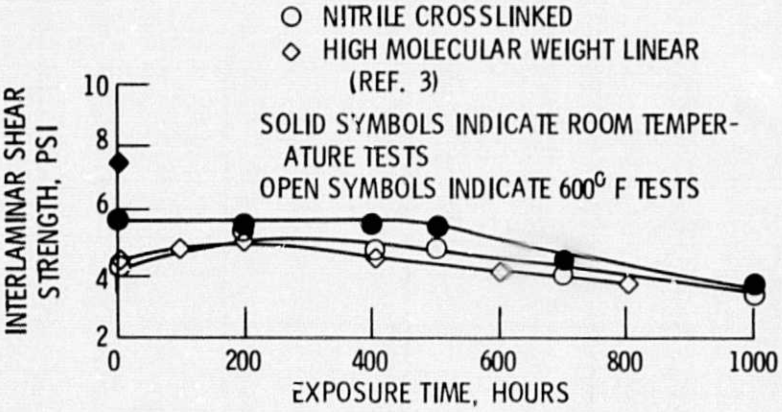


Figure 3. - Room temperature and 600° F interlaminar shear strength of nitrile crosslinked and high molecular weight linear PMR-PPQ/HMS graphite fiber composites, exposed in air at 600° F.

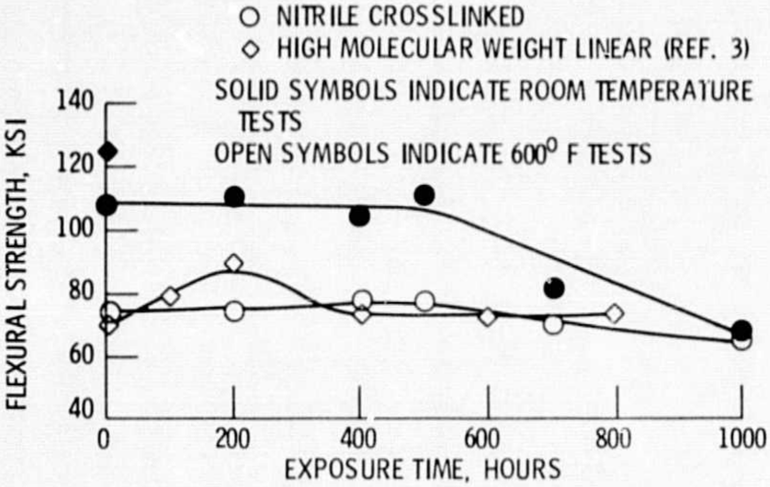


Figure 4. - Room temperature and 600° F flexural strength of nitrile crosslinked and high molecular weight linear PMR-PPQ/HMS graphite fiber composites, exposed in air at 600° F.

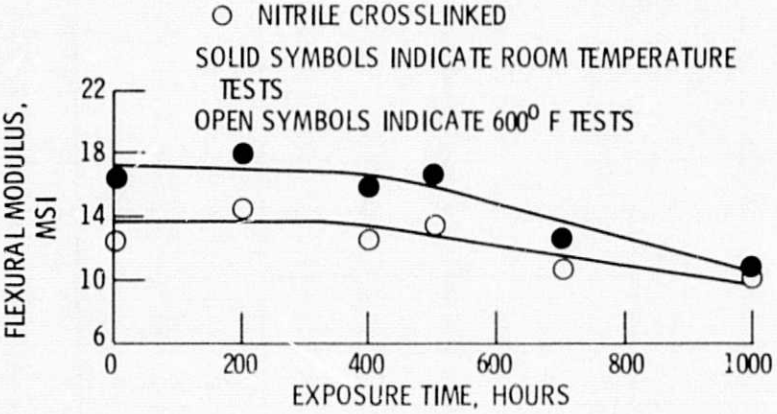


Figure 5. - Room temperature and 600° F flexural modulus of nitrile crosslinked PMR-PPQ/HMS graphite fiber composites, exposed in air at 600° F.

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