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DEVELOPMENT OF HIGH TEMPERATURE RESISTANT GRAPHITE FIBER COUPLING AGENTS

by

R. N. Griffin

General Electric Company
Space Sciences Laboratory
P. O. Box 8555
Philadelphia, Pennsylvania 19101

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS3-17788

William B. Alston, Project Manager

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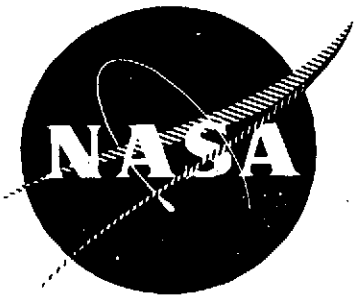

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Project Manager, William B. Alston, Materials and Structures Division, NASA Lewis Research Center, Cleveland, Ohio

16. Abstract

Ten surface treatments were investigated as potential coupling agents to improve the elevated temperature shear strength retention of polyimide/graphite and polyphenylquinoxaline/graphite composites. The potential coupling agents were evaluated by fiber strand tensile tests, fiber and composite weight losses at 533 and 588K, and by interlaminar shear strength retention at 533 and 588K. The two surface treatments selected for more extensive evaluation were a coating of Ventromer T-1, a complex organometallic reaction product of titanium tetrachloride and trimethyl borate, and a polyphenylquinoxaline (PPQ) sizing which was pyrolyzed in nitrogen to form a carbonaceous layer on the fiber.

Pyrolyzed polyphenylquinoxaline is a very satisfactory coupling agent for polyimide/Thornel 300 graphite fiber composites. During 1000 hours aging at 588K such composites lose a little over half their transverse tensile strength, and suffer a slight loss in flexural modulus. However, no degradation of flexural strength or interlaminar shear strength occurs during 1000 hours aging at 588K.

None of the coupling agents examined in the course of this work had a markedly beneficial effect with polyphenylquinoxaline composites. This may indicate simply that none of them were well suited to use with polyphenylquinoxaline, or it may indicate that the weak point of the PPQ composites is not the carbon/resin interface.

17. Key Words (Suggested by Author(s))		18. Distribution Statement
Composites	Polyphenylquinoxaline	
Coupling Agent	Interface	
Fiber	Interlaminar Shear	
Graphite	Flexure	
Polyimide		

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FOREWORD

This document constitutes the final report for the work accomplished between 27 June 1973 and 26 June 1974 by the General Electric Company for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS 3-17788, on Development of High Temperature Resistant Graphite Fiber Coupling Agents.

This work was performed under the technical direction of Dr. William B. Alston of the Lewis Research Center, Cleveland, Ohio.

The Space Processing Programs Section of the Space Sciences Laboratory was responsible for the work performed on this program. Mr. Louis R. McCreight, Manager, Space Processing Programs Section, provided overall program supervision and management. The Principal Investigator responsibilities for the program were performed by Dr. R. N. Griffin. Major technical contributions throughout the program were provided by Mr. E. F. Muziani and Mr. R. J. Grosso.

SUMMARY

The objective of this program was to develop coupling agents or surface treatments to improve the elevated temperature shear strength retention of polyimide/graphite and polyphenylquinoxaline/graphite composites. Ten potential coupling agents or surface treatments were evaluated by fiber strand tensile tests, fiber and composite weight losses at 533 and 588K, and by interlaminar shear strength retention at 533 and 588K. The two of the ten surface treatments selected for more extensive evaluation were a coating of Ventromer T-1, a complex organometallic reaction product of titanium tetrachloride and trimethyl borate, and a polyphenylquinoxaline (PPQ) sizing which was pyrolyzed in nitrogen to form a carbonaceous layer on the fiber.

After the initial screening studies it appeared that the Ventromer T-1 treatment was the best in almost all respects. Considerably different results, however, were obtained in the more thorough evaluation. In almost every instance, the composites made with the carbonized PPQ sizing were more stable than those made with the Ventromer T-1 treatment. The interlaminar shear and flexural strengths at 588K of polyimide/graphite composites made with the carbonized PPQ sizing were the same after 1000 hours at 588K as they were initially.

Differences were also noted in the fracture mechanisms of composites made with the two surface treatments. Polyimide composites of fibers treated with Ventromer T-1 often exhibited brittle tensile initiated failure, not only in the flexural strength tests but also in the interlaminar shear tests. Many of the interlaminar shear tests of polyimide composites with carbonized-PPQ-treated fiber also resulted in tensile initiated failure. In general the failure mode was less brittle.

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I. INTRODUCTION

Rapid progress in the development of high-modulus fiber-reinforced composites, such as those based on carbon, boron and the newer PRD fibers, has been hampered by problems in technology which must be solved if progress is to be maintained. Chief among these problems is the fact that under multiaxial stress conditions, many of these composites appear to fail within the matrix or at the filament-matrix interface rather than by rupture of the filaments. This problem has been emphasized in the reports of contractors working on such structures as horizontal tails and blading for aircraft and on helicopter rotor blades.

The outstanding mechanical properties of graphite fibers become of practical interest only if they can be efficiently translated into a useable composite. Although tensile properties of carbon fibers appear to be directly related to the size and orientation of the graphitic subunits, the properties of a fiber/resin composite depend to a large extent on the adhesion between the fiber and the matrix. Early work with carbon fiber/epoxy composites gave disappointingly low values for the interlaminar shear strength, a general measure of the adhesion at the interface. Spurred by the desire to use such composites as ablation materials, a number of investigators have studied the problem as it applies to graphite/epoxy systems (1, 2). Oxidative treatments, many of them proprietary, have been developed which raise the interlaminar shear strength of graphite/epoxy composites to acceptable values.

The surface treatments that are used for graphite/epoxy systems, however, are not adequate for use with high temperature resins. The short-time elevated temperature strengths of polyimide/graphite composites are significantly lower than the room temperature values. Composites exposed in air to elevated temperatures have exhibited excessive further decreases in these strength values. Degradation of the mechanical properties of polyimide/graphite fiber composites at 588K may be attributed to thermal and/or thermo-oxidative degradation of the resin/fiber interface and/or a lowering of the matrix modulus at high temperature and/or a difference in the coefficients of expansion of the fiber and resin. While investigators in the field (3, 4) have attempted to develop coupling agents for polyimides on glass fibers, no such materials had previously been available for use with graphite fiber composites of high temperature polyimides and polyphenylquinoxalines, particularly those prepared by means of in-situ polymerization of monomeric reactants (PMR). The purpose of this program, therefore, is to develop coupling agents to improve the elevated temperature strength retention characteristics of PMR polyimide and polyphenylquinoxaline/graphite fiber composites.

II. MATERIALS

Two resin systems were used in this work as matrices for unidirectional graphite fiber composites. One was a polyimide (PI), the other a polyphenylquinoxaline (PPQ), both prepared by the in-situ polymerization of monomeric reactants (PMR) (5, 6, 7) technique.

A. Polyimide Matrices

The polyimide used throughout this study was formed from the monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid (NE), 4,4' methylenedianiline (MDA), and the dimethyl ester of 3,3',4,4'-benzophenone-tetracarboxylic acid (BTDE) in the molar ratio of 2/3.09/2.09, giving a "formulated molecular weight" of 1500. (8)

5-Norbornene-2,3,-dicarboxylic anhydride (NA) was made from cyclopentadiene and maleic anhydride according to the literature procedure. (9) A 95% yield of material, m.p. 431-433K (158-160C) (Lit. 164-5C (9) was obtair Its infrared absorption spectrum is shown in Figure 1. The monomethyl ester was prepared according to Walton (10). After two washes with isopropyl ether and two washes with ligroin the product was obtained in 79% yield, m.p. 374-375K (101-102C) (Lit. 375-376K (102-103C) (10). The infrared spectrum is shown in Figure 2.

The dimethyl ester of 3,31,4,4'-benzophenonetetracarboxylic acid was prepared by heating benzophenonetetracarboxylic dianhydride (BTDA) with methanol according to the method of Serafini, Delvigs, and Lightsey (5). The product had a rather indefinite melting point below 350K (77C). The

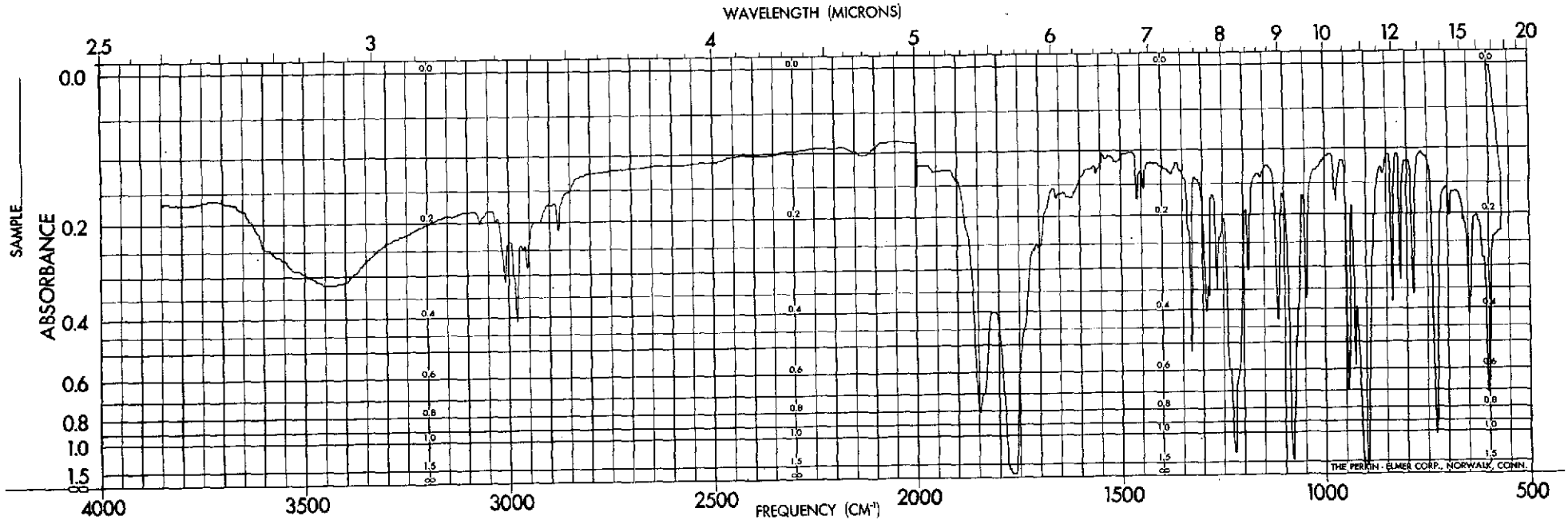


Figure 1 5-Norbornene-2,3-dicarboxylic anhydride, infrared spectrum

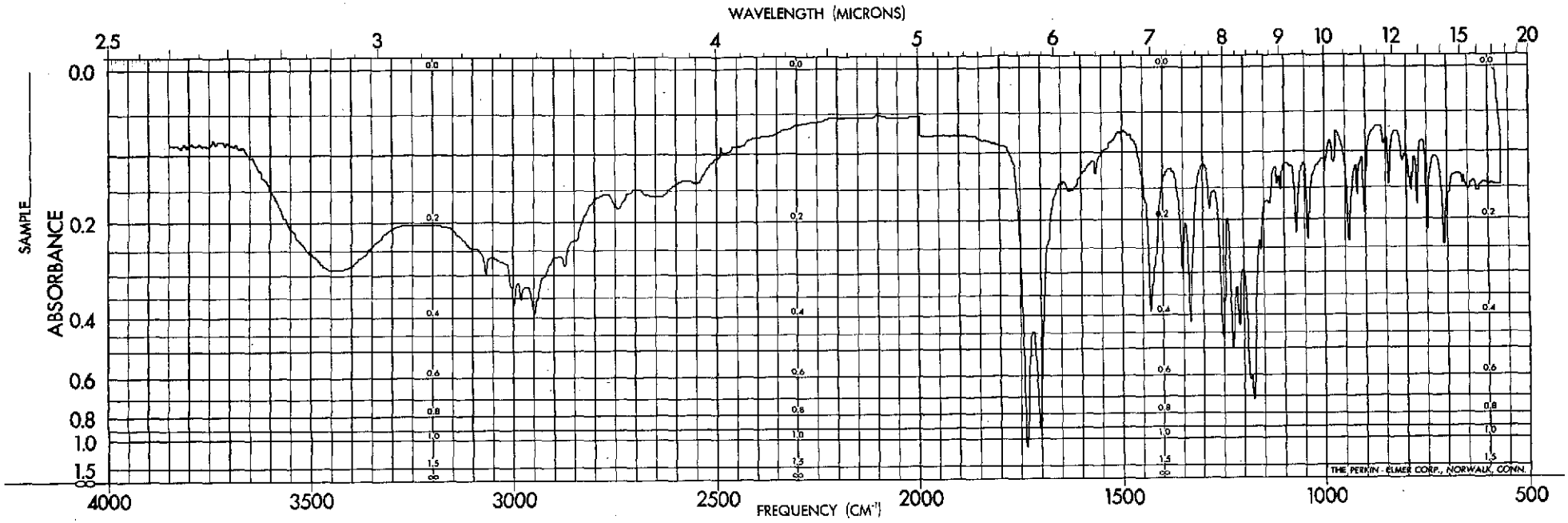


Figure 2 Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid, infrared spectrum in KBr.

infrared spectrum of this material is shown in Figure 3. An attempt was made to purify an analytical sample by vacuum sublimation because we had observed what appeared to be sublimation while determining the melting point on a microscope hot stage. Vacuum sublimation was accomplished easily, giving a light yellow crystalline sublimate and a dark, brittle, glassy residue. As can be seen by comparison of Figures 3 and 4, the sublimate has a markedly different composition than the crude. The "unpurified" material (Figure 3) has an ester carbonyl absorption at 1725 cm^{-1} while the sublimate (Figure 4) has the 1725 cm^{-1} absorption as well as maxima at 1775 and 1850 cm^{-1}, the latter also appearing in the spectrum of BTDA (Figure 5). Thus it appears that under the sublimation conditions some methanol is lost from the diester, giving a mixed ester anhydride. (Because of the relative amounts of material this could not have been a minor impurity in the crude diester.)

During the early part of the program the polyimide was prepared from an assayed stock methanol solution of the dimethyl ester. However, due to long term storage instability of the assayed solution a fresh ester solution was prepared and immediately used for each polyimide formulation. The proper amount of anhydride was heated in refluxing methanol, and the solution used directly in the polymer formulation without isolation of the ester.

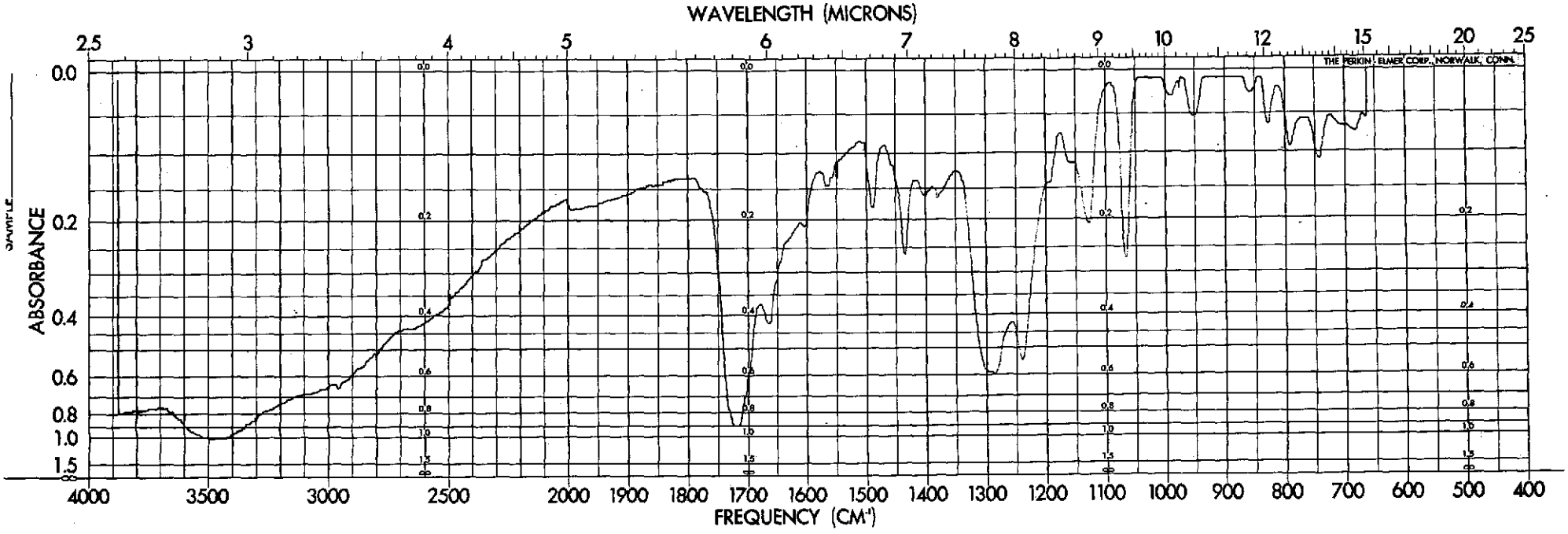


Figure 3 Dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid, infrared spectrum in KBr.

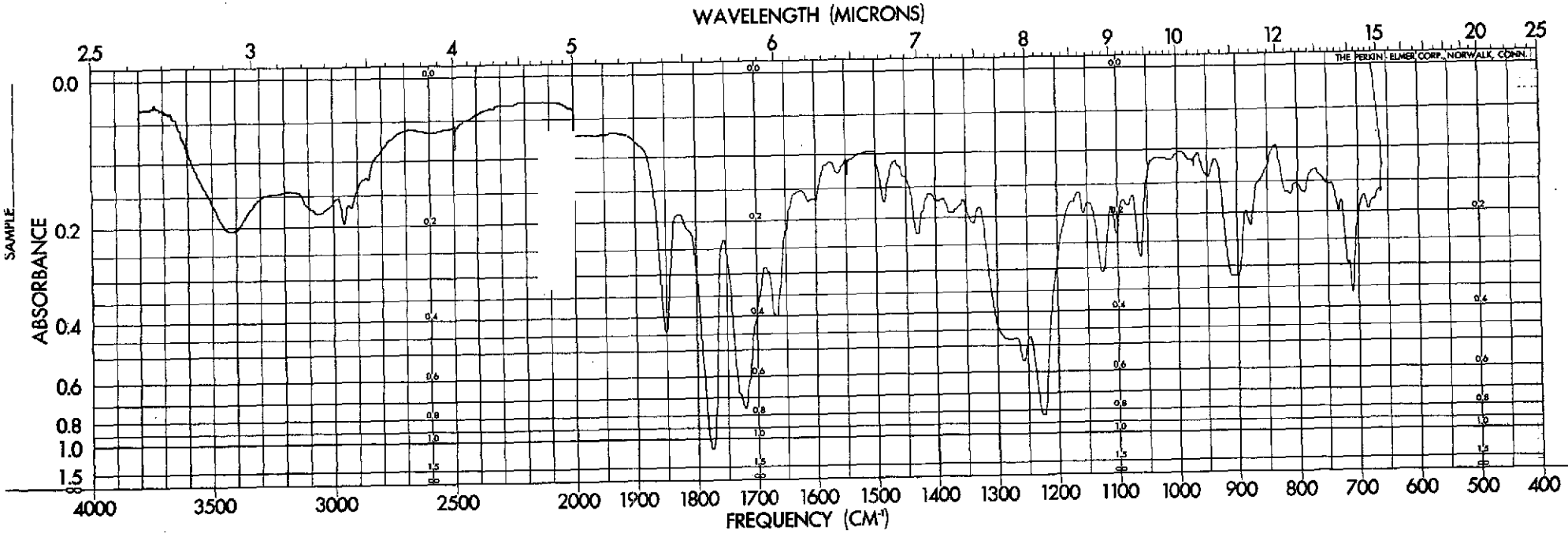


Figure 4 Sublimate from dimethyl ester of 3,3',4,4', -benzophenonetetracarboxylic acid, infrared spectrum in KBr.

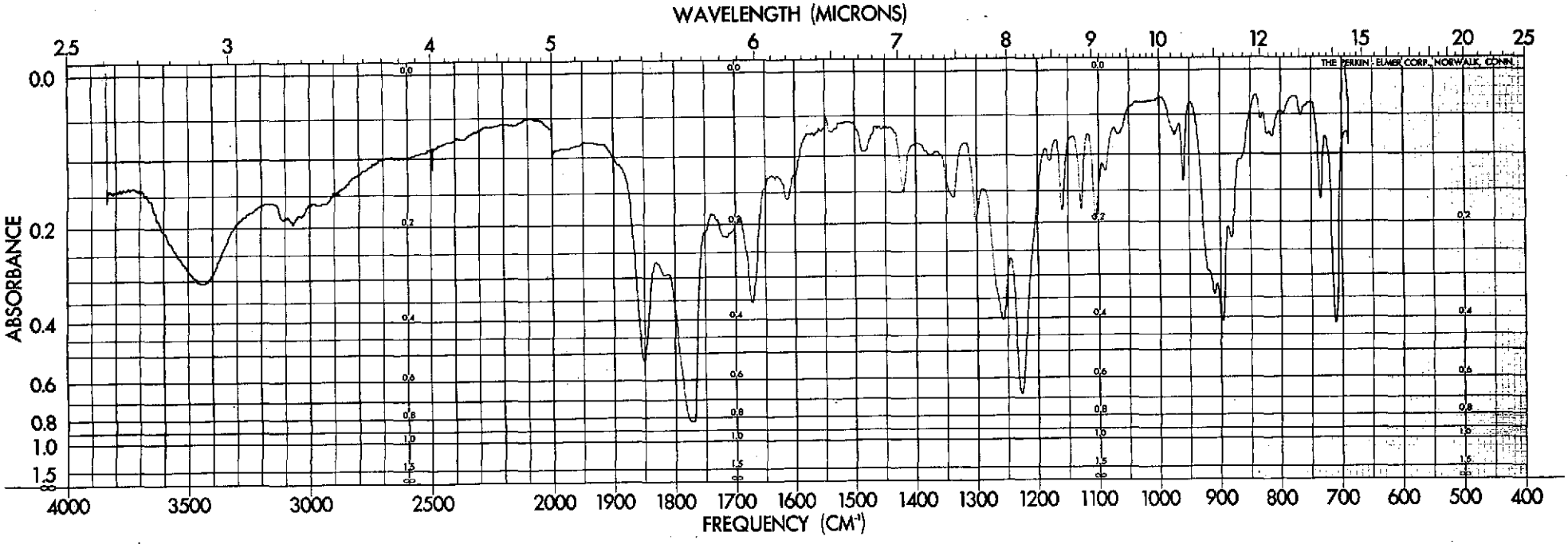


Figure 5 Benzophenonetetracarboxylic dianhydride, infrared spectrum in KBr

Eastman 4,4'-methylenedianiline, 500 g, was dissolved in 2.5 liters of boiling isopropanol containing decolorizing carbon. The mixture was filtered hot through a filter-aid cake and allowed to crystallize. Recovery was 80%, m.p. 365-366 K (92-93 C).

A 40 weight percent solution of the three monomers in methanol was applied to drum wound tapes of graphite fibers. The prepreg was heated at 323 K (50 C) for two hours on the drum to reduce the solvent content to less than 10 percent.

B. Polyphenylquinoxaline Matrices

The polyphenylquinoxaline used in this work was formed by condensation of p-bis(phenylglyoxalyl) benzene (PPGB) with 3,3',4,4'-tetraaminobenzophenone (TABP) (6, 7).

p-Bis(phenylglyoxalyl) benzene was prepared from p-phenylenediacetic acid. After dissolution in sodium hydroxide solution, filtration, and reprecipitation with hydrochloric acid, the p-phenylenediacetic acid melted at 524-525 K (251-252 C).

The procedure of Hergenrother [11] was used except for substitution of selenous acid for selenium dioxide. The oxidation step proceeded so vigorously that cooling of the reaction flask was necessary. The mixture turned black after about one hour of refluxing, and reflux was continued for about 5 hours. The product was recrystallized from isopropanol in 71% overall yield and melted at 397-398 K (124-125 C) (lit. 398-399 K, (125-126 C) [11]. The infrared absorption spectrum is shown in Figure 6.

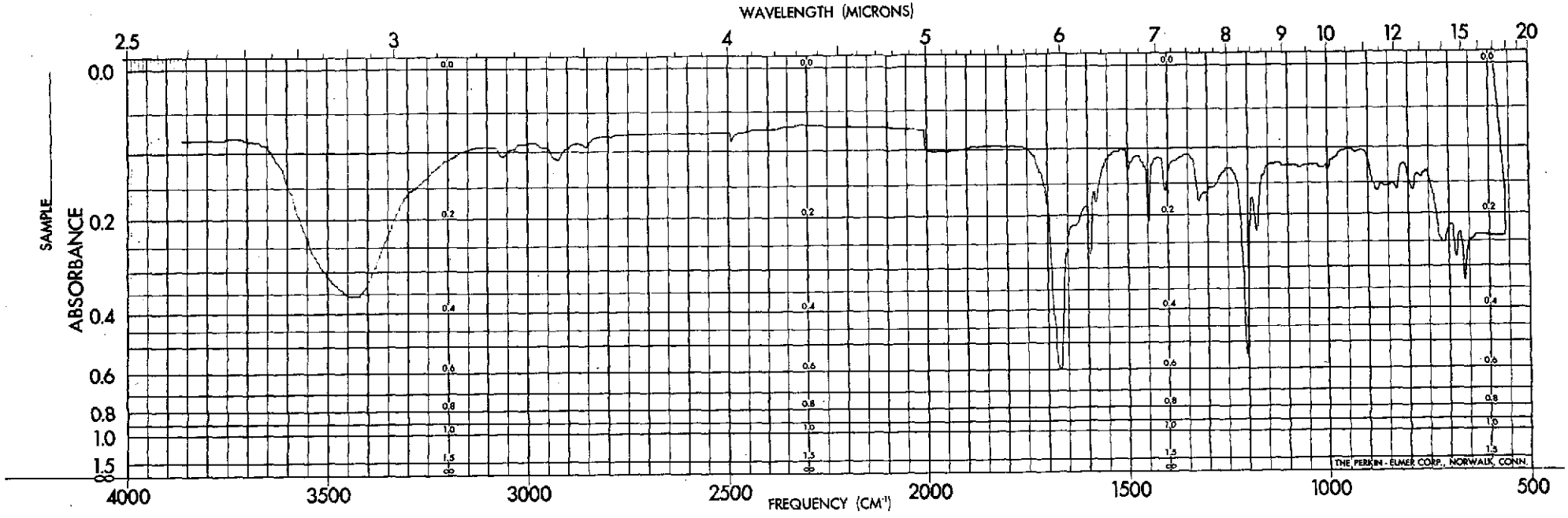


Figure 6 p-Bis(phenylglyoxalyl) benzene, infrared spectrum in KBr

3,3',4,4' - Tetraaminobenzophenone, purchased from Polysciences, Inc., was dissolved in hot, dilute hydrochloric acid containing decolorizing carbon and filter aid. The mixture was filtered hot and potassium hydroxide added to precipitate the product. After being washed with water and dried in a vacuum desiccator the product melted at 489-490 K (216-217 C) and was a mustard yellow color.

An equimolar mixture of the two monomers was dissolved in N-methyl pyrrolidone at 30 percent by weight. This solution was applied to fibers as described in Section III-A above. Solvent removal required somewhat higher temperatures in this case; and a rather delicate balance seemed to exist between inadequate solvent removal which could lead to flashing of solvent during subsequent hot pressing, and excessive advancement of the polymerization which could lead to uneven distribution of fibers in the composite.

C. Graphite Fiber

It was originally intended that HTS graphite fiber would be used in this study. The surface structures of many graphite fibers were examined in our earlier work (12). Others have studied surface morphology, porosity and wetting characteristics. Estimates of pore size and shape in carbon fibers have been obtained from Raman spectroscopy (13, 14, 15) and electron microscopy (14). The latter technique was used for a comparison of the surfaces of treated and untreated, high-strength HT graphite fibers.

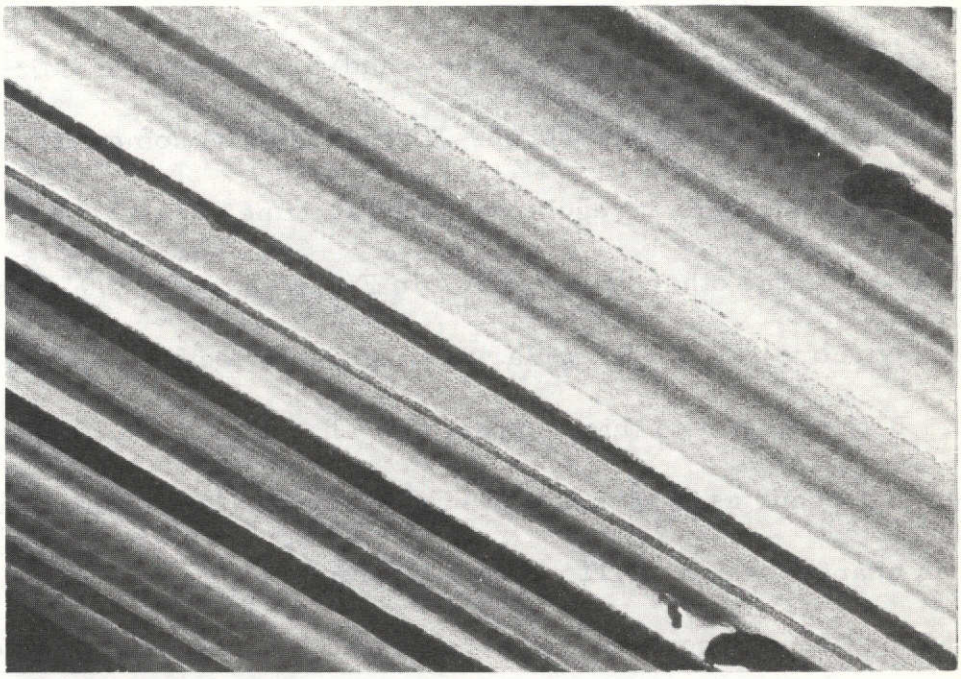


Figure 7. Photomicrograph of HT Graphite Fiber. 30,000 X

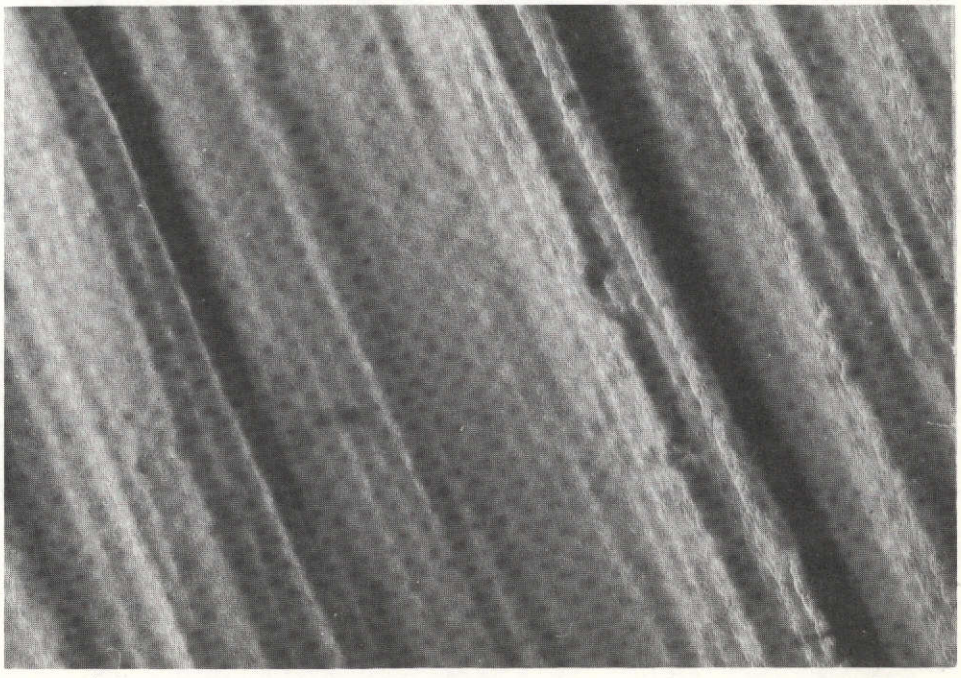


Figure 8. Photomicrograph of Treated HT Graphite Fiber. 30,000 X

This comparison is shown in Figures 7 and 8. The untreated HT fiber surface shown in Figure 7 at 30,000 X appears to be somewhat smooth, with no marks but some irregularity along the fine edges. The treated HT surface, on the other hand, shown in Figure 8 at 30,000 X appears to have many more surface irregularities and imperfections than the untreated fibers. It appears from this comparison, that in addition to chemical changes that occur as a result of fiber surface treatment, there are some physical changes which might enhance bonding.

It has been reported elsewhere that an overall smoothing of the surface of PAN-based fibers follows oxidation by CO_2 (16) or nitric acid(17).

The use of high strength HT fibers was desirable, also, because of continuity with work done with PMR polymers (5, 7). Treated HT fiber may provide better interfacial bonding with coupling agents and treatments as a result of the small crystallite sizes which should theoretically provide more reactive sites. Since the proportion of graphite basal plane present in the fiber surface increases with fiber modulus, it is plausible that the higher shear strengths found with lower modulus fibers are a reflection of the greater chemical bonding of the matrix to edge carbon atoms present in the fiber surface (18).

However, after work had started we found that we were unable to obtain the required amounts of HTS fiber in a reasonable time. Therefore Union Carbide's "Thornel" 300 graphite yarn, grade WYP 30 1/0 was

selected as the most similar, readily-available material. The nominal properties of this material are tensile strength 2.48×10^3 MN/m^2 (360,000 psi) and tensile modulus 2.34×10^5 MN/m^2 (34×10^6 psi). The fiber was obtained with the commercial surface treatment but without the standard epoxy sizing. Instead the fiber was sized with water which was removed as the fiber was used in this study.

D. Coupling Agents or Surface Treatments

Ten methods for improving the elevated temperature stability of graphite/PI or graphite/PPQ composites were selected for evaluation. Eight of these methods involved treatment of the fiber in order to promote adhesion of the resin matrix or to lower the rate of oxidation of the fiber. One was a treatment of the fiber to alter the failure mechanism of the composite, and one the addition of an antioxidant to the fiber surface. The ten treatment methods are shown in Table I.

Treatments #1 and #2, the addition of a thin layer of polymer by immersion of the fiber in a dilute solution of polymer or monomers, were akin to the sizing of Thornel 50-S with polyimide reported by Hanson and Serafini (19). They differed from the formulation of the composite itself primarily in that a very dilute solution was used in order to improve the chance of coating relatively inaccessible edge planes with the polymer.

The third, fourth, and fifth treatments were based on the work of Larsen, Smith, and Erickson (13) who demonstrated as much as three-fold improvement in shear strength of graphite-epoxy composites by pyrolyzing

Table I - Graphite Fiber Treatments Investigated

1. Heat clean and size with PMR-PI.

2. Heat clean and size with PMR-PPQ.

3. Heat clean, size with PMR-PPQ, and carbonize the sizing.

4. Heat clean, size with PMR-PI, and carbonize the sizing.

5. Heat clean, size with an epoxy novolac containing a Lewis acid, and carbonize the sizing.

6. Heat clean and treat with Ventromer T-1.

7. Treat the fiber with ferric chloride and heat.

8. Treat the fiber with ferrocene and heat.

9. Heat clean and size the fiber with PMR-PI containing a mineral filler.

10. Treat the fiber with phosphorus oxychloride.

a layer of polyphenylquinoxaline on the surface of HM graphite fibers.

The rationale for the third and fourth treatments is quite evident in light of the work cited above. The rationale for the fifth treatment, however, deserves some further explanation. The formation of a carbonaceous char by pyrolysis of an aromatic resin is well known (20). However, when an acid of an appropriate type is added to certain resins, the course of the pyrolysis is markedly altered; and the nature and quantity of charred product can be quite different than that which is formed in the absence of the acid. Extensive work on the subject was carried out as a means of developing re-entry ablation materials which were easily fabricable in large pieces by casting with a wide range of available physical properties. These were developed and patented (21) about 10 years ago as the GE Century Series Ablation Materials. Although the application was quite different, the ability to tailor the course of the degradation products from carbonaceous to graphitic would seemingly be of value to the development of high temperature coupling agents. In particular, the use of additional ingredients rather than simply accepting the natural degradation products offers a large amount of control of the process.

Treatment of materials with a reaction product of titanium tetrachloride and trimethyl borate has been reported (22) to improve the wettability of a wide range of substances such as glass, quartz, paper, textiles, and even fluorocarbon polymers. The sixth treatment entailed the use of such material with heat-cleaned fibers.

The seventh and eighth treatments were based on the relatively successful surface reduction techniques reported (13) for carbon fiber/epoxy composites.

In addition to treatments which are coupling agents, surface treatments, or protective agents, the ninth treatment was intended to help to achieve the desired result by mechanical improvement of the interface. Fine particle or flake forms of mineral fillers in small amounts have sometimes been found to improve the properties and to alter the failure mechanisms of composites, especially at elevated temperatures.

Finally, if the degradation of composite properties at elevated temperatures is fundamentally due to oxidative degradation of the fiber-resin interface, it seemed logical to treat the fiber surface with a material to inhibit its oxidation.

The inhibitory effect of halogen compounds -- and in particular, the halides and oxyhalides of phosphorus -- on the oxidation of carbon and graphite has been known for many years (23). Phosphorus oxychloride, which appears to be the most active inhibitor, has found application in the control of oxidation in nuclear graphites (24) and, recently as an additive to retard carbon brush wear in electric motors (25). In spite of several detailed studies of the kinetics and products of the inhibited oxidation reaction, the effect is not completely understood nor is the nature of the interaction of $POCl_3$ with the carbon surface defined. Nevertheless,

treatment with phosphorus oxychloride was chosen as the tenth surface treatment to inhibit oxidation of the fiber/resin interface (26).

A fiber treatment apparatus was set up as shown schematically in Figure 9. The fiber was first heat cleaned in a nitrogen-filled tube furnace at 1353-1393K. Immediately after heat cleaning, the fiber was immersed in a solution of coupling agent. It could then be dried at any temperature up to about 573K and the coupling agent pyrolyzed if so desired. All the surface treatments except phosphorus oxychloride were applied with this apparatus.

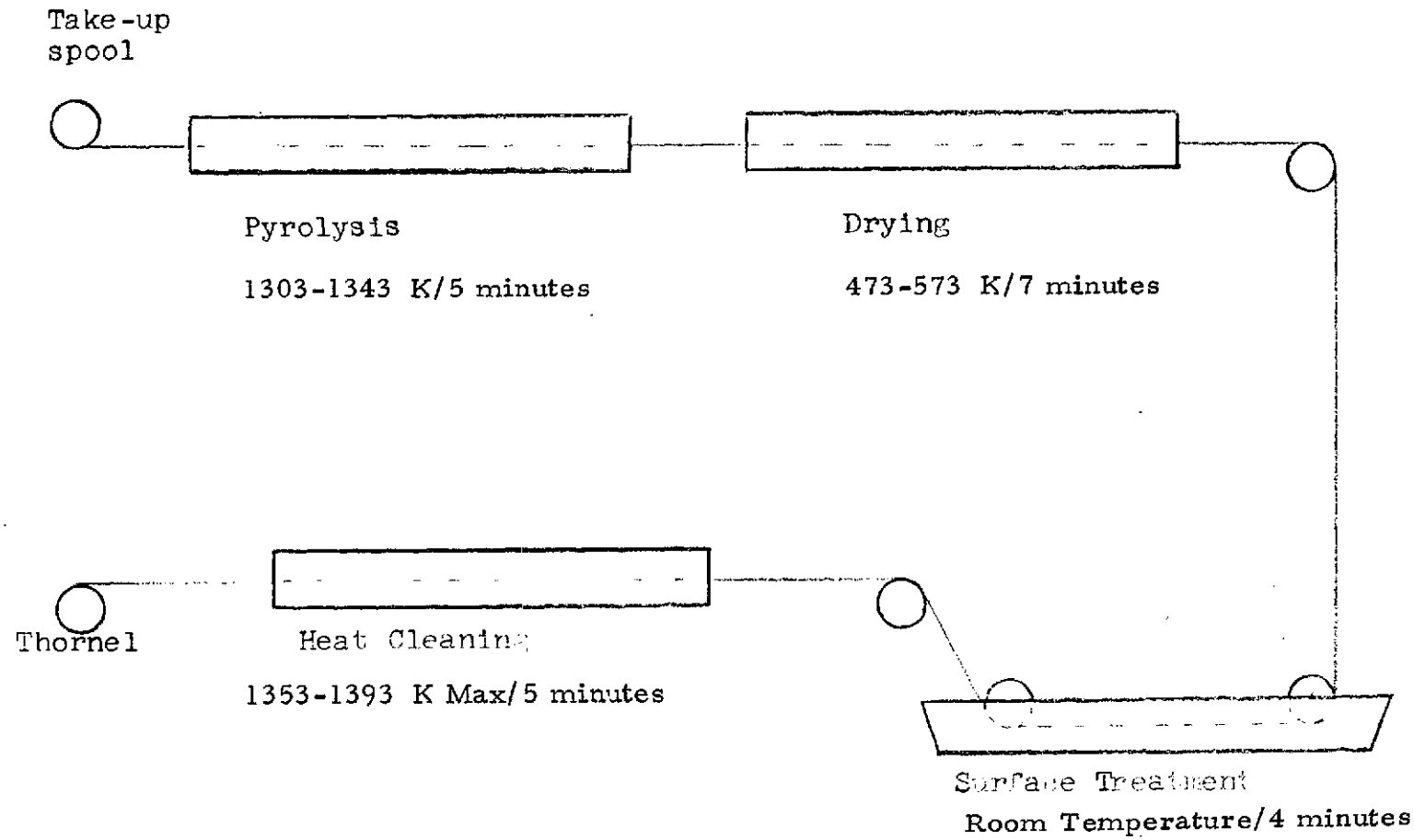
Sizing with PMR polyimide was accomplished by immersion of the fiber in a methanol solution. The fiber was first heat-cleaned in nitrogen at 1373 $\pm$ 20K, immersed for about four minutes in a 0.1% solution of PMR-PI, and the coating was dried at 473-493K.

The PPQ sizing (treatment #2) was applied in much the same way except that a 0.1% solution of monomers in N-methylpyrrolidone was used.

The most successful treatment reported by Larsen, Smith and Ericson (13) for increasing the interlaminar shear strength of graphite-epoxy composites was a PPQ sizing pyrolyzed to produce a carbonaceous coating on the graphite fibers. Our initial attempts to reproduce these results were quite unsuccessful. The fiber was heat-cleaned in nitrogen at ~1373K, immersed in a 0.1% solution of PMR-PPQ (from 3,3',4,4'-tetraamino-benzophenone and p-bis(phenylglyoxalyl) benzene in N-methyl pyrrolidone, dried at 473-493K and pyrolyzed at 1323K. The resulting fiber was extremely brittle in places, resulting in frequent breaks. In addition,

FIGURE 9

Schematic of Fiber Treatment Apparatus



excessive amounts of pilling were observed. This problem was eliminated by passing the fiber between two silicone rubber rolls after it emerged from the treatment bath. In some places the Thornel tows are more open than in others. The coating solution of 0.1% PPQ in N-methyl pyrrolidone apparently had a higher viscosity than the other solutions we had worked with, resulting in excessive pick-up in the open parts of the tow. The end result was carbon bridging between the individual fibers and creation of a brittle section in the tow. The rolls, in effect, squeegeed the excess solution out of the tow, and the coating treatment was completed without further difficulty.

Carbonaceous coatings were similarly produced from PMR-PI in methanol and from epoxy-novolac in DMF.

The epoxy formulation was based on the work of Barry and consisted of

DEN 438 - 100 parts

methyl nadic anhydride - 68 parts

No problems were encountered with treatment #6, the application of Ventromer T-1. The Thornel fiber was simply immersed in an aqueous solution of 0.33% Ventromer T-1 and 0.33% sodium tripolyphosphate, neutralized to pH 7 with ammonium hydroxide.

Since Larsen reported (13) that pyrolysis of iron-containing materials on the surface of graphite fibers leads to improved composite shear strength, ferric chloride was applied to Thornel WYP-30 - $\frac{1}{0}$ as a 1.5% solution in a 2:1 mixture of benzene and methanol. The fiber was first heat-cleaned as above, coated by immersion in the ferric chloride solution, dried and pyrolyzed at 1293-1313K. A great deal of pilling of the yarn was observed after this treatment as well as occasional breakage of the yarn. No mention of this problem was made by Larsen, Smith and Erickson (13), and it may be the case that a more dilute solution of ferric chloride would produce better (or less damaging) results. Just as with ferric chloride, encouraging results have been reported (13) concerning the effects of treatment of graphite fibers with ferrocene. Thornel WYP 30 - $\frac{1}{0}$ was heat cleaned in nitrogen at ~1373K, immersed in a 2% solution of ferrocone in xylene, dried, and pyrolyzed at 1293-1313K. The results were generally similar to those observed with ferric chloride, though to a lesser degree.

It was our original intention in considering treatment #9 to apply a sizing of polyimide filled with aluminum silicate microfibers (DuPont "Fybex D"). The aluminum silicate disperses well in methanol, and remains dispersed for at least several days without agitation. However, when it was added to a 1% PMR-PI solution in methanol it immediately agglomerated and sank. It could not be redispersed by ultrasonic or 60 Hertz (Syntron) vibration. Therefore, the fiber was coated in a

methanol solution of 1% PMR-PI and 0.5% Cab-O-Sil which was constantly agitated by a Syntron vibrator.

Because of the treatment conditions that were apparently necessary for inhibiting oxidation by phosphorus oxychloride (26) (treatment #10), the usual treatment apparatus was not used. Instead, a quantity of Thornel fiber was wrapped on a Pyrex mandrel, and the fiber was treated for 24 hours with 5% sodium hypochlorite solution, washed, dried, and treated for one hour with phosphorus oxychloride. It was then heated overnight, starting at room temperature and increasing slowly to 573 K (300 C). This treatment was expected to reduce the residual absorbed $POCl_3$ to less than 8% by weight and to increase the threshold oxidation temperature of the fiber by about 130^{o}, as was observed by McKee (26) in studies of thermal desorption of phosphorus oxychloride and oxidation temperature of graphitized carbon.

III. SCREENING TESTS

A. Fiber Weight Loss Studies

Changes in the weight of the ten treated fibers were measured during 200 hour exposures in air at 588K and 533K (315 C and 260 C respectively). The results of these studies are tabulated in Appendices A and B. Treatments 1-5, which involved sizing with PI or PPQ or with a polymer-derived pyrocarbon, appeared to be beneficial or at least not significantly harmful to the oxidative stability of the fiber. Treatment number 6, the halotitanate, appeared to offer some protection to the fiber during the first one hundred hours at 588K, but after two hundred hours at 588K the fiber weight loss with this treatment was a little larger than that observed with no treatment or with treatments 1-5.

Treatment of the fiber with ferric chloride (#7) produced catastrophic degradation of the fiber at both 588 and 533K. This treatment was thus discontinued. Similarly, treatment with ferrocene (#8) caused a significant loss of stability at 588K, though it had no particular effect at 533K. Since there did not appear to be any significant counter-balancing virtue in this treatment, it was dropped from further consideration.

Fiber with a sheath coating of silica-filled polyimide (treatment #9) degraded at 588K (315C) at a rate about twice as great as the fiber sized with polyimide alone (treatment #1). Possibly the silica catalyzes the decomposition of the polyimide, the fiber, or both.

Treatment of the fiber with phosphorus oxychloride (treatment #10) caused an initial rapid loss of weight (3-4% in one hour, 9-10% in 24 hours). This was rationalized as removal of residual absorbed $POCl_3$. Unfortunately, the loss of weight continued to be excessive at both 588K and 533K and was essentially a linear function of time at 588K between 24 and 200 hours.

Since these results were so greatly at variance with the results observed with other forms of graphite (23-26), it was thought that inadequate washing had left residual sodium hypochlorite which was causing the degradation. Accordingly, some fiber was treated with $POCl_3$ without the prior hypochlorite treatment. After being heated at 588K for twenty-four hours, the three samples lost an average of 10.8% of their initial weight. During the following 176 hours the three samples lost only an additional 2% of their initial weight, indicating that residual hypochlorite contributed to the degradation.

Two treatments were selected for further study. These were #3, a pyrocarbon sizing derived from PPQ, and #6, a halotitanate. The weight losses of untreated reference fibers and of fibers subjected to treatments 3 and 6 were measured after exposure at 588K and 533K for periods up to 1000 hours. The results of these studies are shown graphically in Figures 10 and 11. Both treatments improved the thermal stability of the fiber, the halotitanate showing slightly greater improvement than the pyrocarbon.

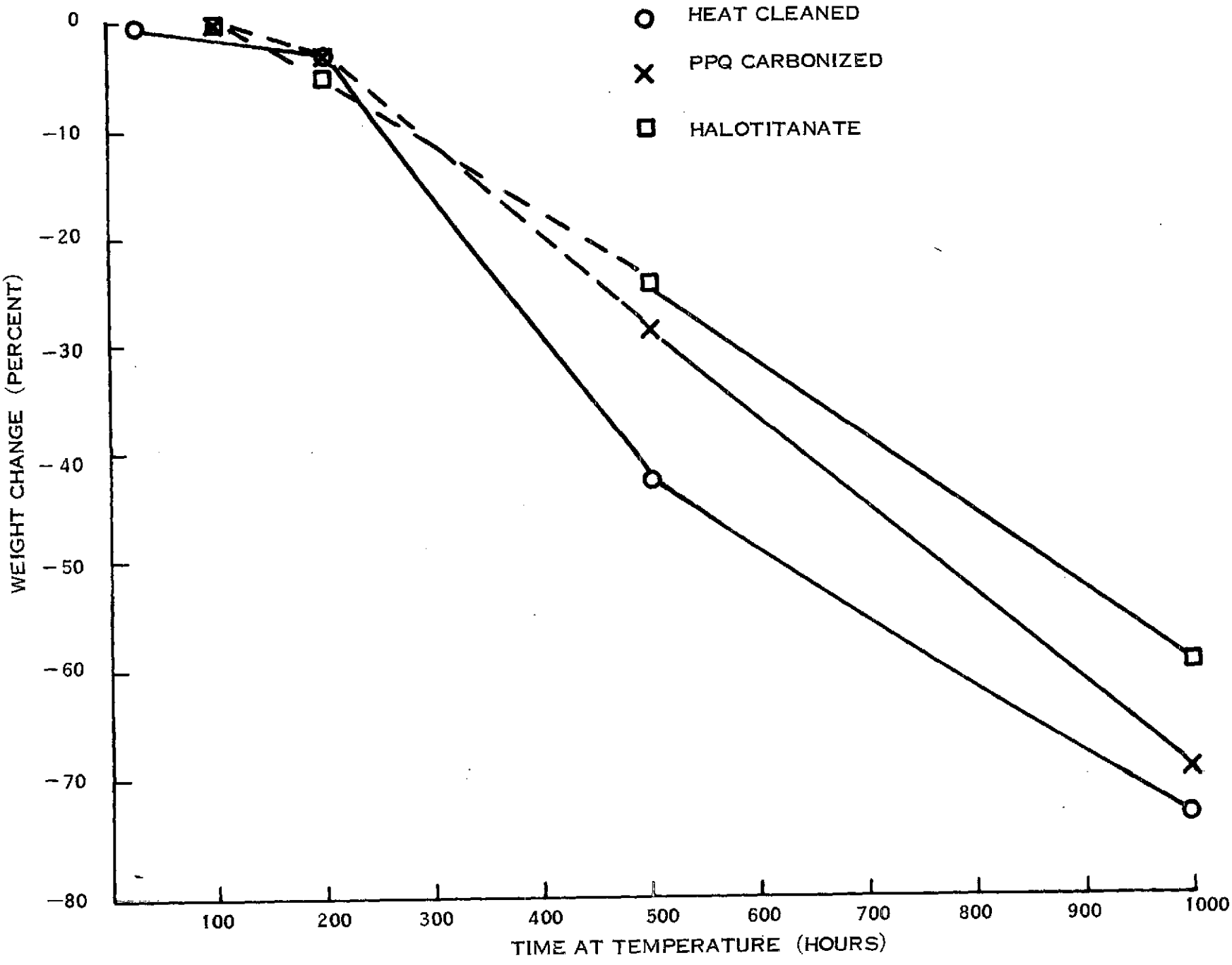


FIGURE 10. FIBER WEIGHT LOSS AT 588°K

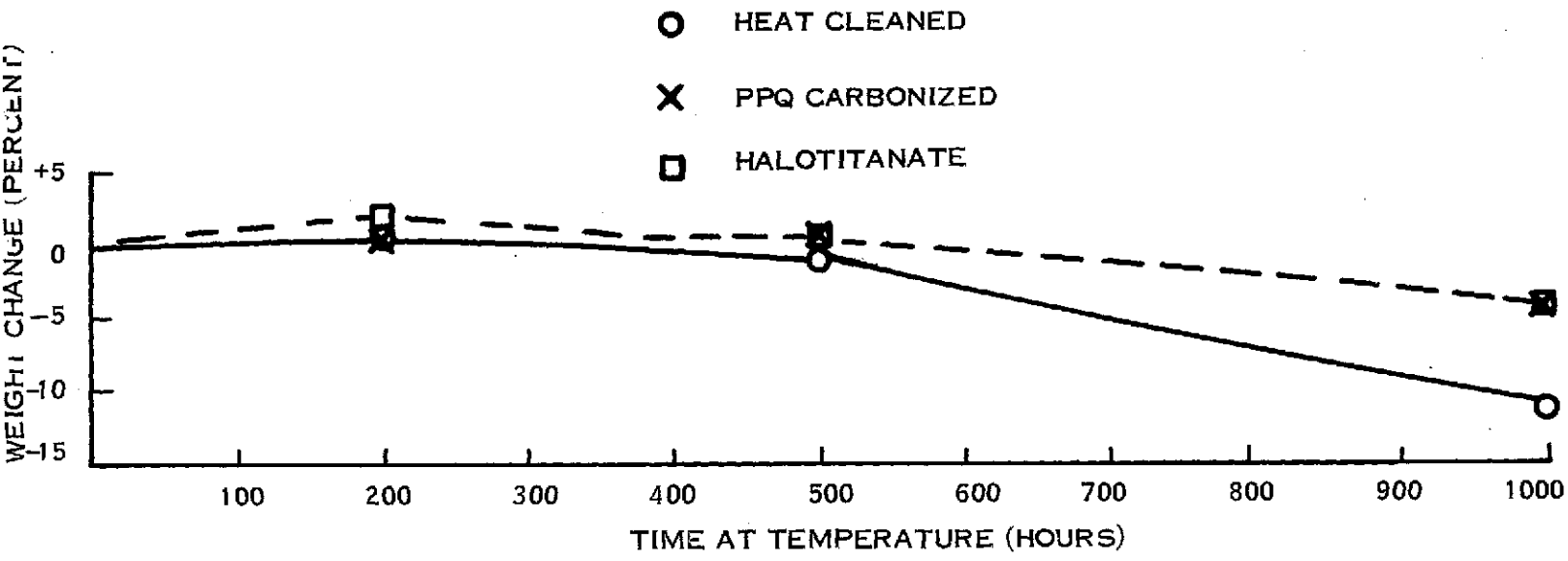


FIGURE 11. FIBER WEIGHT LOSS AT 533°K

B. Fiber Tow Tensile Tests

Fiber tow tensile tests were performed according to Hercules Advanced Composite Test Method ACTP-F-2 wherein the tow is coated with an epoxy to a resin content between 55% and 65% by weight. Acccording to this test ferric chloride (treatment #7) and phosphorus oxychloride (treatment #10) greatly reduced the strength of the tow. This further reinforced the decision to discontinue further investigation of treatment 7 and 10. The other treatments resulted in no change of fiber tow tensile strength within a range of about 10%.

C. Composites Fabrication and Testing

Eight polyimide composites were made with graphite fibers representing seven surface treatments and a control. The matrix was PMR-PI made from 5-norbornene-2, 3-dicarboxylic acid monomethyl ester, 4,4'-methylenedianiline, and 3,3',4,4'-benzophenonetetracarboxylic acid dimethyl ester in the mole ratio of 2/3.09/2.09 (7). The fiber was wound on a mandrel, impregnated with the calculated amount of a 50% methanol solution of monomer mixture, and dried under heat lamps. After the prepreg was dry, it was removed from the mandrel, stacked between Teflon-coated glass and aluminum foil and imidized for 2 hours at 477K in an oven. It was transferred to a preheated (477K) mold, placed in a press at 505K for 10 minutes under contact pressure. Pressure of 3.45 MN/m^2 (500 psi) was

applied and maintained while heating to 588K and holding for 1 hour. The composite was cooled slowly to 477K then rapidly to room temperature. Post-curing was accomplished as shown in Table II.

Table II - Polyimide Post-Cure Cycle

RT $\longrightarrow$ 505K in 8 hours

505K hold for 16 hours

588K hold for 24 hours

588K $\longrightarrow$ RT overnight

The properties of the polyimide composites are summarized in Appendix A. The calculated void contents were low and agreed with the ultrasonic C scans results. The ultrasonic scans showed no difference between composite #O at -1.1% void and composite #1 at 2.7% void. The only fault shown by the ultrasonic C scans of these polyimide composites was a dry area in the center of #2 composite (treatment #4, carbonized epoxy). Measurements made in this dry area indicated a 53.5% fiber volume, 44.4% resin volume, and 2.1% void, certainly not indicative of resin starvation. The interlaminar shear strength (ILS) at that point was 97.2 MN/m^2 which was only slightly lower than the average of the other samples (103 MN/m^2). The ultrasonic C scans also showed that four of the panels were cracked. One was cracked when it was removed from the mold; the other three were cracked during shipment for testing.

In similar fashion eight composites 12.5 cm square were made with a matrix of PMR-PPQ made from 3,3',4,4'-tetraaminobenzophenone and p - bis (phenylglyoxalyl) benzene. The prepreg was heated at contact pressure in a press at 566K for 90 seconds. A pressure of 3.45 - 6.9 MN/m^2 (500-1000 psi) was applied then for 1 hour. The temperature was then raised to 644K for 1 hour, after which the laminate was cooled rapidly to room temperature. Post-curing was accomplished as shown in Table III.

Table III - Polyphenylquinoxaline Post-Cure Cycle

RT ⟶	472K hold for 2 hours
	498K hold for 2 hours
	525K hold for 2 hours
	569K hold for 2 hours
	597K hold for 2 hours
	622K hold for 2 hours
	644K hold for 3 hours
644K ⟶	RT overnight

The PPQ composites all had high volume fractions of fiber as can be seen by inspection of Appendix C. The ultrasonic C scans showed that several of the panels contained defective areas which were avoided when the panels were cut into test specimens.

Photomicrographs of some of the panels showed significant differences between the polyimide panels and the polyphenylquinoxaline panels. Figure 12 is a typical end-view of a polyimide composite. It shows a compact, uniform distribution of fibers with one tow indistinguishable from another. On the other

hand, the PPQ composites had the appearance of Figure 13 with each individual tow separated by a layer of resin. As can be seen in the close-up views of the same composite, Figures 14 and 15, the space between the tows and the area within the individual tows were essentially free of any voids. Defective areas in the PPQ composites were characterized by cracks in the resin between tows as shown in Figure 16. Cracks were not found that carried into or through a tow.

1. Composite Weight Losses

Weight loss measurements were made in triplicate on the eight polyimide composites and the eight PPQ composites. Samples were exposed for 200 hours in circulating air ovens at 588K and 533K. The data are summarized in Appendix D. At 533K none of the samples lost more than one percent of their weight in 200 hours. At 588K, however, the polyimide composites lost between two and three percent of their weight during the 200 hours while the PPQ composites lost between about four and 7-1/2% of their weight at 588K and 200 hours. Inspection of Figures 17 and 18 indicates the type of damage suffered by the PPQ composites at 588K. Figure 17 shows the unaged PPQ composite made with Ventromer T-1 treated graphite fiber. Figure 18 shows the same composite after 500 hours at 588K. The development of internal voids in the composite is obvious. This probably

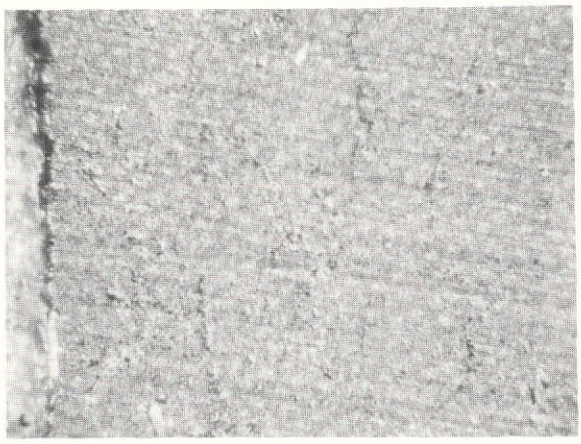


Figure 12. Photomicrograph of a Polyimide/Graphite Fiber Composite.

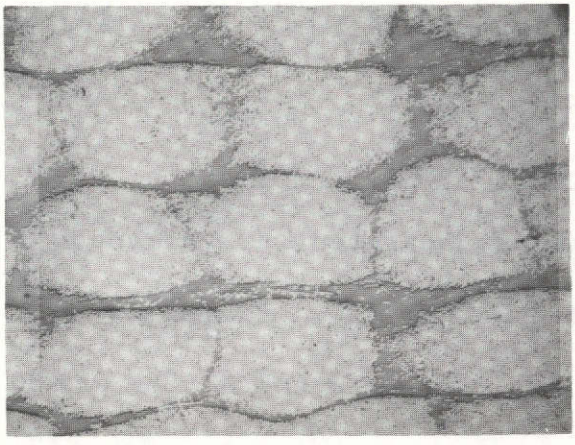


Figure 13. Photomicrograph of a PPQ/Graphite Fiber Composite.

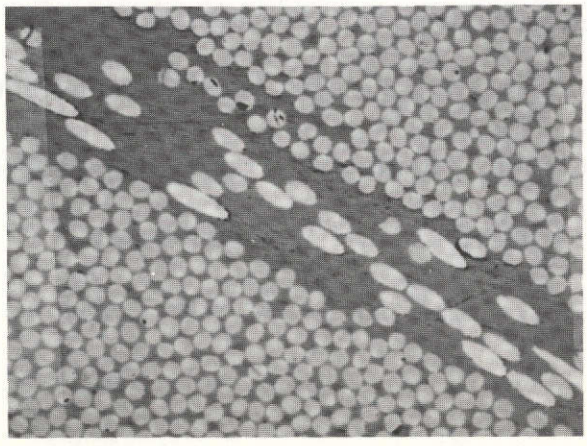


Figure 14. Photomicrograph of the Space Between Tows in a PPQ/Graphite Fiber Composite.

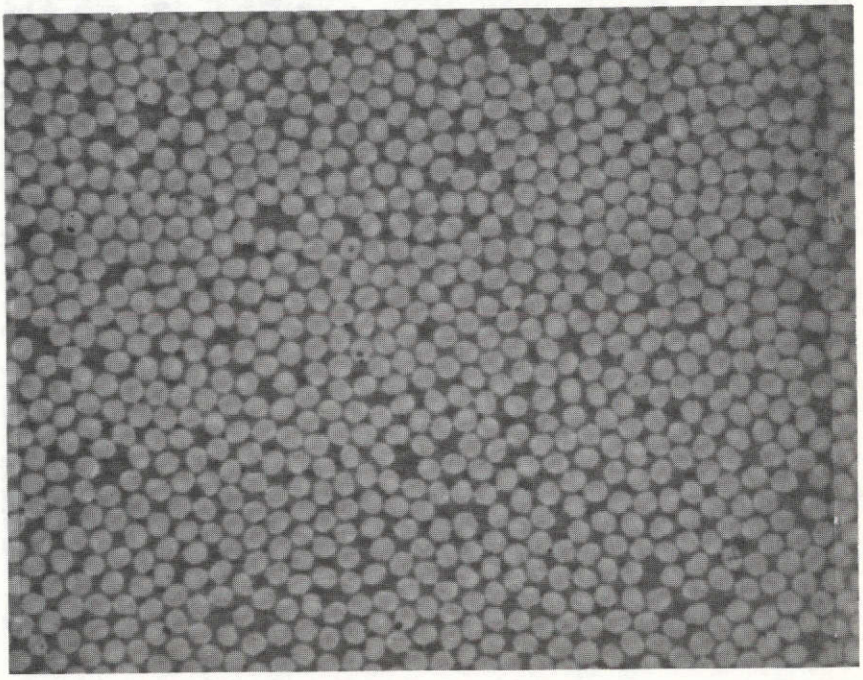


Figure 15. Photomicrograph of One Tow in a PPQ/Graphite Fiber Composite.

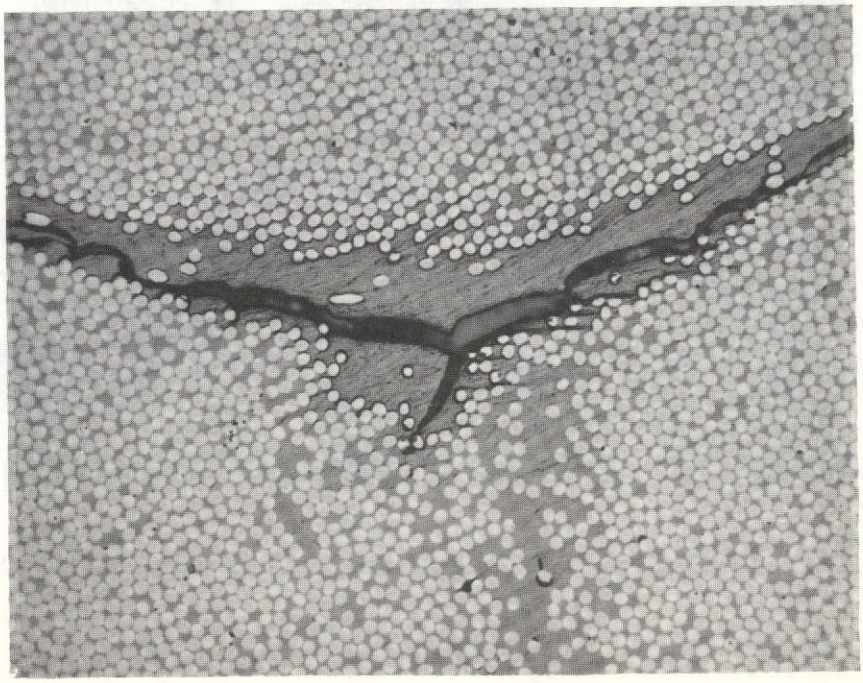


Figure 16. Defect in a PPQ/Graphite Fiber Composite.

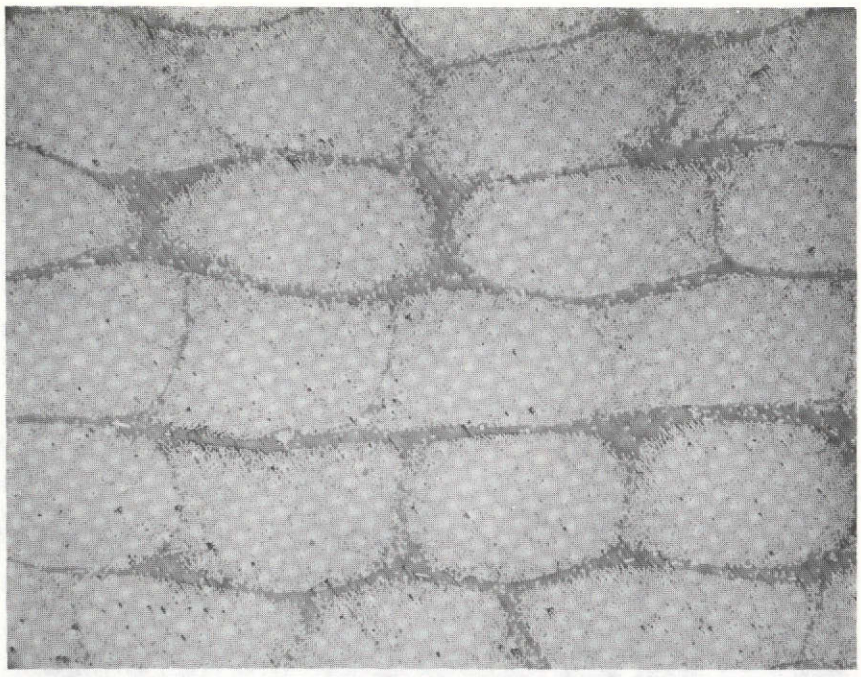


Figure 17. PPQ/Graphite Fiber Composite as Made.

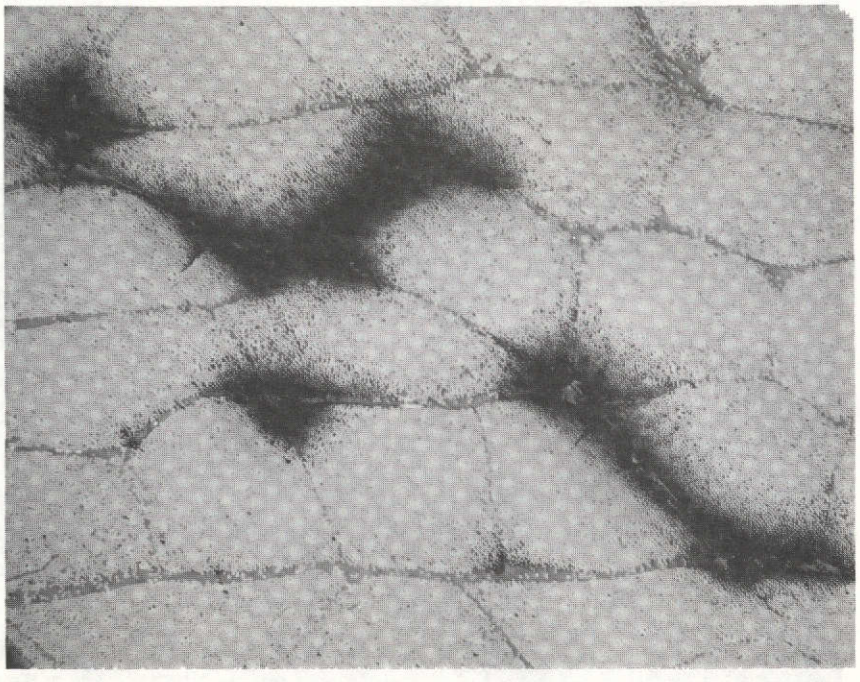


Figure 18. PPQ/Graphite Fiber Composite After 500 Hours at 588K.

accounts for the weight loss observed with PPQ composites at 588K, and for the loss in physical properties at that temperature. Because of the drastic degradation of PPQ composites at 588K, the PPQ composite work was discontinued in the long term 588K aging tests in Task II.

2. Composite Interlaminar Shear Strength

The interlaminar shear strength of the composites was measured according to the Hercules interlaminar shear test and ASTM 2344-67. Sample dimensions were 0.635 cm by 1.8 cm by 0.20 cm. Interlaminar shear was measured in triplicate at room temperature, at 588K, at 533K, and at 588K and 533K after 200 hours exposure at the corresponding test temperature. With the polyimide composites, initial room temperature values between 116 and about 133 MN/m^2 (16,900 to 19,200 psi) were obtained. Corresponding values for the PPQ composites were 92.6 to 117 MN/m^2 (13,400 to 17,000 psi). At 588K the interlaminar shear strength of polyimide composites was approximately one-half the value obtained at room temperature. After exposure at 588K for 200 hours, increases of as much as 34 percent in the interlaminar shear strength at 588K were experienced in all of the polyimide composites. Exposure of the polyimide composites at 533K resulted in about a 40 percent decrease in initial interlaminar shear strength. After exposure at 533K for 200 hours the interlaminar shear strength did not further change. Similar comments apply to the PPQ composites except that the loss in initial interlaminar shear strength on heating to 588K was about 60 to 70 percent.

After exposure at 588K for 200 hours, increases of as much as 50 percent in the interlaminar shear strength at 588K were experienced for all the PPQ composites. Exposure of the PPQ composites at 533K resulted in about a 45 percent decrease in interlaminar shear strength. After exposure at 533K for 200 hours, the interlaminar shear strength did not further change.

For the polyimide composites, the halotitanate treatment appeared to give the best overall performance with carbonized PPQ a very close second. For the PPQ composites, the best results were obtained with a pyrolyzed carbonacous coating on the fibers. It appeared to make little difference if the carbonized coating on the fiber came from pyrolyzed polyimide, epoxy or PPQ.

Tensile failures in the interlaminar shear test were frequently observed with polyimide composites made with untreated fiber. This was true when the composites were tested at room temperature as well as when they were tested at 533 and 588K after having been aged at the corresponding test temperatures for up to 500 hours. A different type of failure was observed when the Ventromertreated graphite fiber composite was aged for 200 hours at 588K and tested at room temperature in an interlaminar shear test. The failure observed was a brittle tension failure. It differed in that the failure occurred suddenly and violently. The fracture surfaces showed

no protruding fibers but did have an almost glassy appearance. The brittle tension failure was later shown in Task II to invariably occur during room temperature and elevated temperature interlaminar shear tests of polyimide/Ventromer-treated graphite fiber composites after prolonged aging (500 to 1000 hours) at 533 or 588K. The brittle tension failure was observed whether the high temperature aging had been conducted in circulating air or in nitrogen.

Data from the interlaminar shear tests conducted in the screening part of this program are summarized in Appendix C.

IV. ADVANCED COMPOSITES EVALUATION

The screening phase of this work described above involved the investigation of ten coatings or treatments to be applied to carbon fiber to improve the thermo-oxidative stability of PMR-PI and PMR-PPQ composites. Three of the treatments originally suggested were eliminated because they proved to be deleterious to the oxidative stability of the carbon fiber. Two of these three also had a markedly adverse effect on the strength of the fiber. The remaining seven treatments (plus an untreated fiber as a control) were evaluated in terms of thermal stability and interlaminar shear strength of PI and PPQ composites made therefrom.

As a result of this screening, Thornel 300 fiber which had been heat cleaned (as a reference material), fiber which had been coated with carbonized PPQ, and fiber which had been treated with a halotitanate (Ventromer T-1) were selected for more thorough investigation.

A. Thermal Stability and Nature of the Treated Fiber Surface

1. Thermal Stability

The Thornel 300 fiber used in this work and subjected to the two selected surface treatments showed a weight loss of about 3 to 4 percent during 200 hours at 588K. Between 200 and 1000 hours an essentially linear and catastrophic degradation took place, resulting in 1000 hour weight losses between 60 and 73 percent as shown in Figure 10. At 533K no loss of weight was observed until after 500 hours, but between 500 and 1000 hours, as much as 12 percent loss was observed as shown in Figure 11.

In light of the oxidative instability of the fiber it is not surprising that after 500 hours at 588K all the polyimide composites lost 5 to 6 percent in weight, albeit with no change in appearance. After 1000 hours at 588K weight losses in the polyimide composites were in the neighborhood of 14 to 18 percent. As is described below, however, degradation of the polyimide composites made with halotitanate-treated fiber was more serious than weight loss alone might suggest. After 500 hours at 588K transverse tensile specimens were sufficiently distorted that meaningful physical tests could not be performed. At 533K the largest weight loss observed with the polyimide composite was approximately 4 percent.

Because of the instability of the PPQ composites noted during the screening portion of this work PPQ composites were tested only at room temperature and at 533K during the second phase of this work. Weight losses of the PPQ composites were less than 1 percent after 500 hours at 533K but increased to between 10 and 15 percent after exposure for 1000 hours at 533K. Figure 19 illustrates the difference between the thermal stability of the polyimide and polyphenylquinoxaline composites. The extreme fuzziness of the PPQ composites (samples 8, 11 and 14) after 500 hours at 588K is evident. The surface degradation of the PPQ composites is reflected in the interlaminar shear data shown in Figure 20. If the sample dimensions at the time of testing are used to calculate the interlaminar shear strength, exposure for 500 hours at 588K appears to have had no adverse effect on the composites. But if the interlaminar shear strength is calculated on the basis of the original sample thickness a marked decrease in strength is seen to occur. This, along with the weight loss data, seems to indicate that fiber and/or resin is lost from the outside of the composite, but that the remaining resin is relatively unaffected by the 500 hour exposure. Figures 17 and 18, however, clearly indicate the opposite is true; that thermal degradation also occurs in the bulk of the PPQ composites during the 500 hour aging at 588K.

2. Nature of the Treated Fiber Surface

X-ray diffraction patterns obtained by a Debye-Sherrer camera showed only minor differences between the crystal structures of Thornel

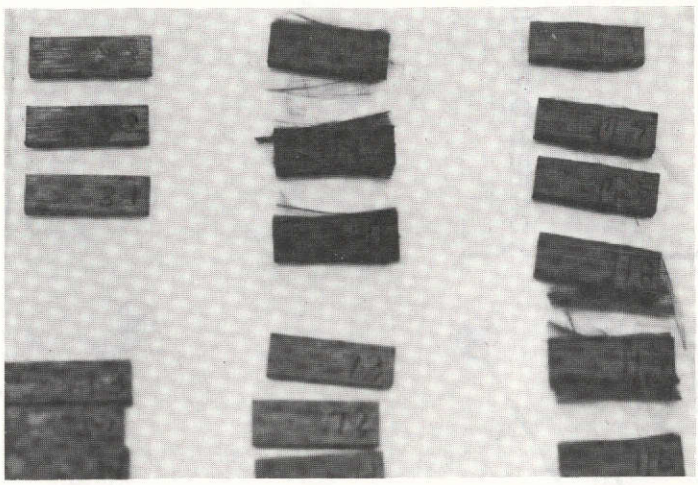


Figure 19. PI and PPQ Composites After 500 Hours at 588K.
Samples 8, 11, and 14 are PPQ Composites.
Samples 1, 3, and 7 are PI Composites.

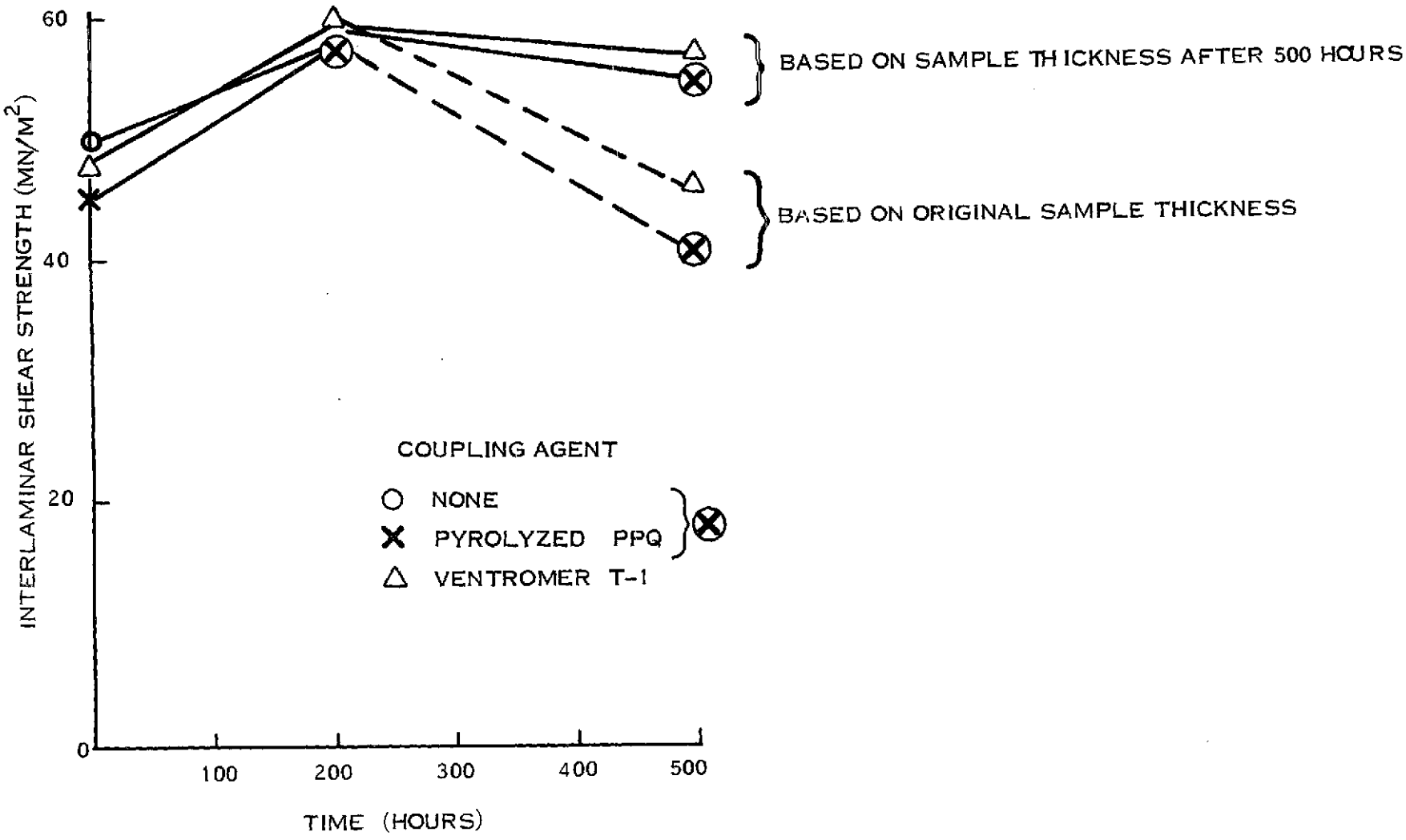


Figure 20. Interlaminar Shear Strength of Polyphenylquinoxaline Composites Aged and Tested at 588K.

fiber "as received" and of Thornel fiber subjected to treatments 3 and 6. Since it has been shown by Raman spectroscopy that surface treatment of graphite fibers with pyrolyzed PPQ diminishes the size of crystallites near the fiber surface (13), it appears that the x-ray diffraction patterns resulted from the interior of the fiber as well as the exterior and the contribution of the exterior layers was relatively small.

Ventromer T-1 is a complex reaction product of titanium tetrachloride and trimethylborate. Films laid down from aqueous solutions of Ventromer T-1 produce water-insoluble titanoxane polymers. An electron microprobe was used in an attempt to locate the titanium on graphite fibers which had been subjected to treatment #6. The amount of titanium present, however, was insufficient for detection by this method.

B. Interlaminar Shear Strength

1. Interlaminar Shear Strength of Polyimide Composites

Quite a remarkable difference was observed between the interlaminar shear strength of the polyimide composites made during the screening phase of this work and the interlaminar shear strength of the polyimide composites made during the advanced composites evaluation phase of this work. For example, the room temperature interlaminar shear strength of the Ventromer-treated composite made during the screening phase of the work

was 129 MN/m^2. This is in sharp contrast to the 99 MN/m^2 obtained for the Ventromer-treated composites made in the second phase of this work. Similarly, the composite made with untreated fiber in the screening effort had an interlaminar shear strength of 123 MN/m^2 while the corresponding composites made in the second phase of the work had an interlaminar shear strength at room temperature of 89 MN/m^2. Corresponding values for the composites made with carbonized PPQ were 133 and 106 MN/m^2. It was tempting to blame these lower values of interlaminar shear strength on the fact that a different lot of Thornel fiber was used during the advanced composites evaluation phase of this work. However, tow tensile tests revealed a fiber strength of 30.6 kg for the fiber used during the second phase of the work, a value slightly higher than that found for the fiber used in the screening work. Nevertheless, the fact that the same effect was observed with the PPQ composites tends to indicate that the difference lies in the fiber even though it is not apparent in the fiber's ultimate strength. The differences are dramatized in the interlaminar shear strength of screening and evaluation samples of the polyimide composites with no coupling agent, with Ventromer T-1, and with pyrolyzed PPQ as shown in Figures 21, 22 and 23. In all three cases the initial interlaminar shear strength at 588K was lower for the evaluation sample than for the corresponding screening sample. The difference in interlaminar shear strengths is most obvious in the case of

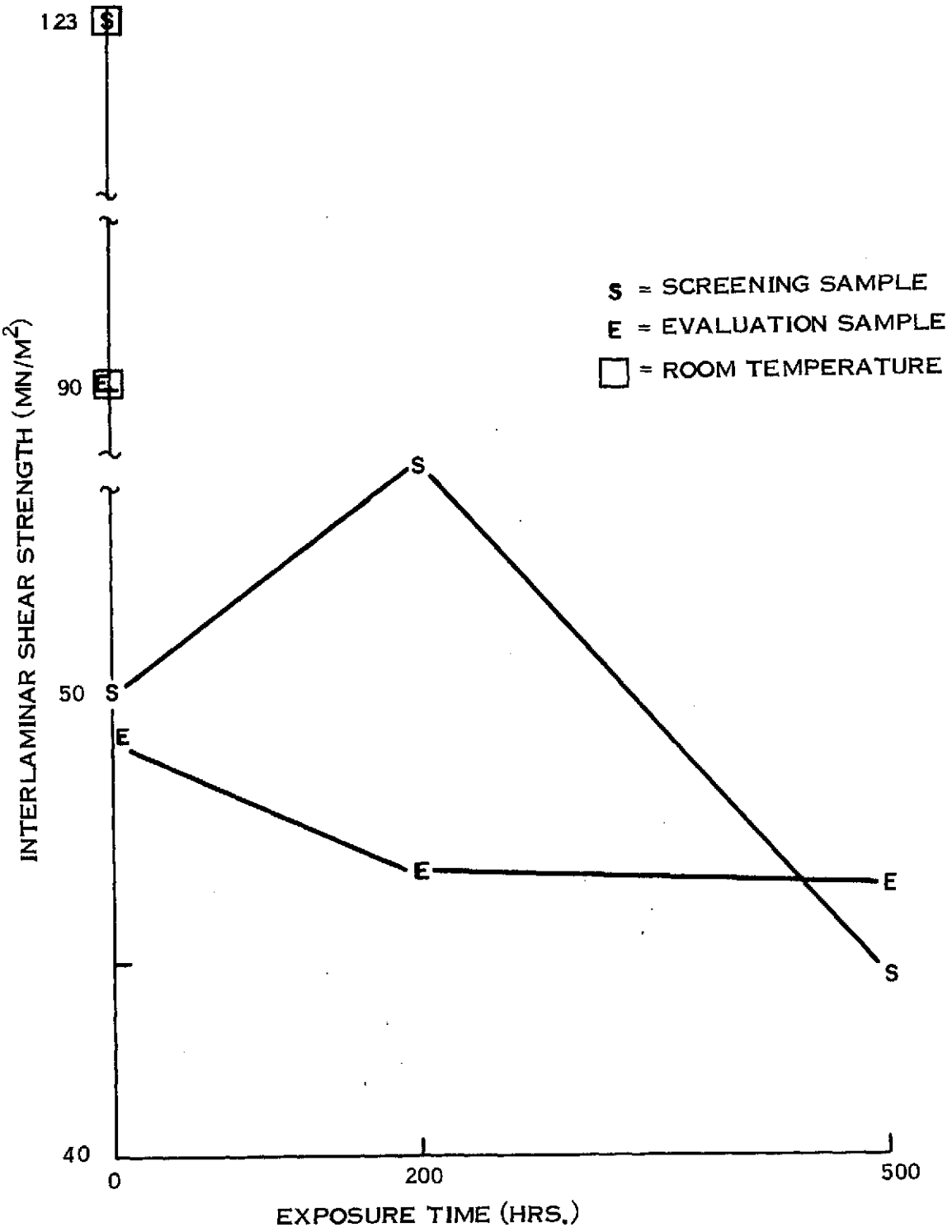


Figure 21. Interlaminar Shear Strength of Screening and Evaluation Polyimide Composites Made With No Coupling Agent, Aged and Tested at 588K.

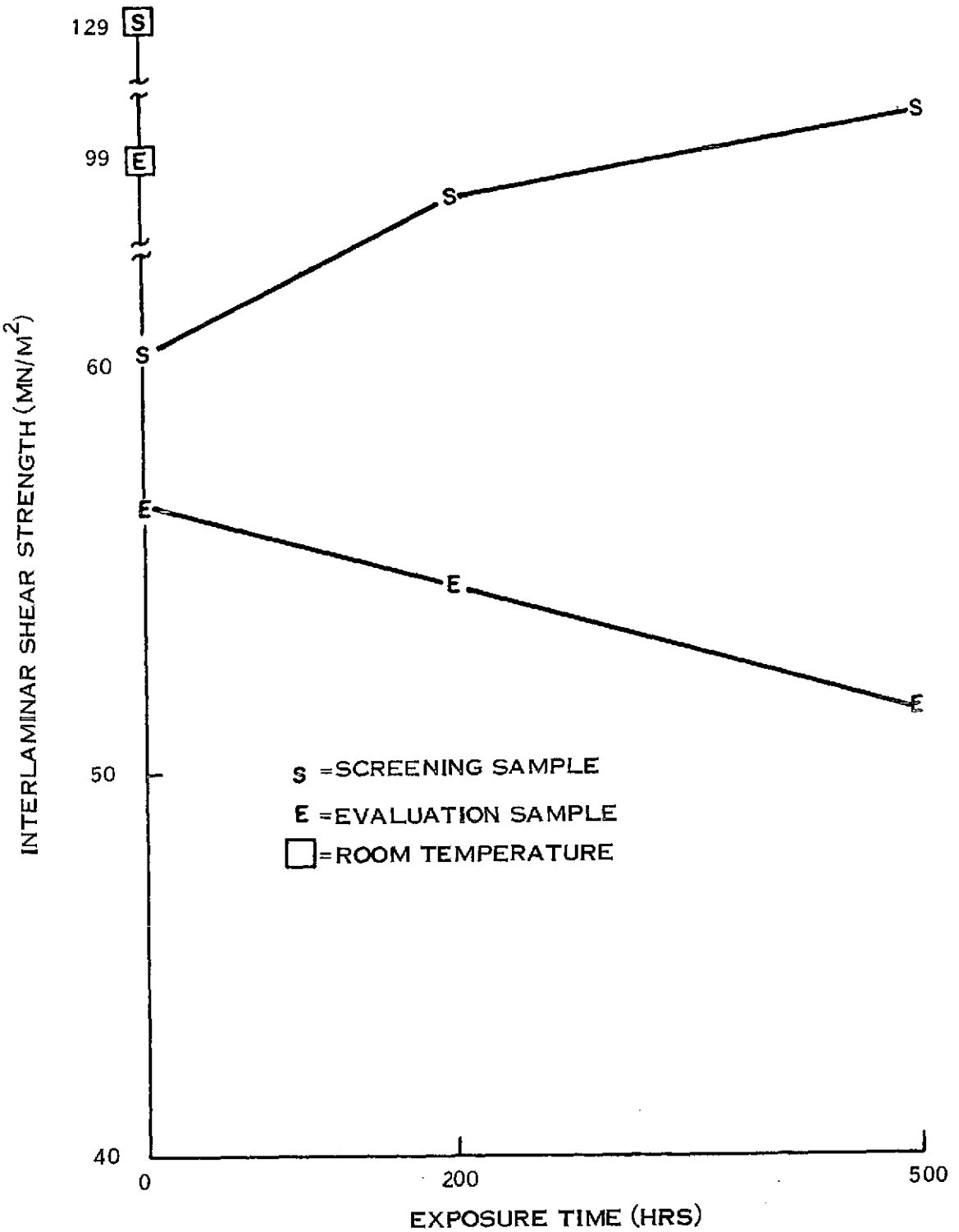


Figure 22. Interlaminar Shear Strength of Screening and Evaluation Polyimide Composites Made With Ventromer T-1 Coupling Agent, Aged and Tested at 588K.

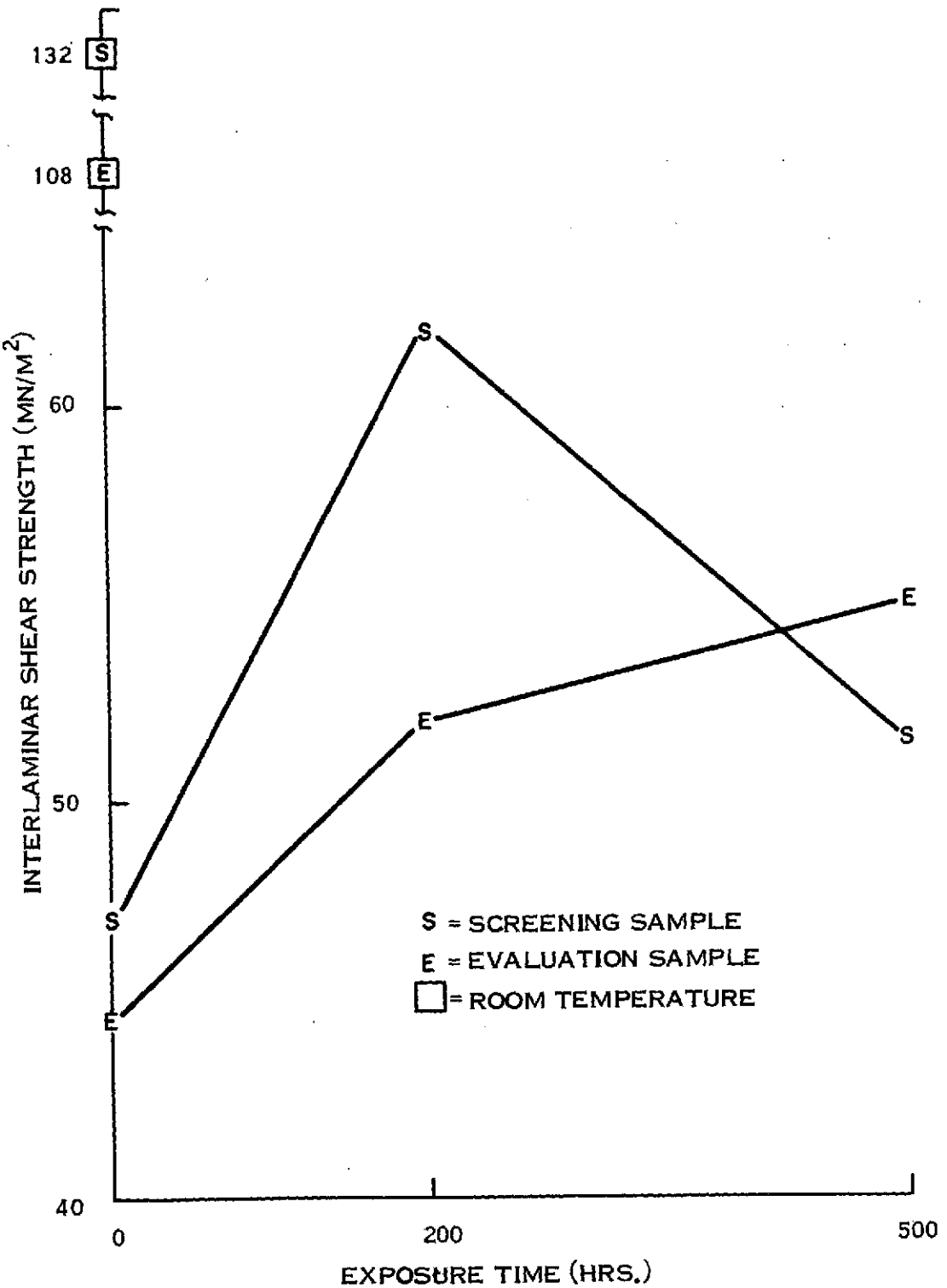


Figure 23. Interlaminar Shear Strength of Screening and Evaluation Polyimide Composite Made With Pyrolyzed PPQ Coupling Agent, Aged and Tested at 588K.

the composites made with Ventromer T-1. As can be seen in Figure 22, interlaminar shear strength of the screening sample continued to increase during 500 hours exposure at 588K. On the other hand, the interlaminar shear strength of the evaluation sample showed a steady decrease with exposure time at 588K. The atmosphere in the aging oven was replenished at a rate of 6 l/hr.

The interlaminar shear strengths of polyimide composites at 588K are shown in Figure 24 in which the steady decrease in the strength of the composite made with Ventromer T-1 is evident. It is also evident that between 500 and 1000 hours the rate of decrease of interlaminar shear strength was approximately the same for the composite made with Ventromer T-1 and for the composite made with pyrolyzed PPQ as a coupling agent. Due to the initial relatively low value of interlaminar shear for the latter composite, the net change in strength during 1000 hours was minimal. In the tests at 588K with minimal thermal exposure, the samples made with no coupling agent all showed brittle tensile failures. After 200 hours exposure at 588K, all the composites made without a coupling agent and all the composites made with Ventromer T-1 showed brittle tensile failures. The composites made with pyrolyzed PPQ as coupling agent also suffered tensile failure, though the failure was not of the brittle type. After 500 hours exposure all the samples underwent tensile failure. After 1000 hours exposure the samples made with pyrolyzed PPQ coupling agent showed a

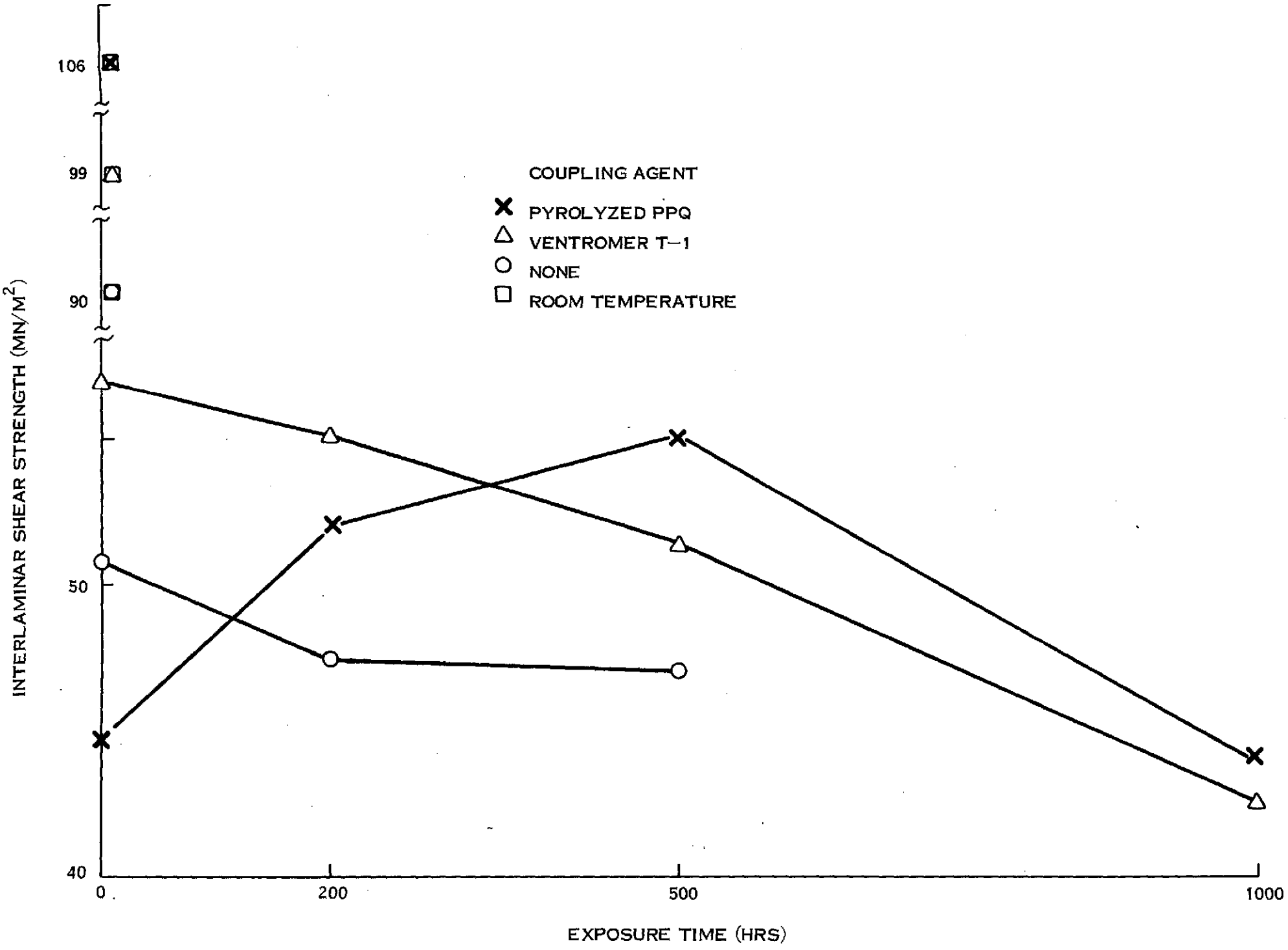


Figure 24. Interlaminar Shear Strength of Polyimide Composites Aged and Tested at 588K.

normal interlaminar shear failure and two of the three samples made with Ventromer T-1 showed a normal interlaminar shear failure. The third Ventromer T-1 sample showed a combination of tensile and shear failure. When the same composites were exposed at 588K but tested at room temperature, tensile failures occurred in all samples after 200 and 500 hours exposure. After 1000 hours exposure all of the Ventromer T-1 samples and two of the three pyrolyzed PPQ samples failed by interlaminar shear. The third PPQ sample failed by a combination of tensile and shear failure. As can be seen in Figure 25 all the composites lost ten to twenty percent of their initial interlaminar shear strength during the first 200 hours exposure at 588K. Between 200 and 1000 hours, however, the composite made with pyrolyzed PPQ showed almost no further change; the retention of interlaminar shear strength being 92.4 percent. The composite made with Ventromer T-1 on the other hand showed a fairly steady decrease in strength from 95 MN/m^2 to about 50 MN/m^2 during the 1000 hour exposure at 588K.

As was to be expected, exposure at 533K of the polyimide composites had relatively little effect on their interlaminar shear strength. Figure 26 indicates a possible slight degradation of the interlaminar shear strength of the composite made with pyrolyzed PPQ over the 1000 hour period. However,

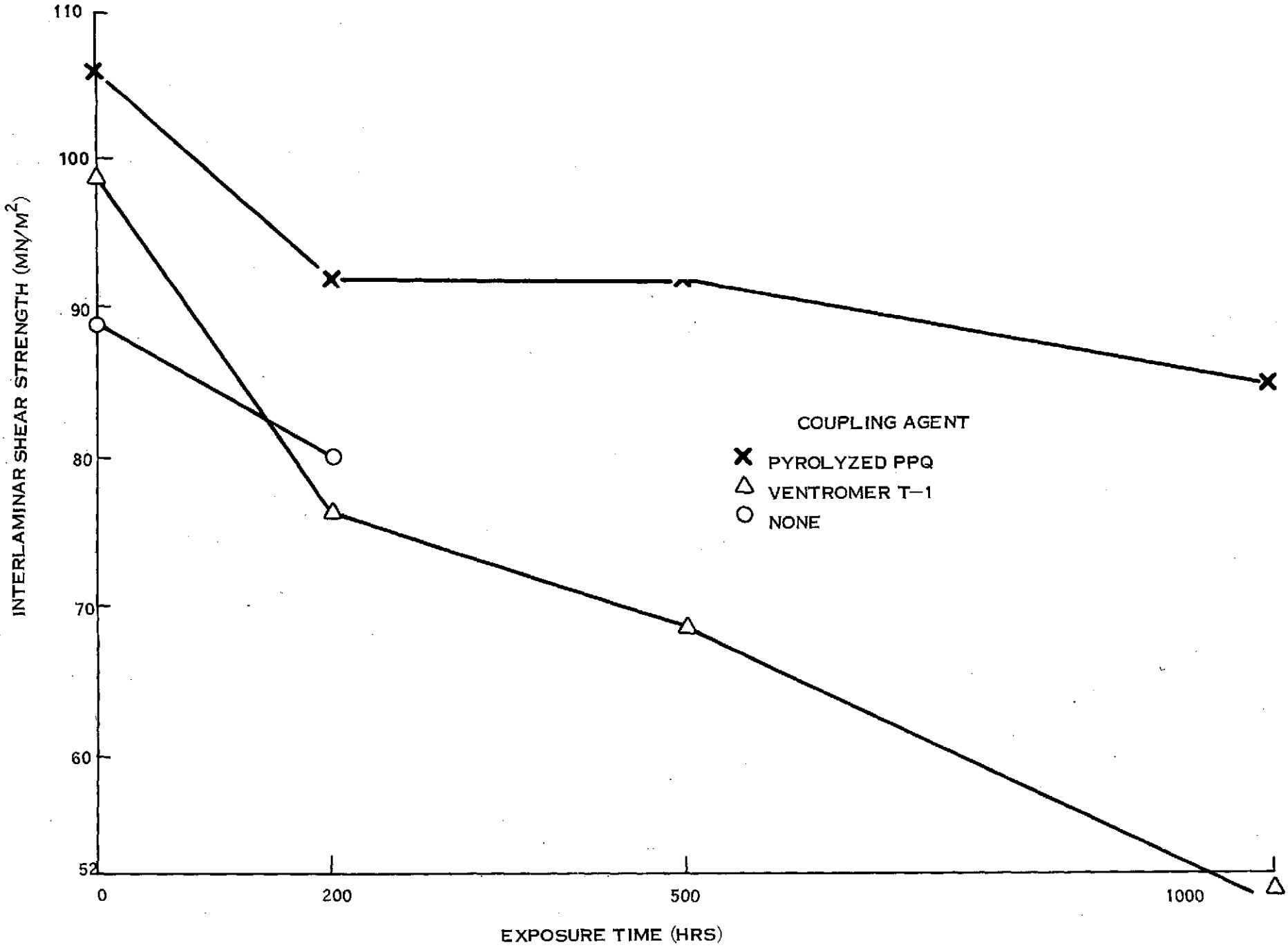


Figure 25. Room Temperature Interlaminar Shear Strength of Polyimide Composites Aged at 588K.

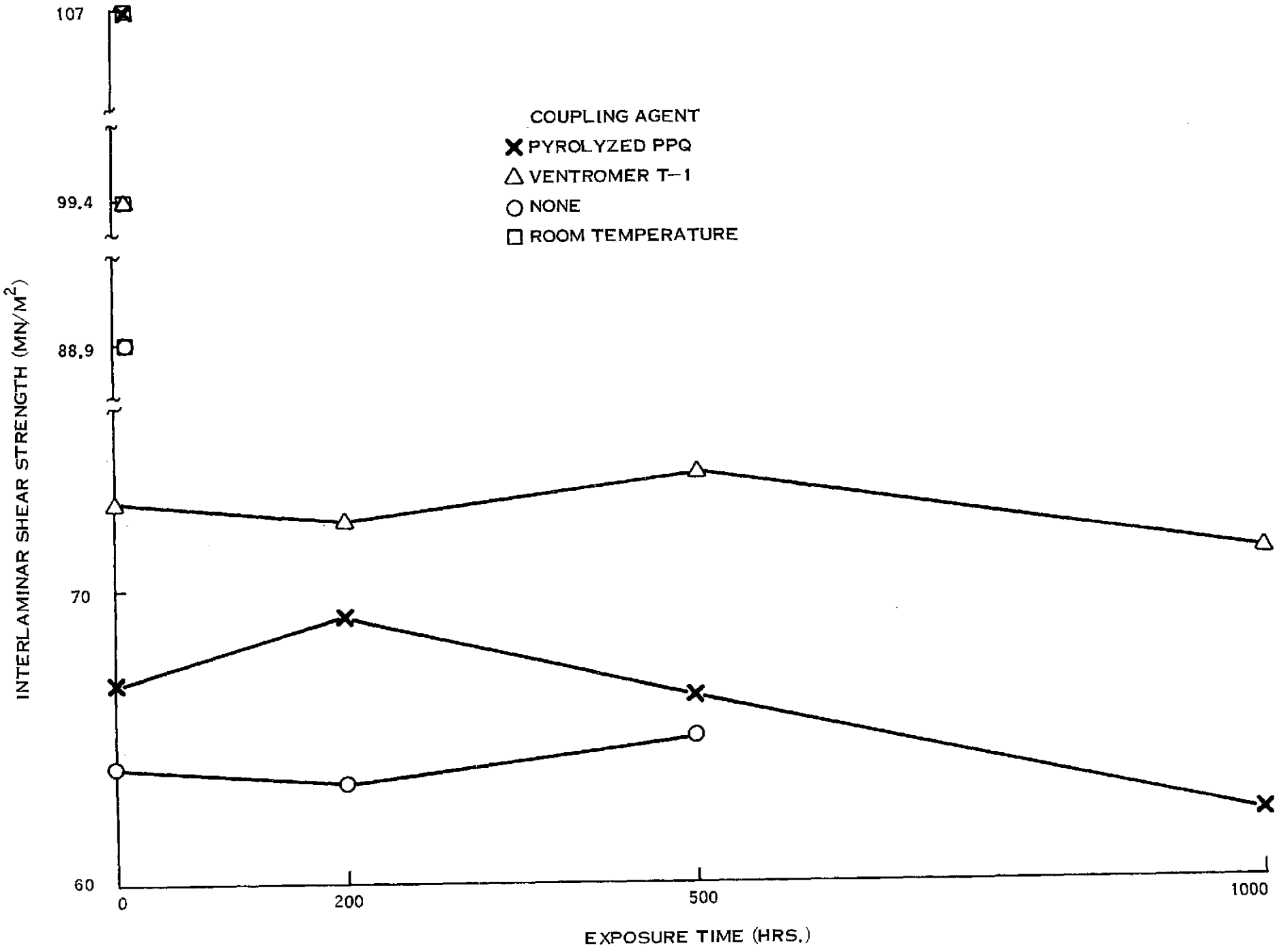


Figure 26. Interlaminar Shear Strength of Polyimide Composites Aged and Tested at 533K.

the composite made with Ventromer T-1 showed almost complete retention of 533K interlaminar shear strength after 1000 hours at 533K. Tensile failures were observed in the nonaged 533K interlaminar shear tests of the composites made with no coupling agent and with the Ventromer T-1 coupling agent. After 200 hours exposure all the composite samples at 533K exhibited tensile failure. After 500 and 1000 hours exposure at 533K, interlaminar shear failure was observed with the composites made without coupling agent and with pyrolyzed PPQ as coupling agent, while the composites made with the Ventromer T-1 showed a brittle tensile failure in all these cases. Quite surprisingly when the interlaminar shear tests were run at room temperature after exposure of the samples for up to 1000 hours at 533K, as shown in Figure 27, a steady decrease in the strength of the composite made with Ventromer T-1 was observed, amounting to approximately 30% loss of interlaminar shear strength after 1000 hours. Tensile failures were observed in all the room temperature interlaminar shear tests after 533K aging. After exposure for 1000 hours at 533K the polyimide composite made with Ventromer T-1 exhibited a brittle tensile failure.

When thermal exposures were performed in nitrogen which was replenished at a rate of 6 l/hr. the results were quite different. As can be seen in Figure 28, exposure in nitrogen at 588K of polyimide composites resulted in a steady increase in strength of both the composite made with Ventromer T-1 and that made with pyrolyzed PPQ as coupling agents.

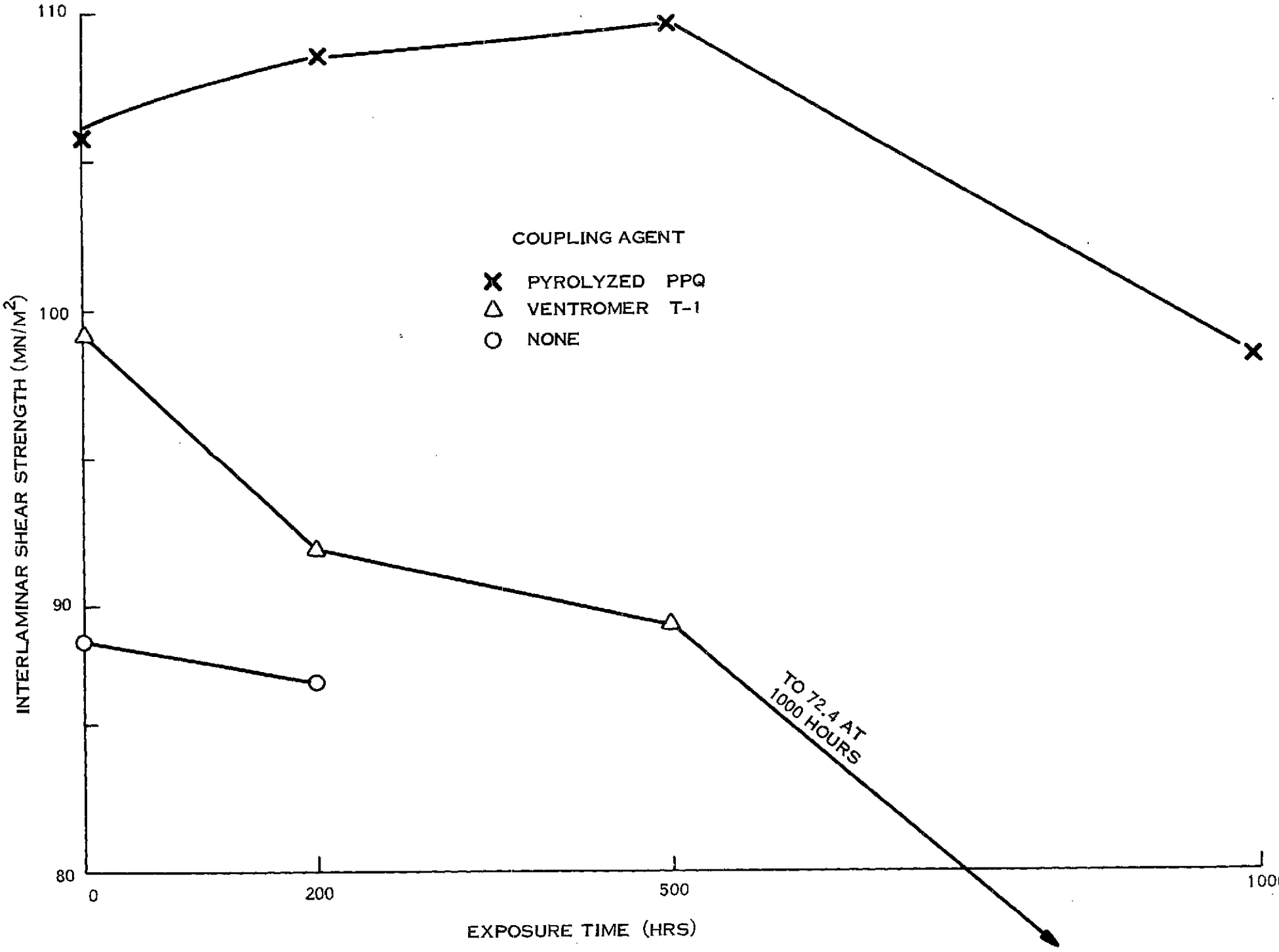


Figure 27. Room Temperature Interlaminar Shear Strength of Polyimide Composites Aged at 533K.

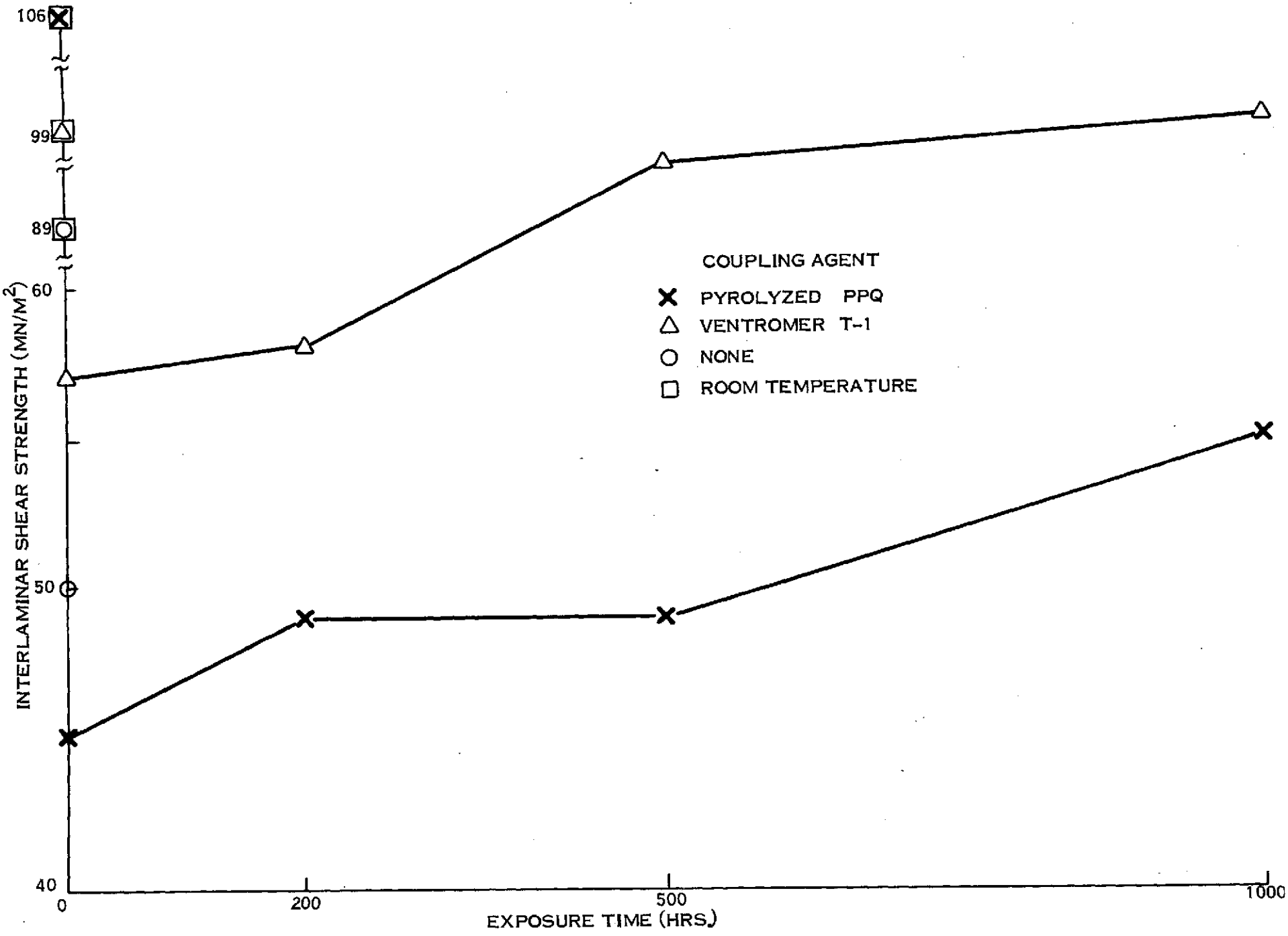


Figure 28. Interlaminar Shear Strength of Polyimide Composites Aged in Nitrogen at 588K and Tested at 588K.

While the interlaminar shear test produced interlaminar shear in all the polyimide samples made with pyrolyzed PPQ, all of the samples made with the Ventromer T-1 coupling agent showed a brittle tensile failure. Aging of the composites in nitrogen at 588K had relatively little effect on the room temperature interlaminar shear strength of the composite made with pyrolyzed PPQ coupling agent. As can be seen in Figure 29 there was an initial drop in interlaminar shear strength followed by a rise between 500 and 1000 hours. The composite made with Ventromer T-1 coupling agent, however, showed a rather large drop in interlaminar shear strength during the first 500 hours followed by no change between 500 and 1000 hours. The net result was a decrease of about 30 percent in the interlaminar shear strength of the Ventromer T-1 composite. This, however, was much less than the loss of almost 50 percent of the strength of the composite made without coupling agent during the first 200 hours exposure. Figures 30 and 31 show that aging in nitrogen at 533K had relatively little effect on the polyimide composites. In most cases the control samples made with no coupling agent were aged only 200 hours, as required.

2) Interlaminar Shear Strength of Polyphenylquinoxaline Composites

Because of the excessive degradation of polyphenylquinoxaline composites at 588K thermal exposure and testing of polyphenylquinoxaline composites in the advanced composites evaluation was limited to 533K. Even at this temperature some degradation was noticeable over a 1000 hour aging period. Inspection of Figures 32 through 35 indicates that the PPQ

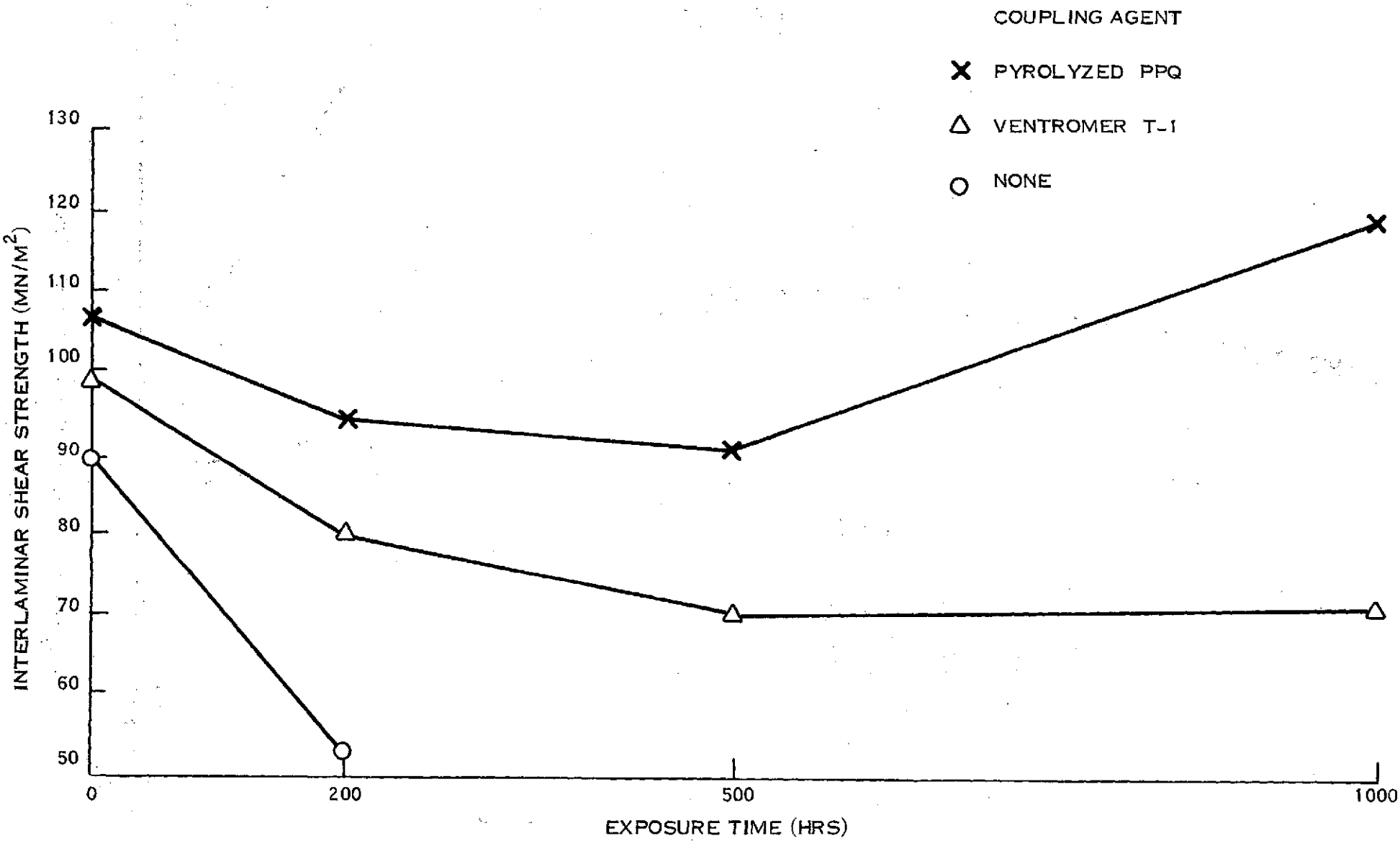


Figure 29. Room Temperature Interlaminar Shear Strength of Polyimide Composites Aged in Nitrogen at 588K.

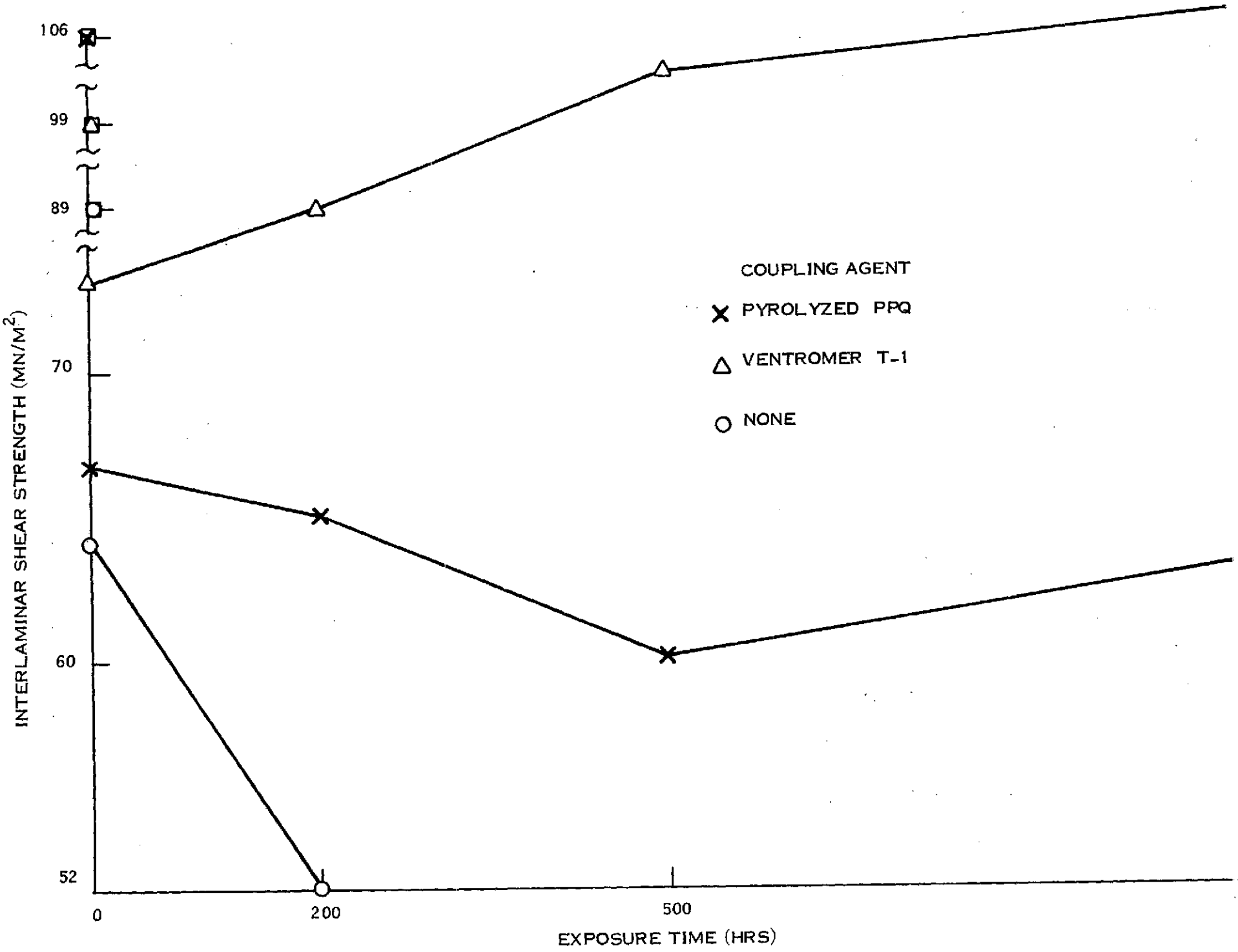


Figure 30. Interlaminar Shear Strength of Polyimide Composites Aged in Nitrogen at 533K, and Tested at 533K.

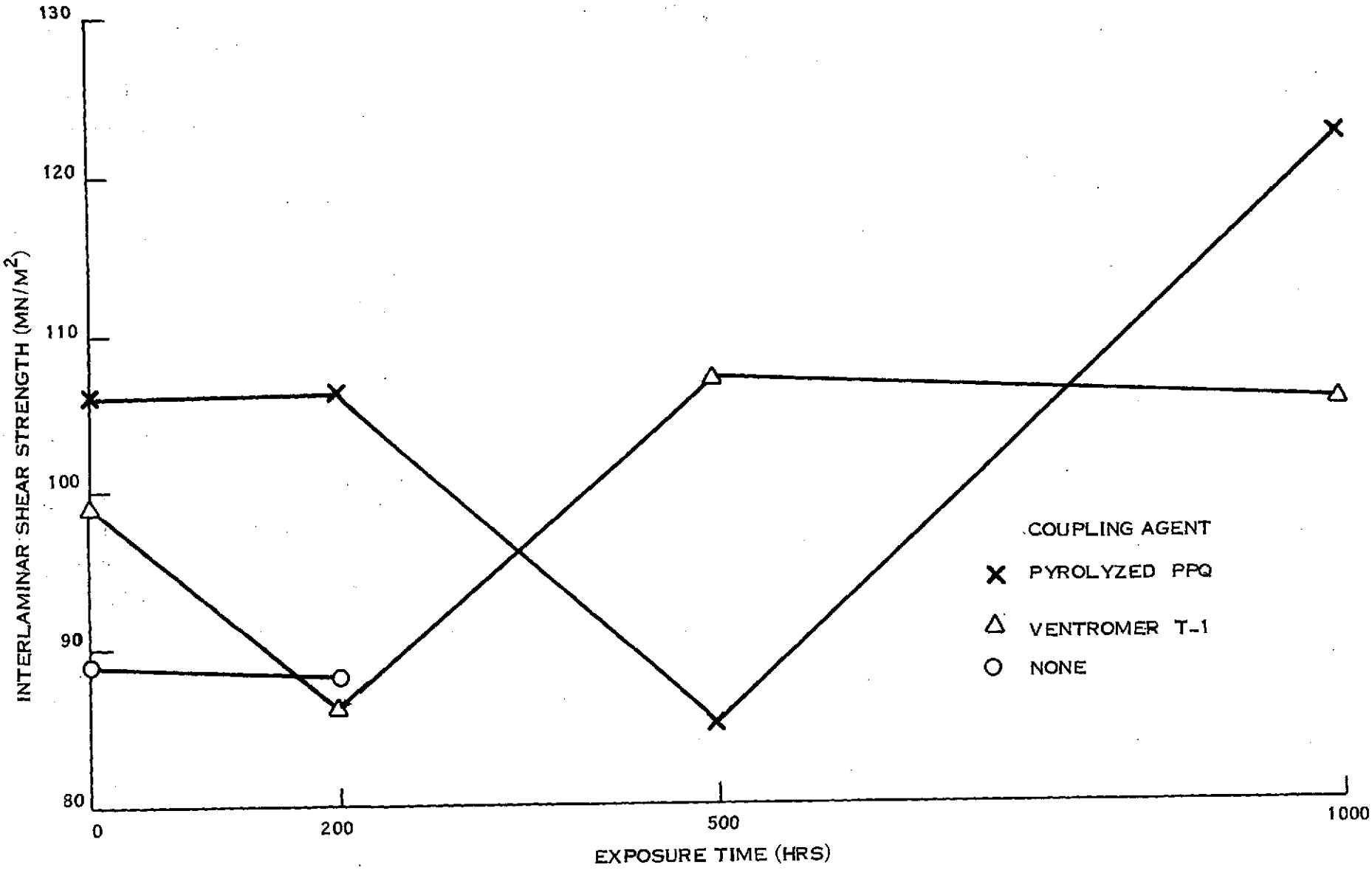


Figure 31. Room Temperature Interlaminar Shear Strength of Polyimide Composites Aged in Nitrogen at 533K.

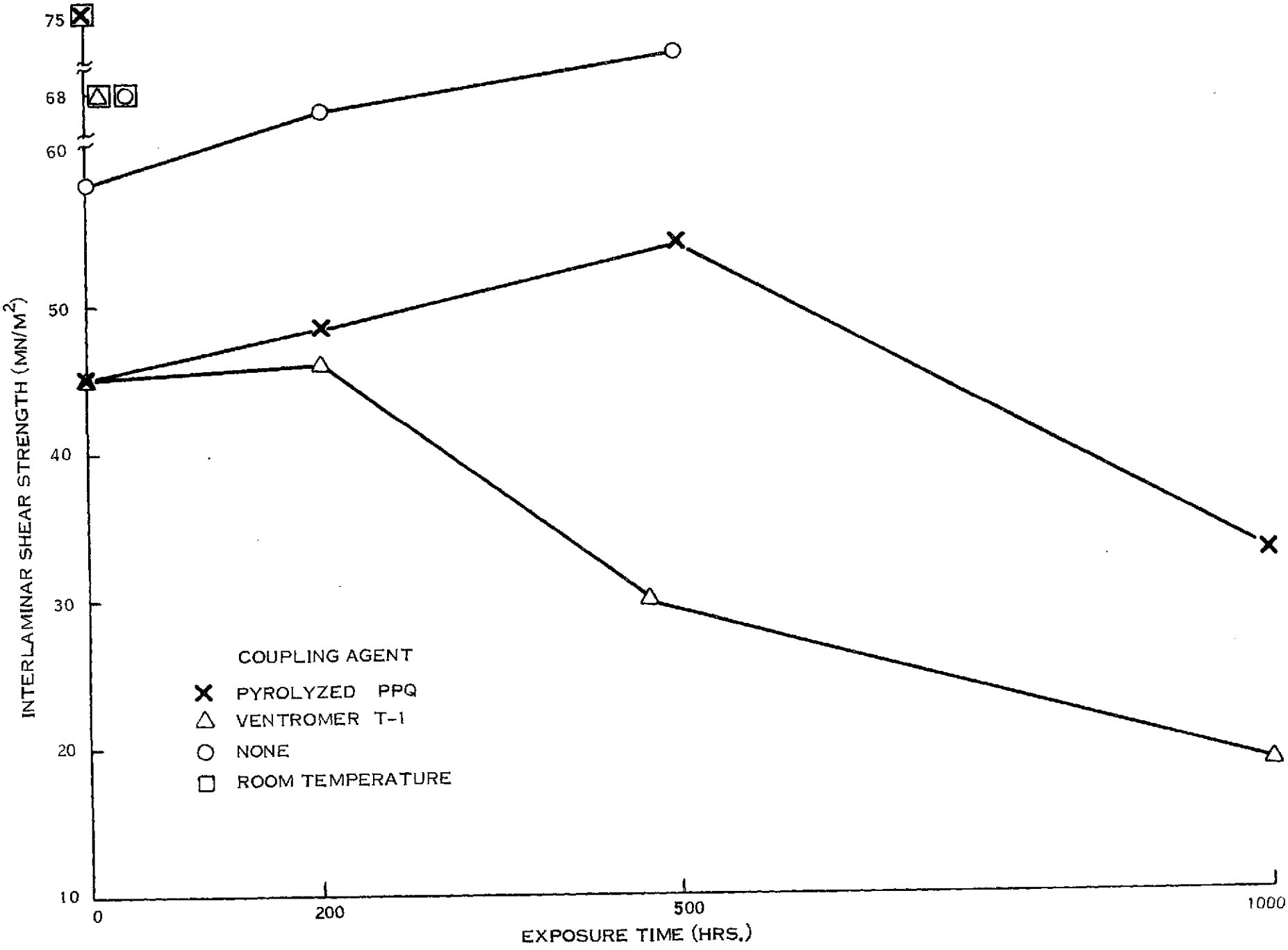


Figure 32. Interlaminar Shear Strength of Polyphenylquinoxaline Composites Aged and Tested at 533K.

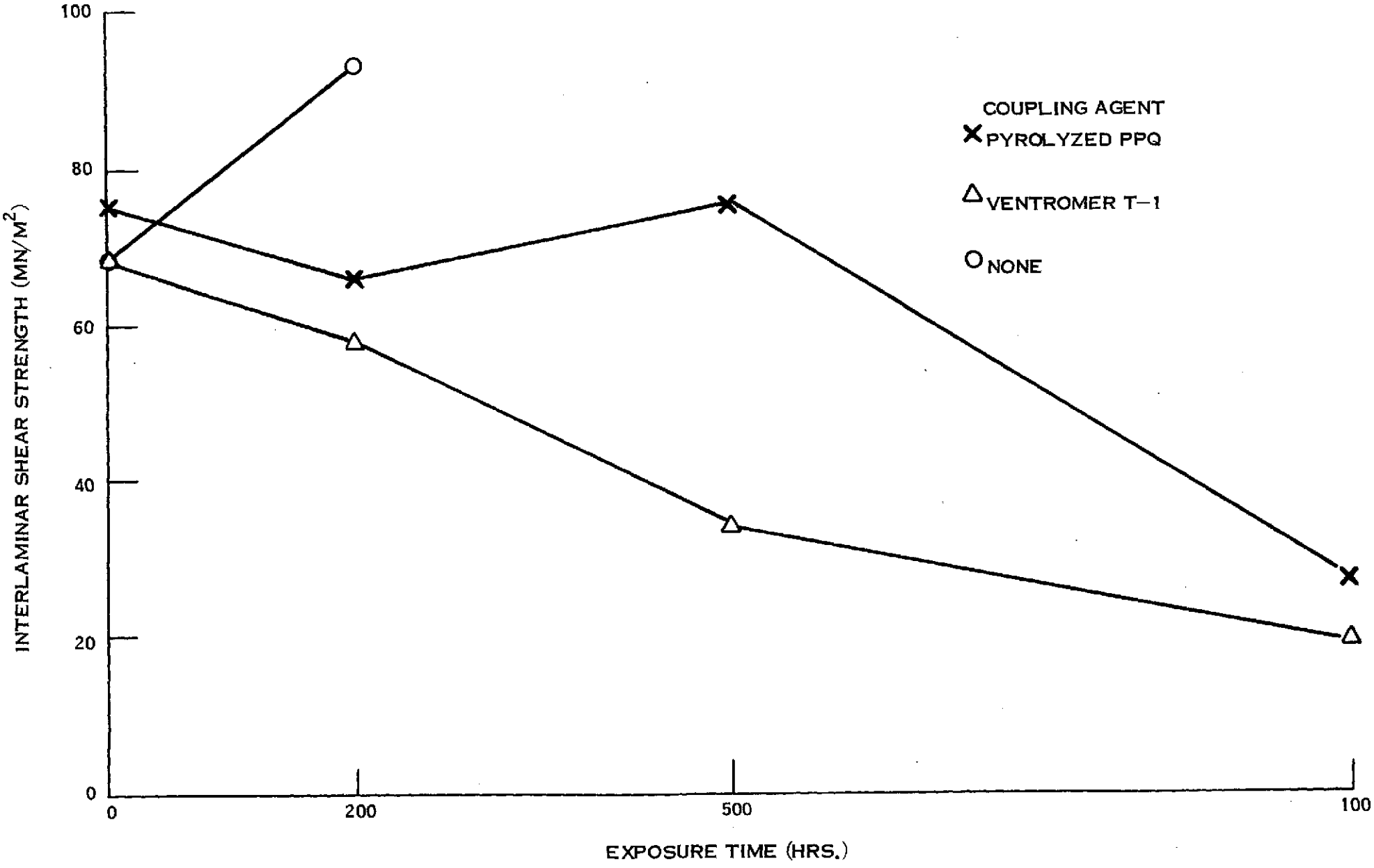


Figure 33. Room Temperature Interlaminar Shear Strength of Polyphenylquinoxaline Composites Aged at 533K.

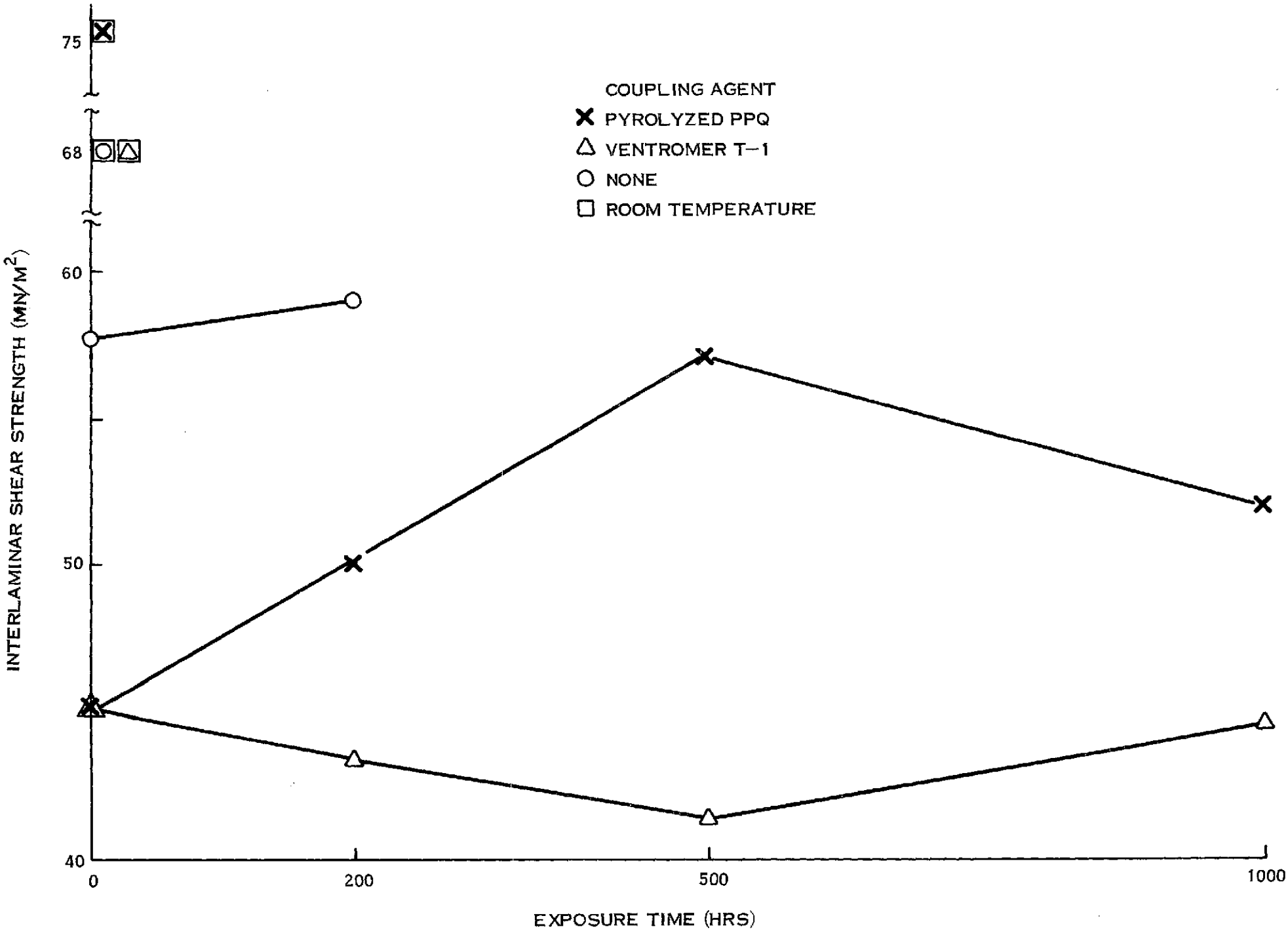


Figure 34. Interlaminar Shear Strength of Polyphenylquinoxaline Composites Aged in Nitrogen at 533K and Tested at 533K.

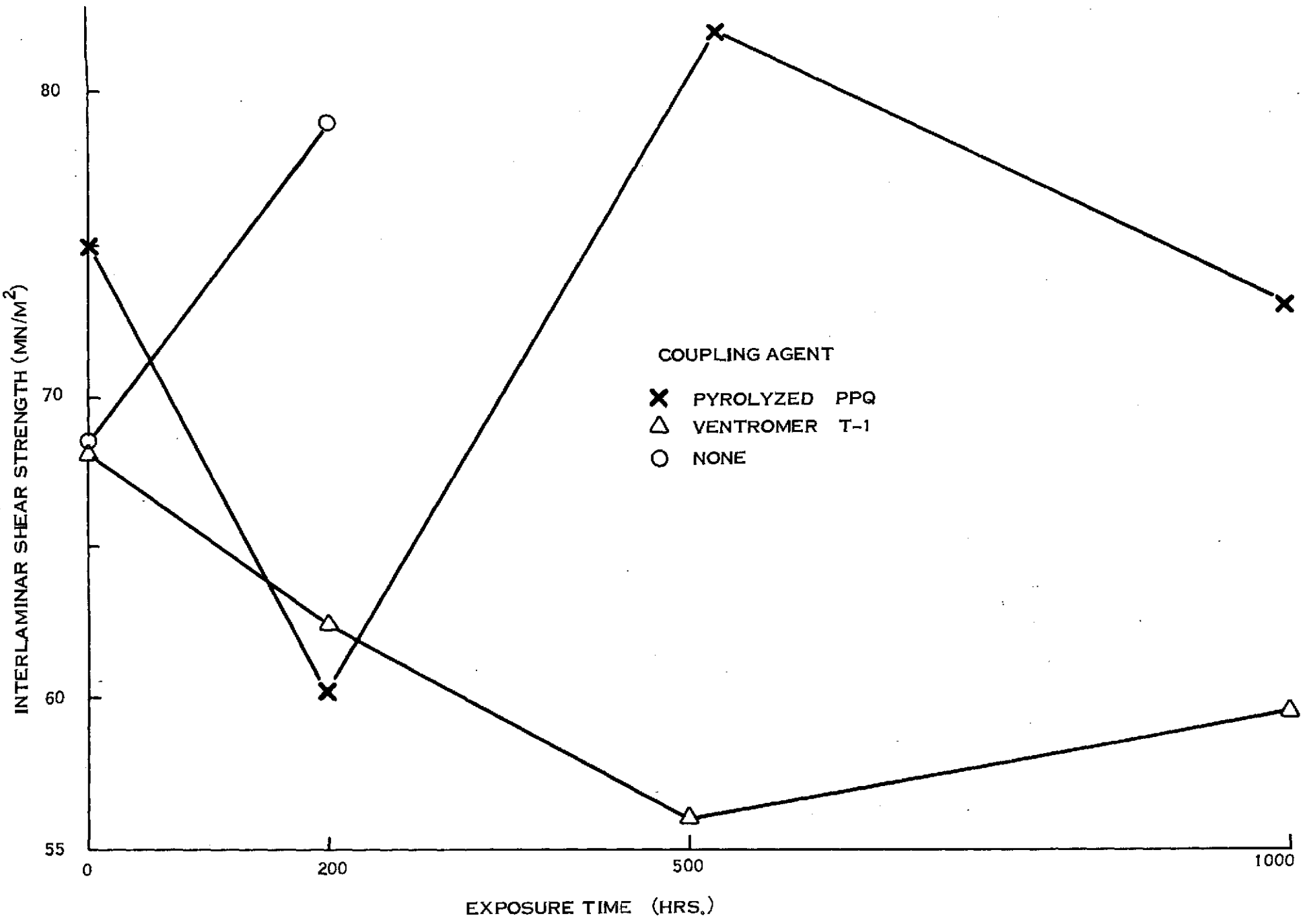


Figure 35. Room Temperature Interlaminar Shear Strength of Polyphenylquinoxaline Composites Aged in Nitrogen at 533K.

composites made without any coupling agent were as good or better than those made with either the pyrolyzed PPQ or the Ventromer T-1 coupling agents in terms of interlaminar shear strength. Although it is not clearly evident from the data, it is believed there is little difference between the effectiveness of the two coupling agents in PPQ composites. All of the 500 hour samples of the Ventromer T-1 composite were inadvertently taken from a defective section of the panel. Therefore the interlaminar shear strengths of the Ventromer T-1 composites at 500 hours are probably not significant.

All interlaminar shear tests of PPQ composites resulted in normal interlaminar shear failure, regardless of the test temperature or previous thermal history of the sample.

C. Flexural Strength and Modulus

The flexural strength and modulus of composites were measured according to Hercules Method ACTP-C-6. Strength and modulus were determined at room temperature and at 533K and 588K after aging at these temperatures for up to 1000 hours. Composites made without coupling agent were aged no longer than 200 hours since longer exposure was not expected to produce significant results.

1. Flexural Strength and Modulus of Polyimide Composites

The initial room temperature flexural strength of the composite made without coupling agent was approximately 830 MN/m^2. The flexural

strength of the composite made with the Ventromer T-1 coupling agent was about 910 MN/m^2, while that made with a pyrolyzed PPQ coupling agent was approximately 1010 MN/m^2. Flexural strengths measured at 533K were of the same order of magnitude, with the composites made without coupling agent and with Ventromer T-1 showing slight increases in strength while the composite made with pyrolyzed PPQ coupling agent showed a 10% lower strength than it had at room temperature. After aging at 533K for 200 hours, the composite made with pyrolyzed PPQ coupling agent increased in flexural strength to about 1120 MN/m^2. Thereafter a moderate decline in strength occurred so that at the end of 1000 hours aging at 533K the flexural strength of this composite was 960 MN/m^2. The flexural strength of the composite made with Ventromer T-1, on the other hand, showed a steady decline in strength throughout the 1000 hours aging at 533K, decreasing from 960 MN/m^2 to 760 MN/m^2 during the 1000 hours. These effects are shown graphically in Figure 36. When these same polyimide composites were aged at 588K, that made with pyrolyzed PPQ coupling agent showed essentially no change in its flexural strength during the 1000 hour aging. On the other hand, the composite made with the Ventromer T-1 coupling agent showed a rapid decrease in flexural strength from about 950 MN/m^2 to 320 MN/m^2 during the first 500 hours. Between 500 hours and 1000 hours there was no further change. Figure 37 illustrates the flexural strength of the composites at 588K.

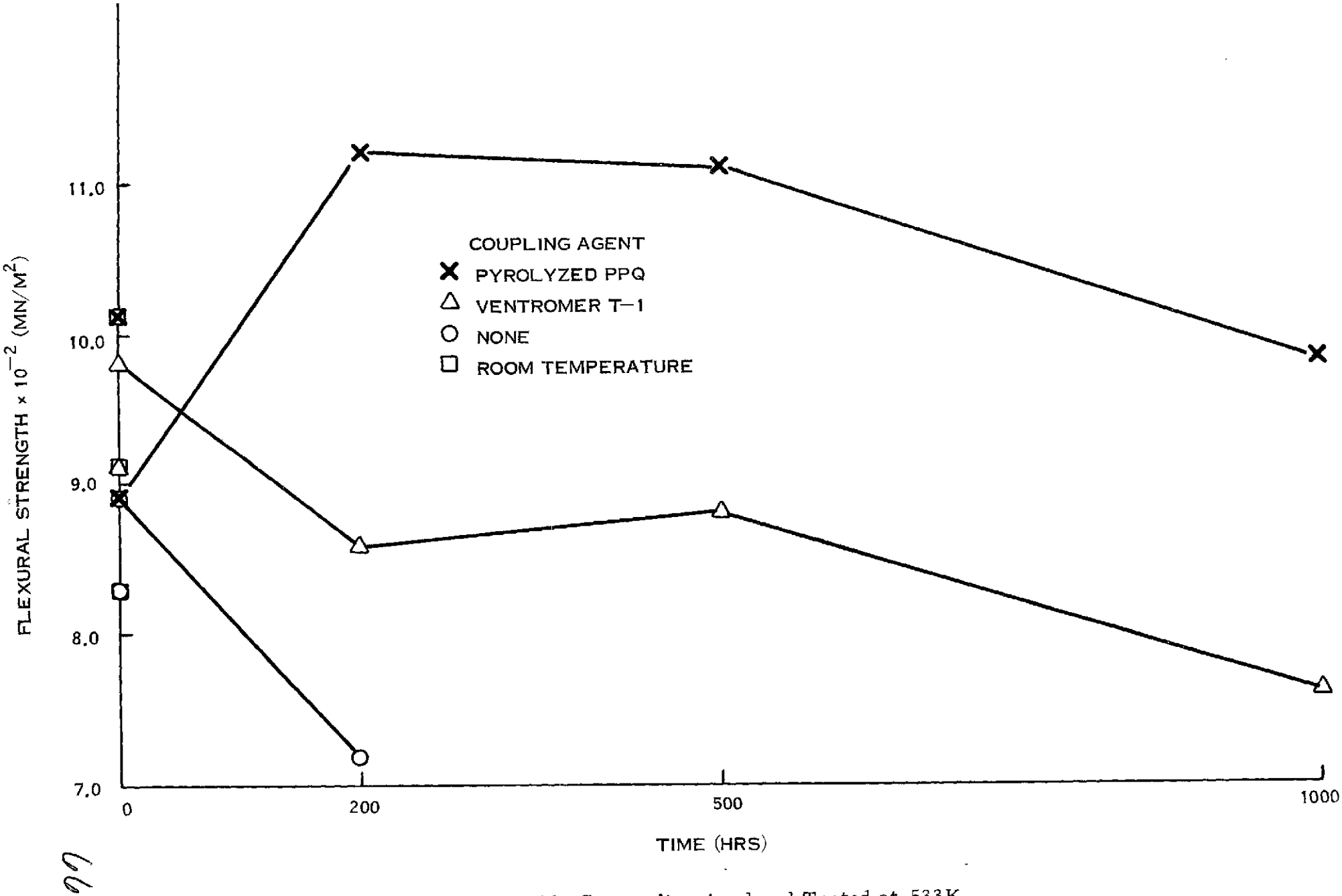


Figure 36. Flexural Strength of Polyimide Composites Aged and Tested at 533K.

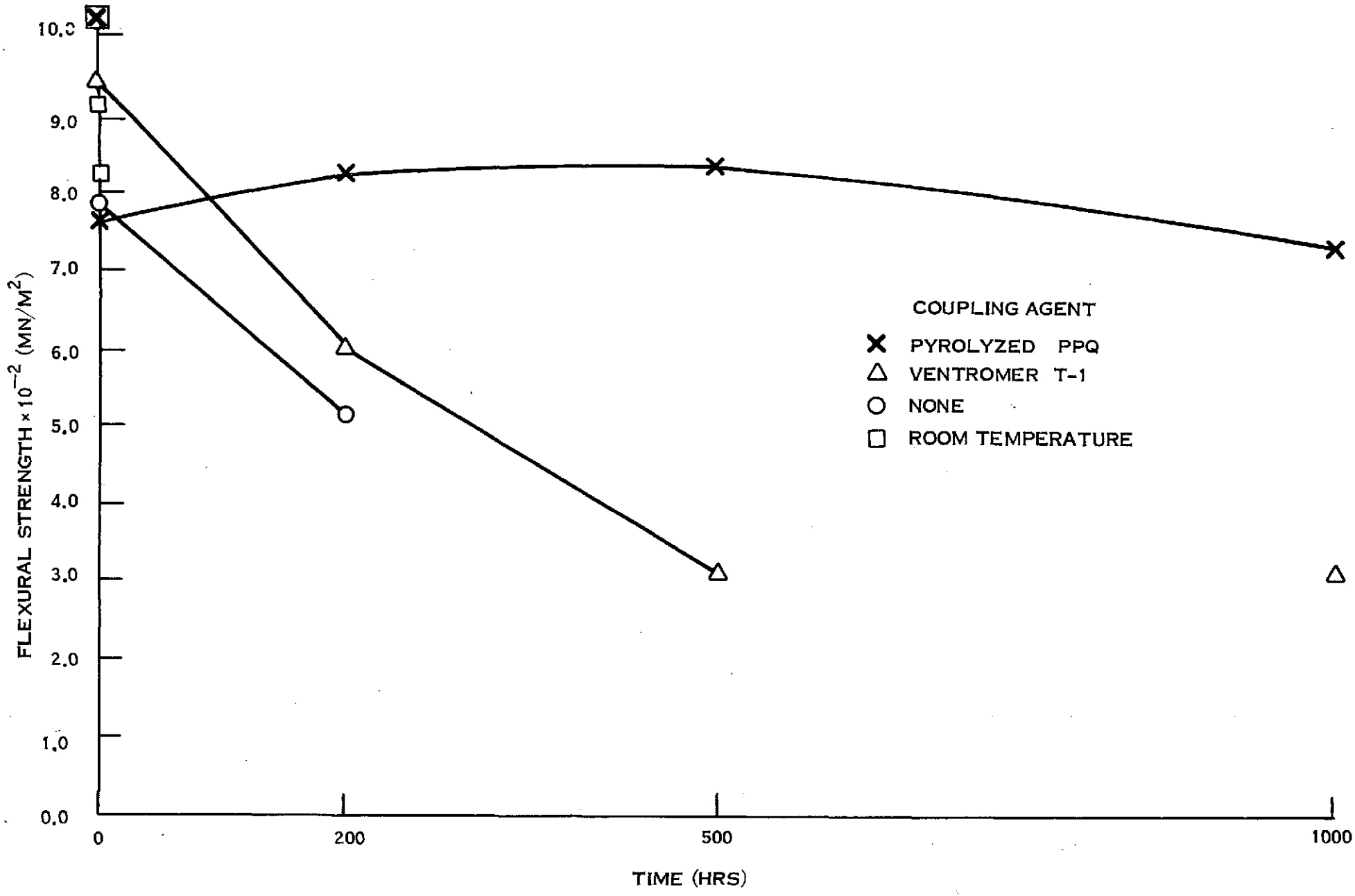


Figure 37. Flexural Strength of Polyimide Composites Aged and Tested at 588K.

The flexural modulus of the polyimide composites at 533K showed effects generally similar to those observed with the flexural strength. Modulus at 533K was not greatly different than that observed at room temperature. The modulus of the composite made with pyrolyzed PPQ remained essentially unchanged during 1000 hours aging at 533K, while the modulus of the composite made with Ventromer T-1 showed an essentially steady decline throughout the 1000 hours. These data are shown in Figure 38.

As shown in Figure 39, the initial flexural modulus of the polyimide composites was essentially the same at 588K as at 533K and room temperature. In this case, again, only a relatively small change was observed in the composite made with pyrolyzed PPQ during the 1000 hours aging at 588K. On the other hand, both the composites made with no coupling agent and that made with the Ventromer T-1 showed a steady decline in flexural modulus during the first 500 hours exposure. This decline was continued between 500 and 1000 hours for the composite made with Ventromer T-1, with the flexural modulus of that composite being of the order of 1/3 of its original value after exposure for 1000 hours at 588K.

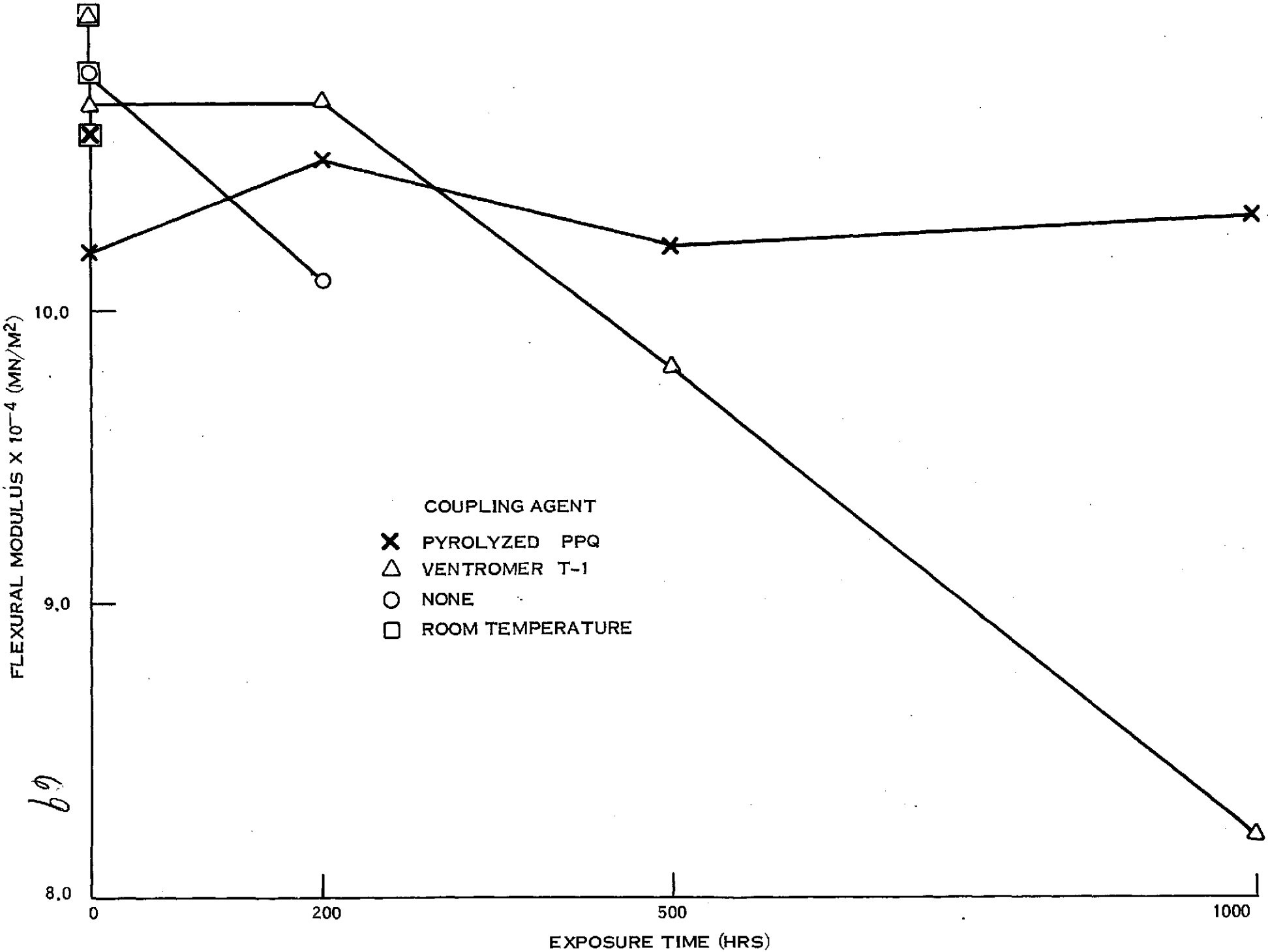


Figure 38. Flexural Modulus of Polyimide Composites Aged and Tested at 533K.

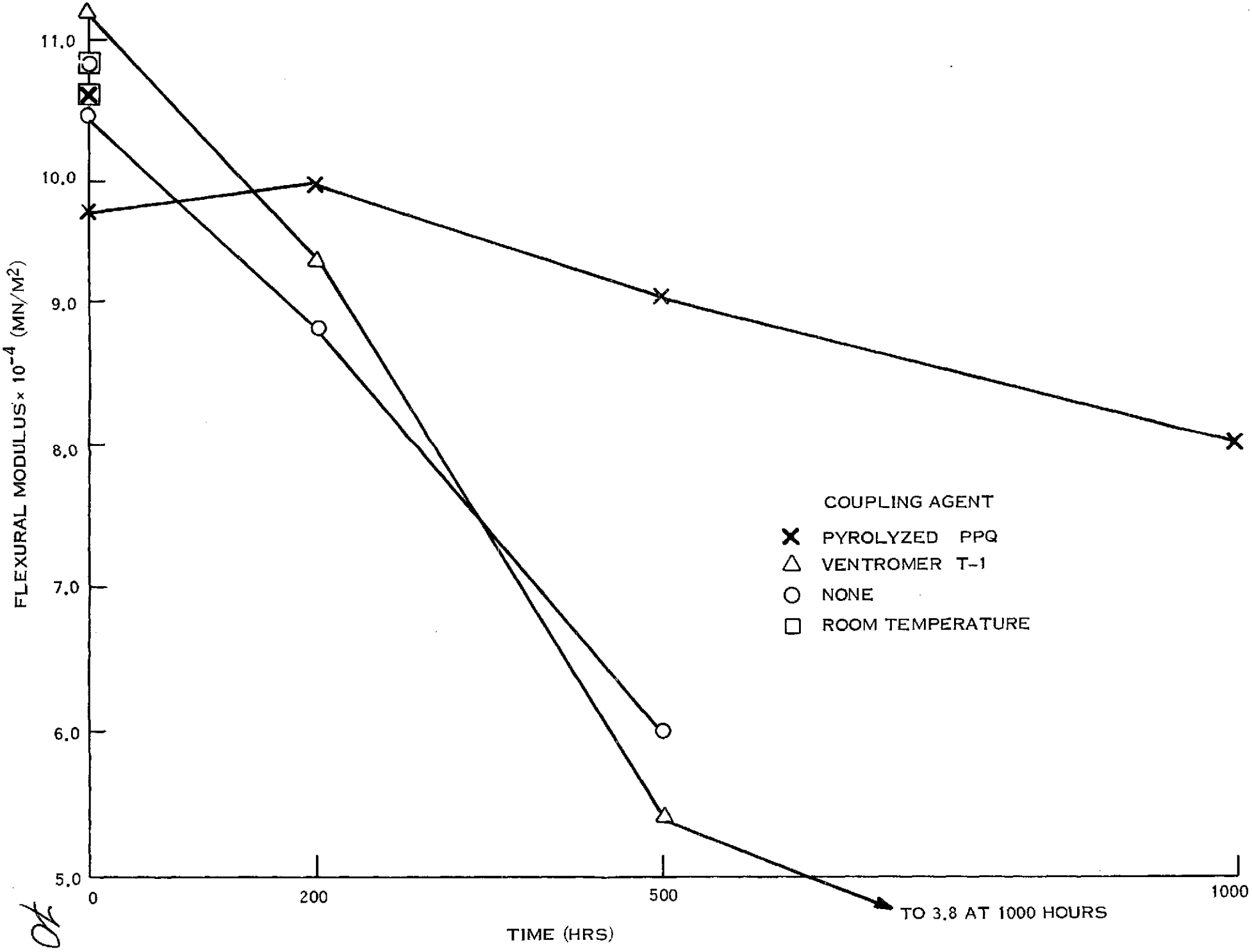


Figure 39. Flexural Modulus of Polyimide Composites Aged and Tested at 588K.

2) Flexural Strength and Modulus of Polyphenylquinoxaline Composites

The initial flexural strengths of PPQ composites were about 20% lower at 533K than at room temperature. Figure 40 shows that the flexural strength of the composite made with pyrolyzed PPQ coupling agent remained fairly constant for the first 500 hours exposure at 533K. However, between 500 hours and 1000 hours, a significant loss in flexural strength occurred in the pyrolyzed PPQ treated composite. The composite made with Ventromer T-1 as a coupling agent showed a steady decline in flexural strength throughout the 1000 hours 533K exposure, with the rate of decrease between 500 and 1000 hours being about the same as that observed with the composite made with pyrolyzed PPQ coupling agent. The difference between the two composites appears to be rather negligible.

The flexural modulus of PPQ composites, shown in Figure 41, was essentially the same at room temperature and at 533K. However, the flexural modulus of all composites decreased markedly during 1000 hours exposure at 533K. The higher initial modulus of th omposite made with Ventromer T-1 was offset by its linear rate of degradation, while the modulus of the composite made with pyrolyzed PPQ coupling agent had a relatively low rate of degradation during the first 500 hours of exposure. Between 500 and 1000 hours of exposure the modulus decreased at about the same rate for both treated composites.

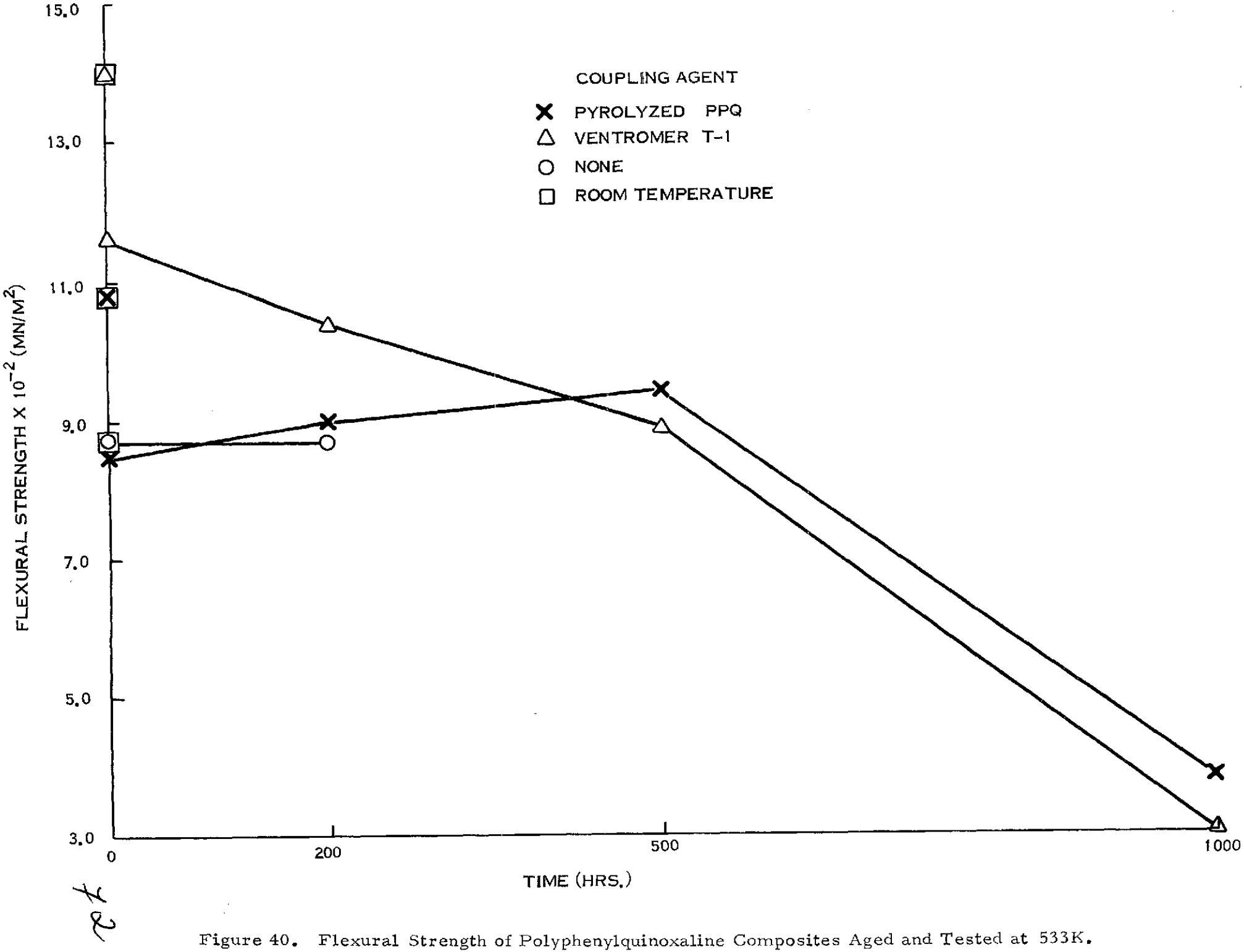


Figure 40. Flexural Strength of Polyphenylquinoxaline Composites Aged and Tested at 533K.

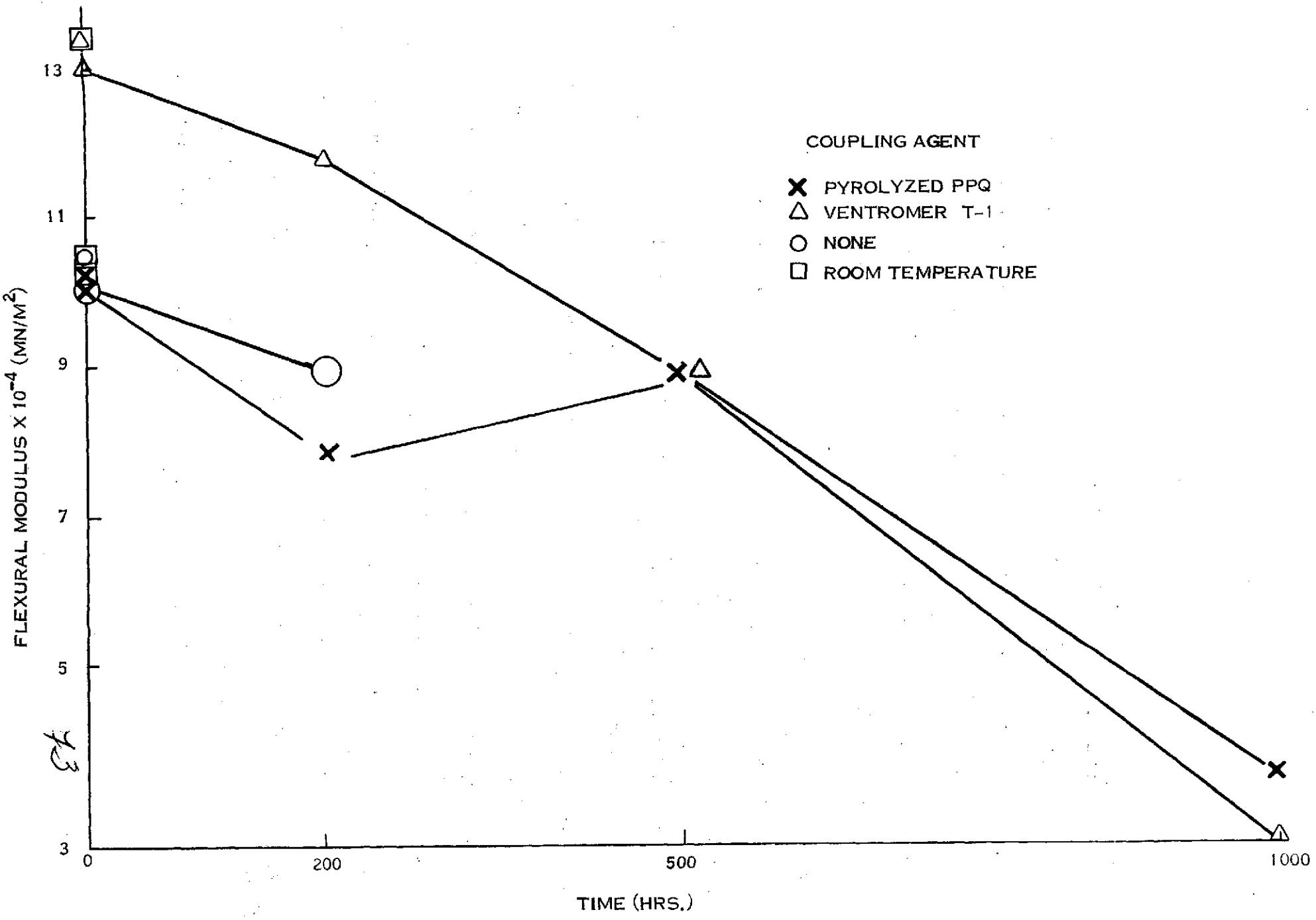


Figure 41. Flexural Modulus of Polyphenylquinoxaline Composites Aged and Tested at 533K.

D. Transverse Tensile Strength

Transverse tensile strengths of all composites were measured in accordance with Hercules Method ACTP-C-5. Unlike the flexural strengths, the transverse tensile strengths of all composites were markedly lower at elevated temperatures than at room temperature. At 588K the transverse tensile strength of polyimide composites was approximately 1/2 of the room temperature value. At 533K the transverse tensile strength of PPQ composites was 1/2 to 1/3 of the room temperature value.

1) Transverse Tensile Strength of Polyimide Composites

The transverse tensile strength of polyimide composites decreased about 50% during 1000 hours aging at 533K regardless of whether the composite was made with a coupling agent of Ventromer T-1 or of pyrolyzed PPQ. The data shown graphically in Figure 42 do not indicate a clear superiority for either coupling agent.

It was during aging at 588K that the most striking difference was observed between the stability of polyimide composites made with pyrolyzed PPQ coupling agent and Ventromer T-1. While the composite made with pyrolyzed PPQ coupling agent lost 60% of its transverse tensile strength during 1000 hours aging at 588K, that made with Ventromer T-1 coupling

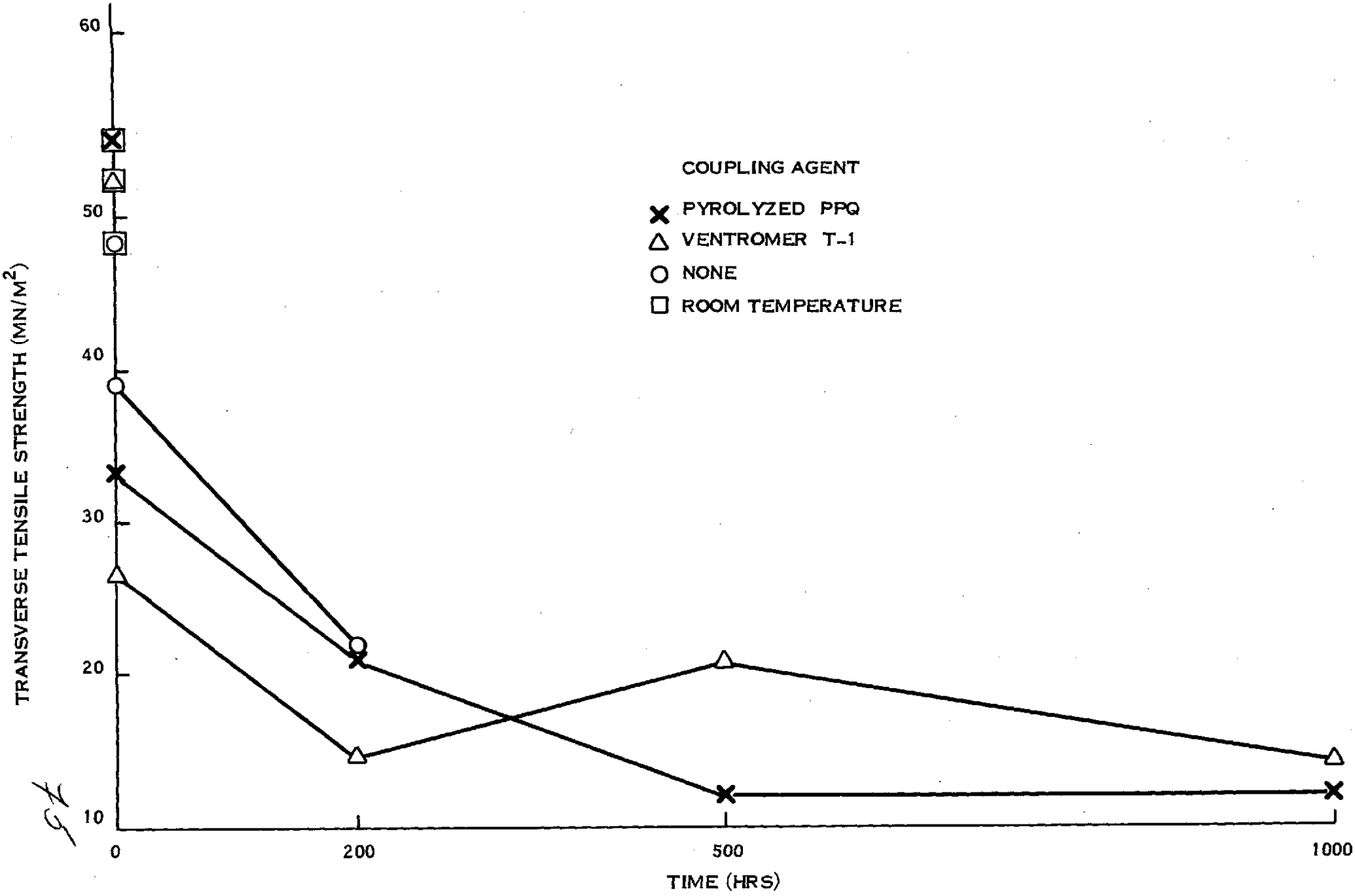


Figure 42. Transverse Tensile Strength of Polyimide Composites Aged and Tested at 533K.

agent degraded so badly that no tensile strength could be measured at periods exceeding 200 hours exposure. Figure 43 therefore shows data for the composite made with Ventromer T-1 only as far as 200 hours exposure. Also, the composite made without coupling agent is shown only to 200 hours exposure because longer exposure was not called for. Figures 44 and 45 show the type of distortion suffered by the polyimide composites made with Ventromer T-1 coupling agent after exposure at 588K for 500 and 1000 hours respectively. The samples designated as Panel 45 PI6 are the composite samples made with Ventromer treated fiber after exposure for 500 hours at 588K. The samples designated Panel 47 PI6 are the composite made with Ventromer T-1 treated fiber after exposure for 1000 hours at 588K. Panels 23 and 25 in Figures 44 and 45 are the transverse tensile specimens of the polyimide composite made with pyrolyzed PPQ coupling agent. A photomicrograph of the edge of one of the transverse tensile specimens made with Ventromer T-1 coupling agent is shown in Figure 46. The extent of degradation is evident. However, the edge of the corresponding aged polyimide composite made with pyrolyzed PPQ coupling agent also showed a similar degradation as shown in Figure 47.

In an effort to determine the cause of the distortion seen in the polyimide composites made with Ventromer T-1 coupling agent, resin

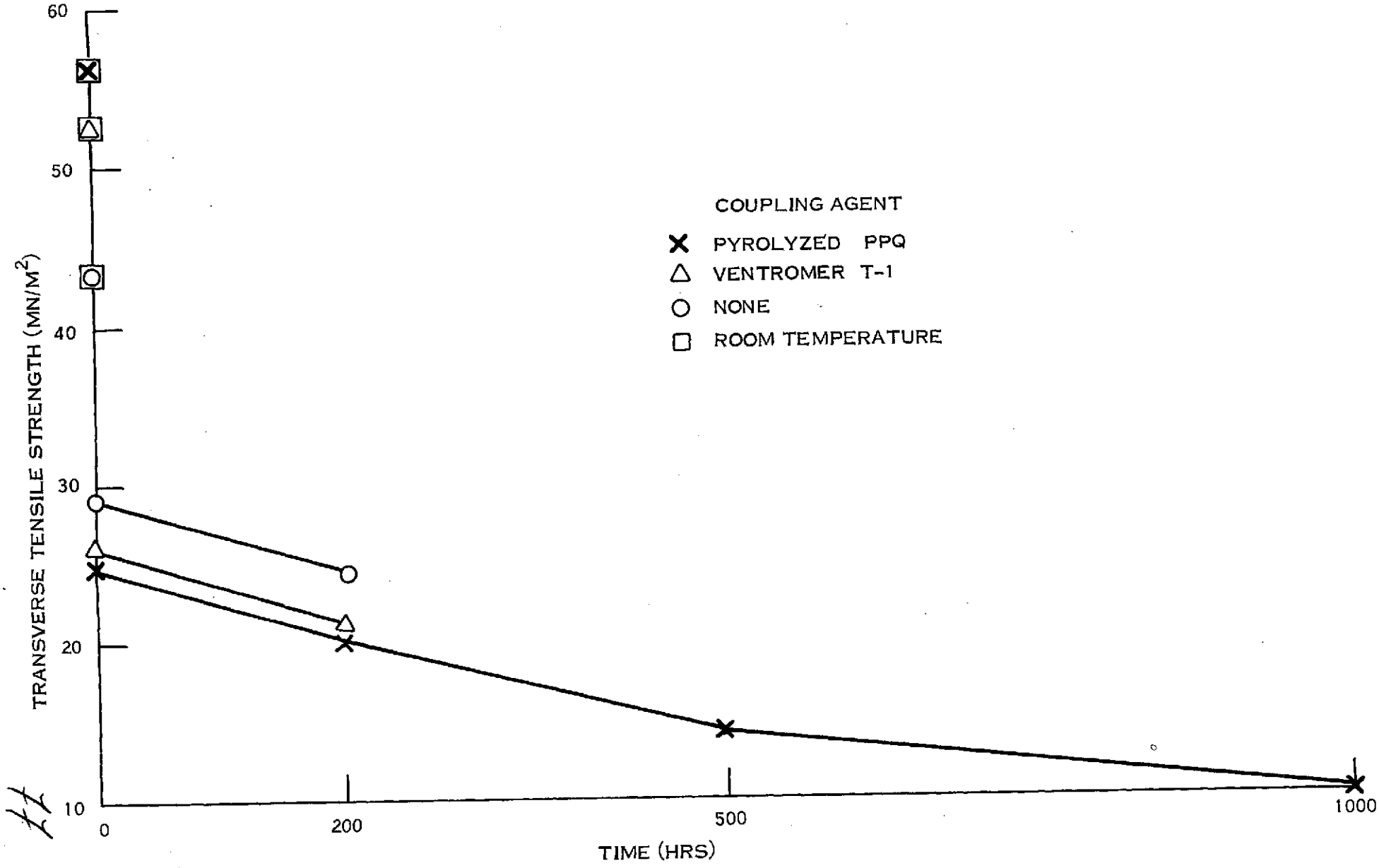


Figure 43. Transverse Tensile Strength of Polyimide Composites Aged and Tested at 588K.

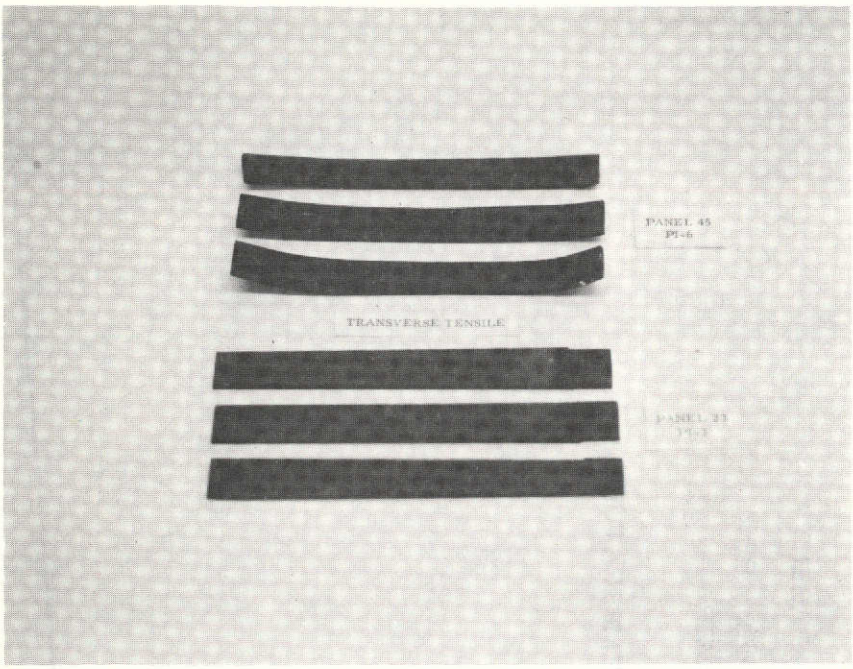


Figure 44. Polyimide Transverse Tensile Specimens After 500 Hours at 588K.

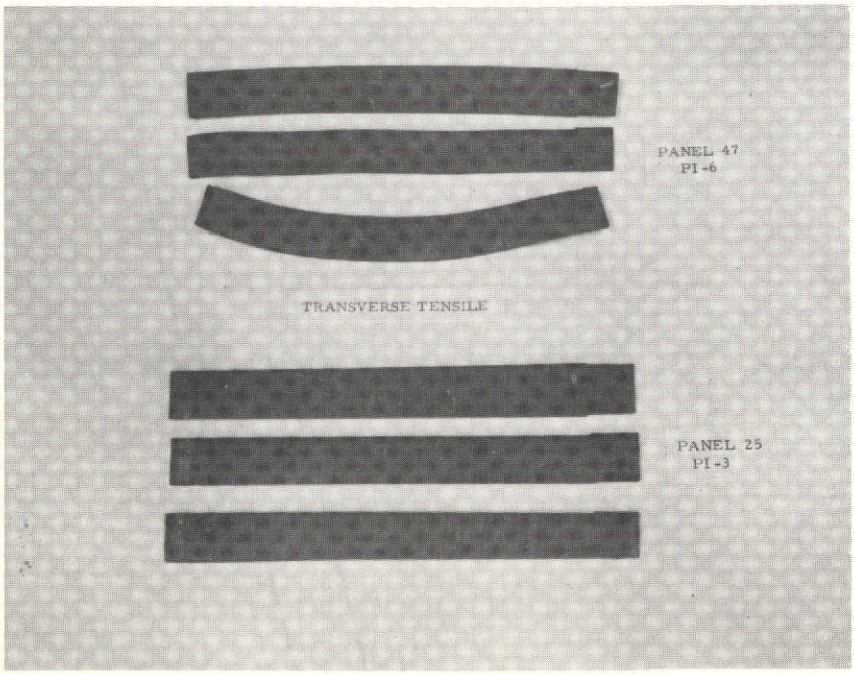


Figure 45. Polyimide Transverse Tensile Specimens After 1000 Hours at 588K.

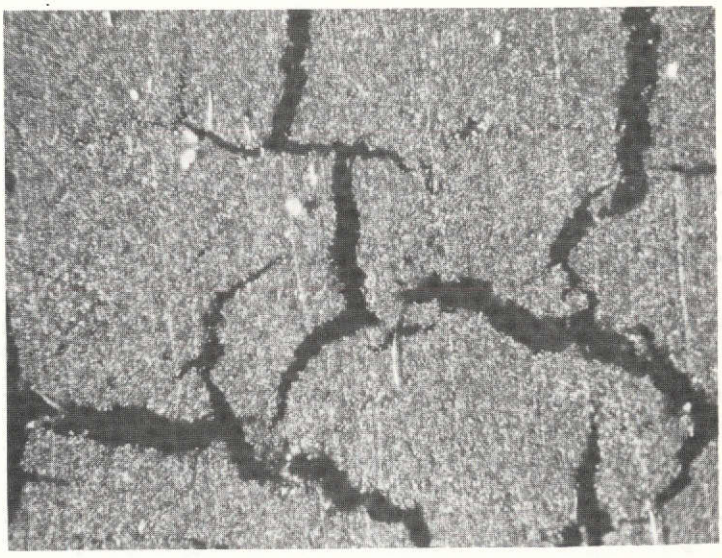


Figure 46. Photomicrograph of the Edge of Ventromer T-1 Treated Transverse Tensile Specimen 45-42 After 500 Hours at 588K.

Figure 47. Photomicrograph of the Edge of Pyrolyzed PPQ Treated Transverse Tensile Specimen 23-40 After 500 Hours at 588K.

content was measured on sample 45-40, the third from the top in Figure 44 and on sample 47-54, the third from the top in Figure 45. The concave side of sample 45-40 had a resin content of 51 wt. %, while the convex side of the same sample had a resin content of 42.6 wt. %. The concave side of sample 47-54 had a resin content of 80.5 wt. %, and the convex side of the same sample a resin content of 68.5 wt. %. These composites as made had resin contents of 34 or 35 wt. %. This indicates that the catastrophic degradation of these samples was due to preferential oxidation of the fiber. It was noted however that in the sulfuric acid digestion of these samples it was not possible to obtain clear solutions by addition of hydrogen peroxide. There appeared to be a significant amount of graphite too fine to be retained by a sintered glass filter. Therefore the measured percentages of resin may be unrealistically high, but they do indicate that little useful fiber remains in these particular samples after aging.

2) Transverse Tensile Strength of Polyphenylquinoxaline Composites

As can be seen in Figure 48, the polyphenylquinoxaline composite made without coupling agent had initially only about half the transverse strength at 533K that it had at room temperature. However, after aging for 200 hours at 533K, this composite had a 533K transverse tensile strength

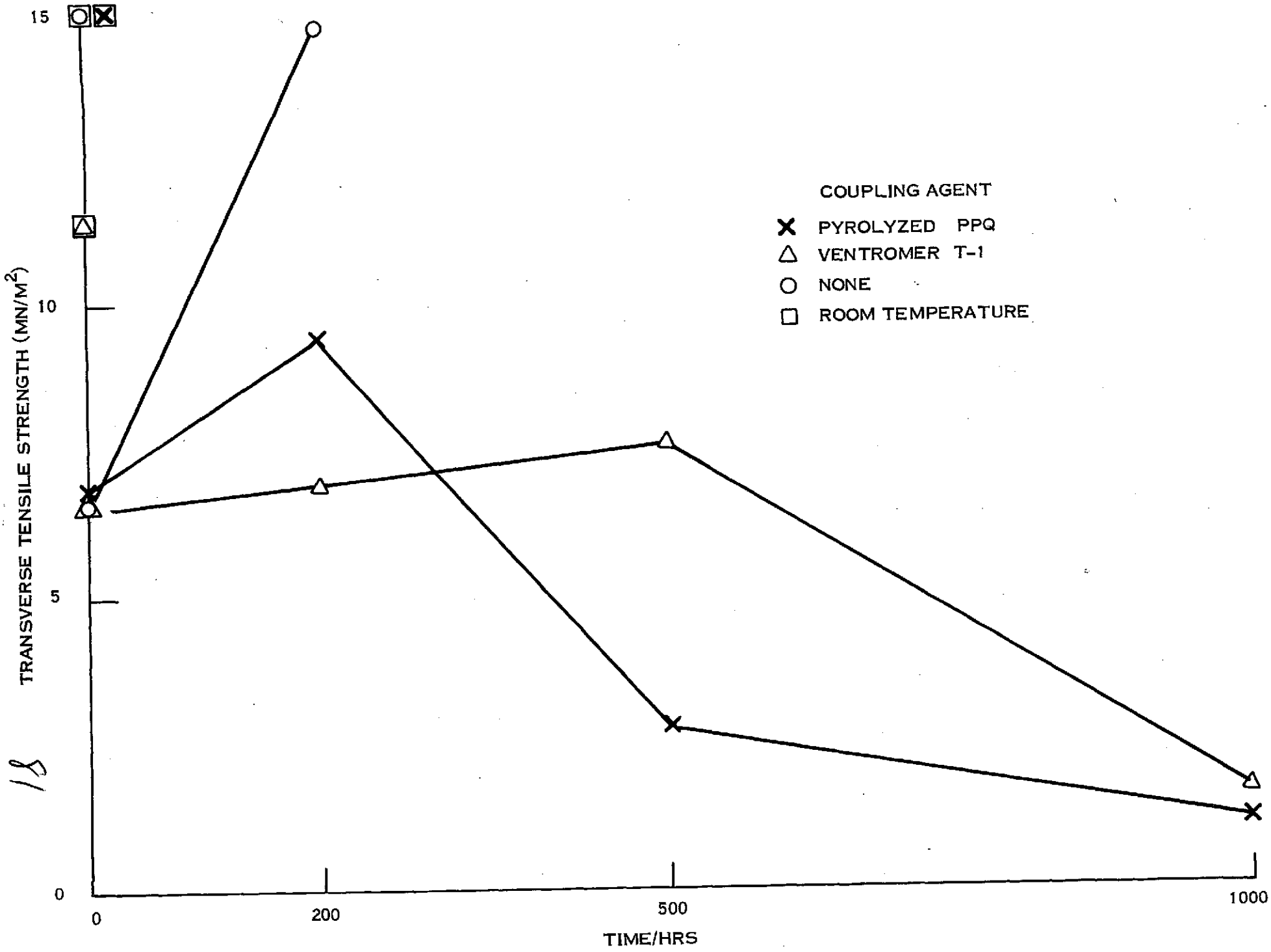


Figure 48. Transverse Tensile Strength of Polyphenylquinoxaline Composites Aged and Tested at 533K.

approximately equal to the strength determined at room temperature. These data were reliable because the scatter among the triplicate determinations of each point was small. However, consistency among the triplicate data points for the composite made with pyrolyzed PPQ coupling agent was unaccountably poor. For example, measurements of unaged transverse tensile strength at 533K gave values of 2.8, 6.2, and 11.3 MN/m^2. After 200 hours aging at 533K, the three values of transverse tensile strength were 6.7, 8.2, and 13.2 MN/m^2; somewhat more consistent though still scattered. Nevertheless it is clear from inspection of Figure 48 that significant loss of transverse tensile strength occurred during the course of 1000 hours exposure at 533K for both the composite made with pyrolyzed PPQ and made with Ventromer T-1 coupling agents.

E. Composite Weight Loss

Weight losses of composites used in the evaluation study were measured at intervals up to 1000 hours exposure at 533 and 588K. As can be seen in Figure 49, both the composite made with pyrolyzed PPQ coupling agent and that made with Ventromer T-1 coupling agent lost approximately 16 to 17% of their weight during 1000 hours exposure at 588K. The loss of weight was relatively linear over the entire 1000 hours. The similarity of the weight losses of the two composites tends to reinforce the belief that the resin contents described above in Section D were unrealistically high.

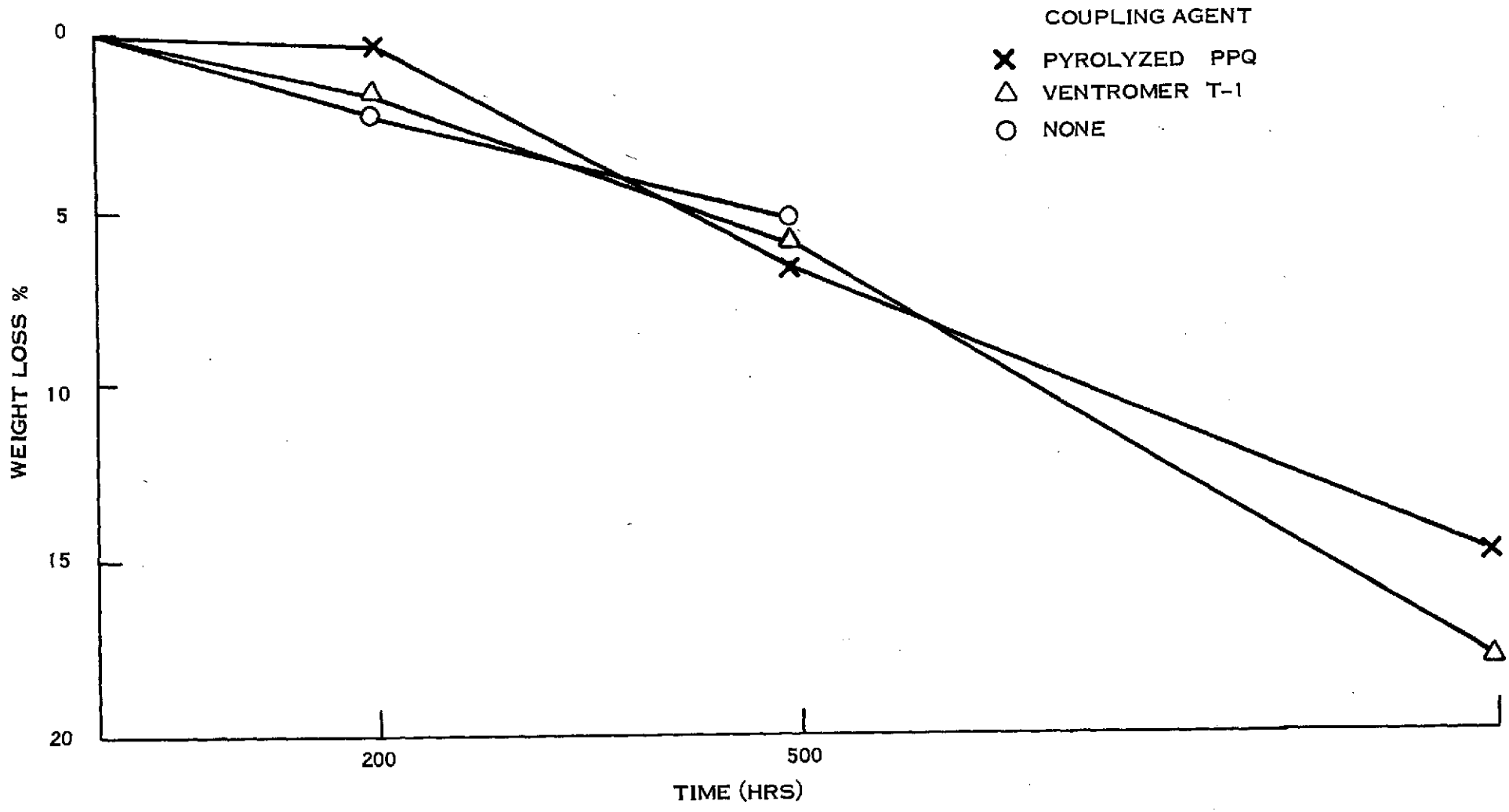


Figure 49. Weight Loss of Polyimide Composites at 588K.

The observed weight loss can not account for the apparent loss of fiber. Therefore the weight loss studies reinforce the opinion mentioned above, that a significant part of the degraded fiber remained in the composite as colloidal particles.

At 533K the polyimide composites all showed approximately the same high degree of stability for the first 500 hours, as illustrated in Figure 50. However, between 500 and 1000 hours at 533K, the composite made with Ventromer T-1 showed an additional 3% weight loss. Although small, this loss tends to confirm the generally observed instability of the composites made with Ventromer T-1 evaluated during the advanced composite study.

The weight loss observed with the polyphenylquinoxaline composites was much greater than was observed with the polyimide composites at 533K, as shown in Figure 51. During the first 500 hours exposure at 533K, the weight loss of the polyphenylquinoxaline composites was the same as that observed with the polyimide composites. However, during the second 500 hours exposure at 533K the composites made with the pyrolyzed PPQ coupling agent and the composites made with the Ventromer T-1 coupling agent underwent catastrophic degradation, both losing during the second 500 hours exposure at 533K 9 to 12% of their weight.

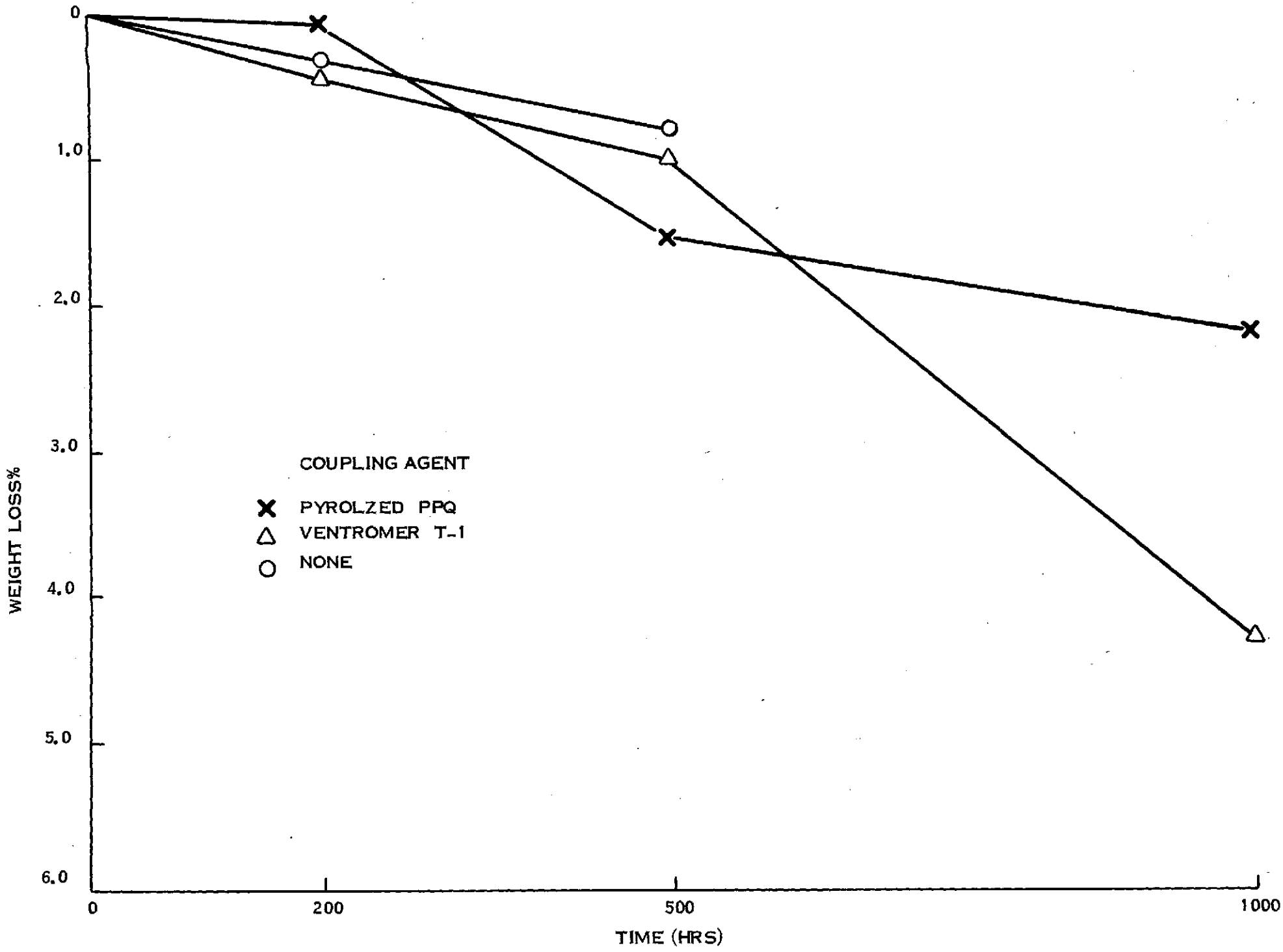


Figure 50. Weight Loss of Polyimide Composites at 533K.

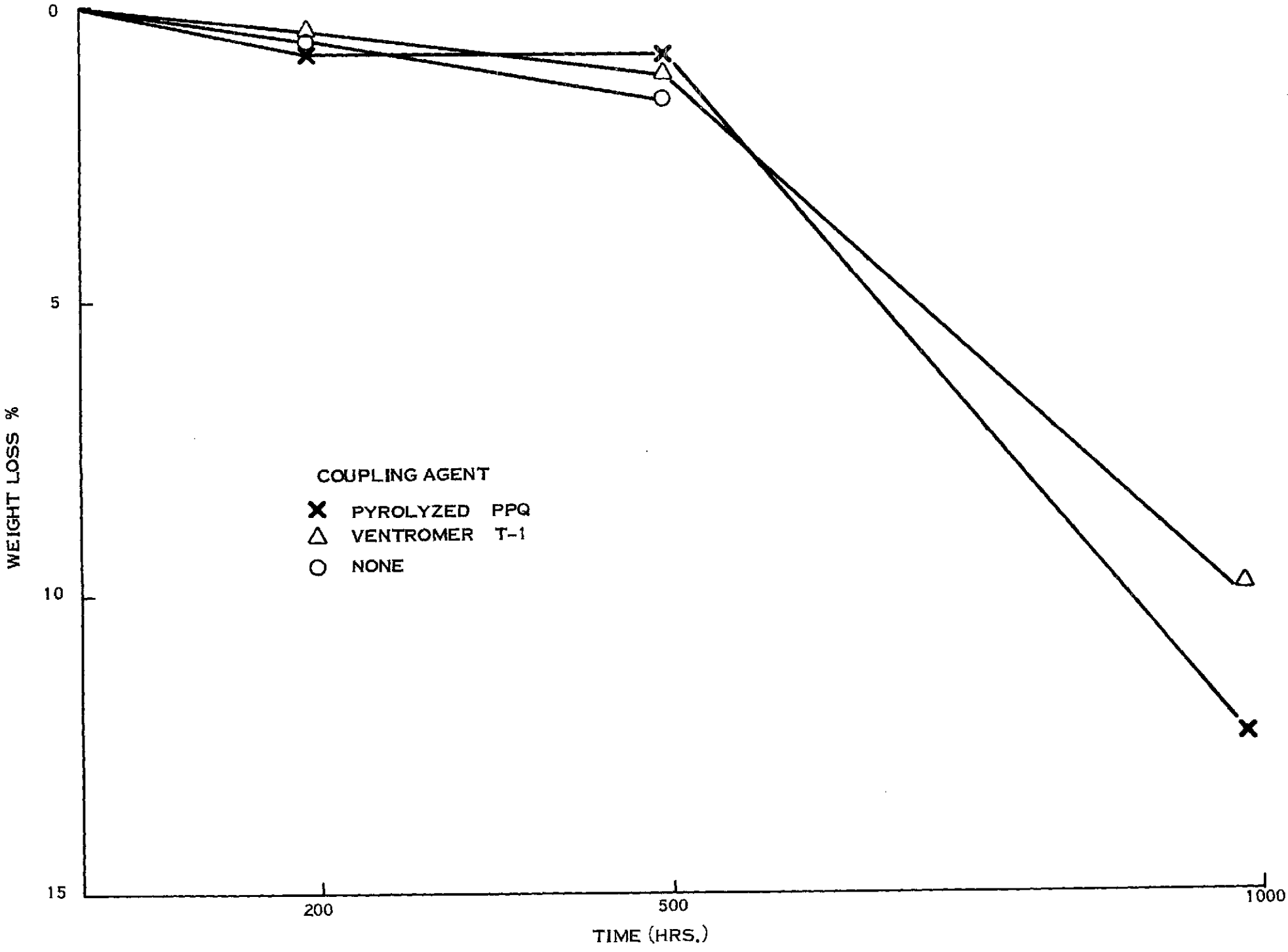


Figure 51. Weight Loss of Polyphenylquinoxaline Composites at 533K.

V. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this experimental study to develop high temperature resistant graphite fiber coupling agents for use with PMR polyimides and polyphenylquinoxalines. Based on the conclusions, recommendations are given for further studies.

A. Conclusions

1) It was found that pyrolyzed polyphenylquinoxaline made a very satisfactory coupling agent for polyimide/Thornel 300 graphite fiber composites. During 1000 hours aging at 588K such composites lose a little over half their transverse tensile strength, and suffer a slight loss in flexural modulus. However, no degradation of flexural strength or interlaminar shear strength occurs during 1000 hours aging at 588K.

2) It was found that Ventromer T-1 was a satisfactory coupling agent in the initial screening evaluation of PMR-polyimide/Thornel 300 composites. However, in the later advanced composite evaluations a reproducibility problem occurred in which the advantages of Ventromer T-1 as a coupling agent were not observed.

3) None of the coupling agents examined in the course of this work had a markedly beneficial effect with polyphenylquinoxaline composites.

B. Recommendations

1) It is recommended that work be continued to determine the general applicability of pyrolyzed PPQ coupling agent for polyimide/graphite fiber composites with graphite fibers other than Thornel 300 used in this study.

2) It is recommended that efforts be made to optimize the Ventromer T-1 treatment, because of the inconsistency between the excellent screening results and the unsatisfactory advanced composites evaluation.

3) It is recommended that Ventromer T-1 coupling agent and similar Ventromer treatments be investigated on graphite fibers other than the Thornel 300 used in this study.

VI. NEW TECHNOLOGY

Rapid progress in the development of high-modulus fiber-reinforced composites, such as those based on carbon, boron and PRD fibers, has been hampered by problems in technology which must be solved if this rapid progress is to be maintained. Chief among these problems is the fact that under multiaxial stress conditions, many of these composites appear to fail within the matrix or at the filament-matrix interface rather than by rupture of the filaments. This problem has been emphasized in the reports of contractors working on such structures as horizontal tails and blading for aircraft and on helicopter rotor blades.

The outstanding mechanical properties of graphite fibers become of practical interest only if they can be efficiently translated into a useable composite. Although tensile properties of carbon fibers appear to be directly related to the size and orientation of the graphitic subunits, the properties of a fiber/resin composite depend to a large extent on the adhesion between the fiber and the matrix.

The surface treatments that are used for graphite/epoxy systems, however, are not adequate for use with high temperature resins. The short-time elevated temperature interlaminar shear and transverse tensile strengths of polyimide/graphite composites are significantly lower than the room temperature values. Composites exposed in air to elevated temperatures exhibit excessive further decreases in these strength values due to oxidation degradation of the resin/fiber interface. While investigators in the field (1, 2) have attempted to develop coupling agents for polyimides on glass fibers, no such materials are available for use with graphite fiber composites of high temperature polyimides and polyphenylquinoxalines.

At least two coupling agents or surface treatments have been shown to improve the interlaminar shear strength and thermal stability of polyimide/graphite composites. Formation of a carbonaceous char on the fiber surface by pyrolysis of an aromatic resin sizing has been shown (27) to improve the interlaminar shear strength of polyimide/graphite composites. It has now been shown that this type of treatment can provide substantial improvement in the thermal stability of such composites. After 1000 hours at 588K a polyimide/graphite composite made with fiber treated with pyrolyzed polyphenylquinoxaline had the same interlaminar shear strength

at 588K as it did before aging (44/MN/m^2). The room temperature interlaminar shear strength decreased from 106 MN/m^2 to 85 MN/m^2 after 1000 hours aging at 588K, with 67% of the decrease occurring during the first 200 hours.

A second coupling agent was found which has produced some very encouraging results. A polyimide/graphite composite made from fiber treated with a reaction product of titanium tetrachloride and trimethyl borate (Ventromer T-1, Ventron Corporation) had an initial interlaminar shear strength of 61 MN/m^2 at 588K. After 500 hours aging at 588K the interlaminar shear strength at 588K was 67 MN/m^2. The problem with this coupling agent is that other composite panels made in ostensibly the same manner as the first panel did not demonstrate the same improved thermal stability.

At present both surface treatments represent a modification to existing technology. If the latter treatment can be made to perform reproducibly in a beneficial manner, it will represent a substantial advance in the art.

APPENDIX A

PROPERTIES OF POLYIMIDE COMPOSITES

#	Treatment	Panel #	Fiber Weight Loss, % in 200 hours 588°K	533°K	Fiber Tow Tensile, Kg	Composite Density, $Kg/m^3 \times 10^{-3}$	Resin Content, %	Void Content, %	Fiber Volume, %
0	None	1	3.1	-0.4*	24.2	1.56	47.1	-1.1	54.0
1	PMR-PI Sized	3	2.3	0.13	23.4	1.53	40.8	2.7	56.5
2	PMR-PPQ Sized	4	3.4	0.5	24.5	1.54	45.6	0.5	53.9
3	PMR-PPQ Carbonized	5	3.1	-0.3	24.5	1.54	41.1	1.8	57.1
4	PMR-PI Carbonized	6	1.5	-0.3	19.2	1.52	44.3	1.8	53.9
5	Epoxy Carbonized	2	2.3	0.6	21.8	1.52	45.2	1.8	53.0
6	Halotitanate	7	4.4	-2.5	21.2	1.55	42.9	0.5	56.6
7	Ferric Chloride		25.1	7.4	13.9				
8	Ferrocene		8.1	0.6	24.0				
9	PMR-PI + Filler	16	4.8	0.7	23.1	1.51	41.5	3.5	54.9
10	Phosphorus Oxychloride		15.2	10.6	11.5				

* Minus indicates gain in weight

APPENDIX B

PROPERTIES OF POLYPHENYLQUINOXALINE COMPOSITES

#	Treatment	Panel #	Fiber Weight Loss, % in 200 hours		Fiber Tow Tensile, Kg	Composite Density, $Kg/m^3 \times 10^{-3}$	Resin Content, %	Void Content, %	Fiber Volume, %
			588°K	533°K					
0	None	8	3.1	0.4*	24.2	1.54	35.5	2.6	61.9
	PMR-PI Sized	9	2.3	0.13	23.4	1.54	36.9	1.4	60.8
2	PMR-PPQ Sized	10	3.4	0.5	24.5	1.54	39.3	3.3	57.4
3	PMR-PPQ Carbonized	11	3.1	-0.3	24.5	1.55	31.1	2.9	66.0
4	PMR-PI Carbonized	12	1.5	-0.3	19.2	1.54	36.7	1.9	61.4
5	Epoxy Carbonized	13	2.3	0.6	21.8	1.55	36.8	1.5	61.7
6	Halotitanate	14	4.4	-2.5	21.2	1.54	37.0	1.8	61.2
7	Ferric Chloride		25.1	7.4	13.9				
8	Ferrocene		8.1	0.6	24.0				
9	PMR-PI + Filler	15	4.8	0.7	23.1	1.51	37.1	3.9	59.0
10	Phosphorus Oxychloride		1[illegible].2	10.6	11.5				

*Minus indicates gain in weight

APPENDIX C-1

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hr.	ILS, MN/m^2		
None	PI	298/0	123	121	123
		533/0	64.1	66.2	65.5
		588/0	50.2	52.2	53.6
		533/200	67.6	68.2	70.3
		588/200	57.2	56.5	58.6
	PPQ	298/0	116	116	113
		533/0	69.0	69.0	70.3
		588/0	51.0	49.6	47.6
		533/200	69.0	67.6	65.5
		588/200	57.2	58.6	57.9

APPENDIX C-2

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hr.	ILS, MN/m^2		
Polyimide	PI	298/0	130	131	132
		533/0	64.1	64.8	65.5
		588/0	43.3	45.4	46.1
		533/200	68.2	62.7	61.4
		588/200	55.8	57.2	58.6
	PPQ	298/0	107	111	113
		533/0	61.3	61.3	62.7
		588/0	35.8	37.9	33.8
		533/200	58.6	57.2	59.3
		588/200	53.8	54.5	52.0

APPENDIX C-3

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hr.	ILS, MN/m^2		
PPQ	PI	298/0	125	128	130
		533/0	64.1	64.1	64.8
		588/0	48.1	48.1	49.5
		533/200	65.5	63.4	63.4
		588/200	59.3	60.0	60.7
	PPQ	298/0	116	117	114
		533/0	66.2	64.1	62.0
		588/0	46.2	46.9	44.8
		533/200	62.0	62.7	61.4
		588/200	57.9	56.5	56.5

APPENDIX C-4

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hr.	ILS, MN/m^2		
Pyrolyzed PPQ	PI	298/0	132	132	134
		533/0	66.2	66.9	67.6
		588/0	45.4	45.4	48.8
		533/200	66.9	66.2	66.9
		588/200	60.7	62.7	63.4
	PPQ	298/0	111	110	120
		533/0	62.0	60.0	64.8
		588/0	44.8	44.1	46.2
		533/200	61.4	60.0	62.7
		588/200	53.8	53.1	57.9

APPENDIX C-5

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hr.	ILS, MN/m^2		
Pyrolyzed PI	PI	298/0	115	116	117
		533/0	62.7	63.4	64.1
		588/0	47.4	49.5	50.2
		533/200	60.7	59.3	59.3
		588/200	51.7	53.1	53.8
	PPQ	298/0	116	118	117
		533/0	62.0	63.4	64.1
		588/0	48.3	46.9	44.8
		533/200	64.8	64.1	62.7
		588/200	57.2	58.6	56.5

APPENDIX C-6

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hr.	ILS, MN/m^2		
Pyrolyzed Epoxy	PI	298/0	125	117	121
		533/0	62.7	67.6	68.3
		588/0	50.2	52.9	53.6
		533/200	62.0	63.4	62.7
		588/200	56.5	57.2	59.3
	PPQ	298/0	117	120	115
		533/0	65.5	65.5	61.4
		588/0	48.3	47.6	43.4
		533/200	66.9	65.5	63.4
		588/200	57.9	58.6	55.

APPENDIX C-7

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hrs.	ILS, MN/m^2		
Ventromer T-1	PI	298/0	123	131	132
		533/0	74.5	71.0	75.2
		588/0	59.1	61.2	62.6
		533/200	68.2	67.6	66.9
		588/200	62.0	64.8	66.9
	PPQ	298/0	111	111	114
		533/0	63.4	63.4	64.1
		588/0	48.3	48.9	47.6
		533/200	65.5	64.8	64.1
		588/200	58.6	59.3	60.0

APPENDIX C-8

INTERLAMINAR SHEAR STRENGTH OF SCREENING COMPOSITES

Coupling Agent	Matrix	Temperature, °K/Time, hrs.	ILS, MN/m^2		
PI/Cab-O-Sil	PI	298/0	126	125	119
		533/0	67.6	69.0	69.0
		588/0	55.2	53.8	55.2
		533/200	72.4	72.4	71.0
		588/200	59.3	60.7	59.3
	PPQ	298/0	92.4	92.4	93.1
		533/0	57.2	57.9	58.6
		588/0	45.5	45.5	44.8
		533/200	60.7	60.0	56.5
		588/200	55.8	55.8	56.5

APPENDIX D

COMPOSITES FOR TASK II

Panel	Type	Wt. pre-pregs (g)	Wt. cured (g)	Wt. loss (g)	Dimensions: Length	Dimensions: Width	Dimensions: Thickness	Trimmed Wt. of Panel (g)	Bulk Density	Density of Resin Content Sample (1)	(2)	(3)	Resin Content, % (1)	(2)	(3)	Resin Content Vol. %	Resin Vol. %	Voids Vol. %
22	PI/carbonized PPQ	62.5	56.0	6.5	4.824"	4.970"	0.0913"	55.4	1.54	1.54	1.55	1.54	35.18	35.84	36.11	42.06	56.37	1.56
23	"	63.0	56.2	6.8	4.850"	4.975"	0.0901"	55.7	1.56									
24	"	64.9	57.4	7.5	4.88"	4.97"	0.0922"	57.2	1.56	1.51	1.54	1.56	34.33	34.16	33.98	40.06	57.48	2.45
25.	"	66.0	57.2	8.8	4.998"	4.979"	0.0900"	57.0	1.55									
26	"	67.2	59.3	7.9	4.848"	4.968"	0.0966"	59.0	1.55									
27	"	67.0	59.2	7.8	4.88"	4.975"	0.0949"	58.8	1.56	1.54	1.55	1.54	34.37	34.18	35.20	40.74	57.35	1.90
28	"	65.8	59.0	6.8	4.863"	4.971"	0.0955"	58.6	1.55	1.54	1.54	1.54	31.39	36.81	36.33	42.99	55.49	1.51
29	"	62.8	57.2	5.6	4.805"	4.970"	0.0952"	56.8	1.53									
30	PPQ/none	81.5	58.2	23.3	4.809"	4.974"	0.0965"	57.7	1.524	1.53	1.52	1.53	32.40	32.65	27.32	37.29	60.03	2.68
31	"	85.6	60.2	25.4	4.829"	4.984"	0.1021"	60.0	1.49									
32	"	76.3	56.9	19.4	4.729"	4.938"	0.0979"	55.7	1.49	1.47	1.48	1.47	36.43	35.41	36.17	42.6	54.3	3.1
33	"	73.0	56.2	16.8	4.776"	4.796"	0.1015"	55.0	1.44									
34	PI/none	65.5	59.3	6.2	4.813"	4.971"	0.0050"	58.7	1.58									
35	"	67.0	60.6	6.4	4.837"	4.972"	0.0989"	60.3	1.55	1.57	1.56	1.54	35.89	34.34	34.36	41.47	57.58	1.53
36	PPQ/carbonized PPQ	69.2	52.3	16.9	4.851"	4.982"	0.8395"	51.8	1.56	1.57	1.58	1.58	25.82	27.05	26.98	33.31	65.73	0.93
37	"	71.0	53.0	18.0	4.801"	4.886"	.0906"	52.0	1.49									
38	"	81.4	59.4	22.0	4.806"	4.940"	0.1012"	58.5	1.485									
39	"	80.8	58.5	22.3	4.796"	4.965"	0.1048"	57.8	1.412	1.43	1.47	1.49	29.34	30.38	30.44	34.91	58.15	6.94
40	"	78.2	59.4	18.8	4.938"	4.974"	0.0982"	59.1	1.494	1.56	1.49	1.49	28.56	29.70	29.51	35.12	60.84	4.04
41	"	82.3	61.0	21.3	4.941"	4.983"	0.1030"	60.6	1.46									
42	PI/none	68.6	59.9	8.7	4.83"	49.75"	0.0954"	59.9	1.59	1.61	1.61	1.60	32.38	31.68	32.53	39.48	61.89	(0)
43	"	68.7	60.4	8.3	4.845"	49.78"	.0.0971"	60.4	1.57									
44	PI/Ventromer	64.0	56.4	7.6	4.855"	4.982"	0.0889"	56.4	1.60	1.60	1.60	1.60	34.02	35.10	35.13	42.44	59.31	(0)
45	"	63.7	56.0	7.7	4.873"	4.983"	0.0908"	56.0	1.55									
46	"	62.0	55.6	6.4	4.859"	4.985"	0.08735"	55.6	1.59	1.59	1.61	1.60	32.60	34.03	34.36	41.12	60.30	(0)
47	"	64.0	56.7	7.3	4.875"	4.986"	0.0903"	56.7	1.58									
48	"	62.5	55.2	7.3	4.914"	4.976"	0.0868"	55.2	1.58									
49	"	63.0	55.0	8.0	4.899"	4.984"	0.0868"	55.0	1.58	1.61	1.61	1.60	32.68	33.62	33.21	40.68	61.0	(0)
50	"	63.3	57.0	6.3	4.899"	4.981"	0.0891"	57.0	1.59	1.61	1.62	1.62	32.11	32.08	32.39	39.73	62.28	(0)
51	"	63.4	56.7	6.7	4.881"	4.983"	0.0908"	56.7	1.565									
52	PPQ/Ventromer	73.7	57.0	16.7	4.871"	4.969"	0.0998"	57.0	1.44	1.44	1.46	1.47	34.38	34.39	35.46	40.17	54.00	5.83
53	"	73.3	57.5	15.8	4.866"	4.982"	0.1005"	57.5	1.44									
54	"	66.2	49.2	17.0	5.011"	4.957"	0.0747"	49.2	1.62	1.62	1.64	1.63	21.21	21.63	21.99	27.95	72.59	
55	"	65.6	46.3	19.3	4.817"	4.959"	0.0738"	46.3	1.60									
56	"	69.5	55.0	14.5	4.857"	4.975"	.0967"	55.0	1.44	1.46	1.47	1.48	34.12	33.29	32.66	38.91	55.66	5.42
57	"	66.8	53.6	13.2	4.854"	4.981"	.0974"	53.6	1.39									

APPENDIX E-1

ADVANCED COMPOSITES EVALUATION

Coupling Agent - None
Matrix - Polyimide

Temp °K/Time	ILS at Temp., MN/m^2			ILS at Room Temp., MN/m^2			Aged in N_2 ILS at Temp., MN/m^2			Aged in N_2 ILS at RT, MN/m^2			Flex Strength $MN/m^2 \times 10^{-2}$			Flex Modulus, $MN/m^2 \times 10^{-4}$			Transverse Tensile MN/m^2			Composite Wt. Loss, %			Fiber Wt. Loss, %
298/0 hr.	77.2	90.3	99.3										7.98	8.11	8.66	11.1	10.3	10.9	34.2	44.8	49.3				
533/0 hr.	63.4	64.8	63.4										8.74	9.31	8.64	11.0	10.9	10.4	41.9	33.4	42.0				
588/0 hr.	54.2	47.6	50.4										8.05	8.47	6.58	10.5	10.7	10.2	25.5	31.3	29.9				
533/200 hr.	65.2	63.9	61.3	73	89	100.6	59.2	66.4	65.0	90.3	86.2	87.6	7.38	7.86	6.38	10.4	10.6	9.17	22.6	26.2	16.8	.46	.58	.44	
588/200 hr.	47.5	46.2	48.9	86.2	77.2	76.5	50.1	54.1	52.9	53.8	56.5	50.3	5.13	5.44	4.98	8.89	8.83	8.62	24.1	27.8	21.4	2.13	2.04	2.15	3
533/500 hr.	65.6	65.6	67.0																			.80	.85	.64	1
588/500 hr.																						5.85	6.26	5.79	42
533/1000 hr.																						2.36	2.54	2.45	11
588/1000 hr.																						20.4	20.1	18.0	74

APPENDIX E-2

ADVANCED COMPOSITES EVALUATION

Coupling Agent - None
Matrix - Polyphenylquinoxaline

Temp, °K/Time	ILS at Temp., MN/m^2	ILS at Room Temp., MN/m^2	Aged in N_2 ILS at Temp., MN/m^2	Aged in N_2 ILS at RT, MN/m^2	Flex Strength, $MN/m^2 \times 10^{-2}$	Flex Modulus $MN/m^2 \times 10^{-4}$	Transverse Tensile, MN/m^2	Composite Wt. Loss, %	Fiber Wt. Loss, %
298/0 hr.	62.0 71.0 72.4				7.59 8.40 8.85	10.1 10.3 11.2	16.1 13.2 16.5		
533/0 hr.	59.3 55.2 58.6				8.36 8.45 9.39	10.2 10.1 10.3	6.8 7.7 5.0		
588/0 hr.									
533/200 hr.	59.1 64.6 64.0	97.2 95.8 92.4	61.2 60.3 55.0	79.2 75.8 81.4	9.63 8.76 8.43	9.65 9.38 9.38	14.0 14.6 15.5	.71 .67 .62	-
588/200 hr.								6.12	3
533/500 hr.	67.0 67.0 67.8							1.86 1.42 1.71	1
588/500 hr.									42
533/1000 hr.								14.4 13.7 15.1	11
588/1000 hr.									74

APPENDIX E-3

ADVANCED COMPOSITES EVALUATION

Coupling Agent - Pyrolyzed PPQ
Matrix - Polyimide

Temp °K/Time	ILS at Temp., MN/m^2			ILS at Room Temp., MN/m^2			Aged in N_2 ILS at Temp., MN/m^2			Aged in N_2 ILS at RT, MN/m^2			Flex Strength $MN/m^2 \times 10^{-2}$			Flex Modulus, $MN/m^2 \times 10^{-4}$			Transverse Tensile MN/m^2			Composite Wt. Loss %			Fiber Wt. Loss %
298/0 hr.	106	105	109										9.07	9.74	11.4	11.0	10.1	10.9	54.1	55.4	5.75				
533/0 hr.	65.5	66.9	67.6										9.26	8.96	8.54	10.5	10.1	10.1	37.6	28.6					
588/0 hr.	43.6	45.2	45.4										7.97	7.18	7.67	8.89	9.72	10.1	20.0	23.8	30.9				
533/200 hr.	69.2	68.1	69.4	111	106	109	64.0	64.7	66.1	104	105	109	10.9	11.1	11.5	10.3	10.8	10.5	21.4	21.4	21.2	.05	.03	.08	
588/200 hr.	51.6	53.2	51.4	93.1	94.5	88.2	48.6	48.9	50.8	94.5	100	87.6	8.10	8.52	8.05	9.86	9.93	10.1	17.3	21.3	22.3	.51	.51	.54	3.1
533/500 hr.	66.0	66.7	66.9	107	110	112	58.8	60.3	59.7	86.9	84.8	84.8	10.6	11.5	11.0	10.1	10.0	10.8	7.17	12.3	18.5	1.57	1.58	1.48	
588/500 hr.	54.2	54.3	54.4	93.8	92.4	89.6	48.7	49.1	49.8	84.1	91.7	91.0	8.43	7.95	8.95	9.72	9.10	8.89	14.0	14.0	13.9	6.39	6.51	6.07	28
533/1000 hr.	60.5	62.5	63.8	101	100	94.6	63.1	61.4	64.3	118	126		9.99	9.96	9.65	10.7	10.1	10.1	15.0	11.8	10.3	2.29	2.21	2.17	4
588/1000 hr.	44.1	43.9	43.2	80.8	86.9	86.6	55.0	53.9	54.5	120	121	116	7.48	7.35	7.40	7.72	8.00	8.41	11.3	10.1	8.3	14.2	14.0	14.3	70

APPENDIX E-4

ADVANCED COMPOSITES EVALUATION

Coupling Agent - Pyrolyzed PPQ
Matrix - Polyphenylquinoxaline

Temp, °K/Time	ILS at Temp., MN/m^2	ILS at Room Temp., MN/m^2	Aged in N_2 ILS at Temp., MN/m^2	Aged in N_2 ILS at RT. MN/m^2	Flex Strength $MN/m^2 \times 10^{-2}$	Flex Modulus $MN/m \times 10^{-4}$	Transverse Tensile MN/m^2	Composite Wt. Loss %	Fiber Wt. Loss %
298/0 hr.	76.5 76.5 71.7				11.1 10.6 10.9	10.0 10.5 10.5	19.6 12.3 14.5		
533/0 hr.	48.2 47.6 40.0				8.01 8.47 9.76	10.3 10.1 10.2	2.8 6.2 11.3		
588/0 hr.									
533/200 hr.	44.5 48.8 50.9	63.4 64.8 69.6	53.5 50.5 46.1	56.5 70.3 53.1	9.63 8.34 4.75	9.03 8.76 6.0	8.2 6.7 13.2		
588/200 hr.								.97 .91 .84	
533/500 hr.	55.8 52.8 54.4	87.6 75.8 74.5	59.0 55.1 56.8	92.4 82.0 81.4	9.45 9.46 9.23	9.17 8.76 8.83	3.1 3.3 -	2.3 2.2 2.6	3.1
588/500 hr.								.82 .83 .90	
533/1000 hr.	43.2 31.3 25.1	42.0 32.0 19.9	55.8 50.8 48.4	85.6 66.5 65.9	4.06 4.14 3.25	3.86 3.86 2.90	1.6	12.3 11.9 11.7	28
588/1000 hr.								11.1 11.8 14.1	4
									70

APPENDIX E-5

ADVANCED COMPOSITES EVALUATION

Coupling Agent - Ventromer T-1
Matrix - Polyimide

Temp °K/Time	ILS at Temp., MN/m^2			ILS at Room Temp., MN/m^2			Aged in N_2 ILS at Temp., MN/m^2			Aged in N_2 ILS at RT, MN/m^2			Flex Strength $MN/m^2 \times 10^{-2}$			Flex Modulus, $MN/m^2 \times 10^{-4}$			Transverse Tensile, MN/m^2			Composite Wt. Loss, %			Fiber Wt. Loss, %
298/0 hr.	110	97.9	90.3										9.11	8.78	9.36	11.2	11.2	11.2	54.8	52.8	49.8				
533/0 hr.	70.3	73.8	75.1										9.72	10.2	9.72	10.6	10.8	10.6	30.4	29.7	21.5				
588/0 hr.	59.7	52.7	58.0										9.08	9.42	9.81	13.2	13.2	13.4	15.7	29.1	34.6				
533/200 hr.	71.1	72.4	73.8	84.8	92.4	98.6	75.3	78.1	73.2	89.6	86.9	84.1	8.25	8.60	9.04	10.6	10.7	11.0	17.6	13.9	12.0	.41	.43	.38	-
588/200 hr.	53.2	60.7	51.4	63.4	80.0	85.5	57.4	61.9	54.3	85.5	81.4	73.8	5.67	6.07	6.23	9.17	9.72	9.10	74.4	17.6		1.92	1.83	1.80	4
533/500 hr.	70.9	77.0	74.9	111	85.5	71.7	79.1	78.8	82.0	111	105	106	8.91	8.63	9.01	9.86	9.72	9.79	25.6	27.2	11.3	1.05	.97	.95	-
588/500 hr.	48.2	55.1	51.3	73.8	78.6	53.1	65.9	62.5	64.1	74.5	75.8	60.0	3.21	4.02	3.09	6.07	5.93	4.21				5.41	5.85	5.92	24
533/1000 hr.	69.9	73.5	69.4	64.8	79.8	72.6	81.2	82.9	82.5	102	106	107	6.66	8.54	7.56	8.34	8.34	8.07	12.5	15.8		4.27	4.24	4.42	4
588/1000 hr.	43.4	44.9	39.1	46.0	56.8	49.0	68.8	71.0	60.2	75.6	69.7	68.7	3.45	3.56	3.03	3.86	3.86	3.54				17.6	17.3	17.6	60

APPENDIX E-6

ADVANCED COMPOSITES EVALUATION

Coupling Agent - Ventromer T-1
Matrix - Polyphenylquinoxaline

Temp °K/Time	ILS at Temp., MN/m^2	ILS at Room Temp., MN/m^2	Aged in N_2 ILS at Temp., MN/m^2	Aged in N_2 ILS at RT, MN/m^2	Flex Strength $MN/m^2 \times 10^{-2}$	Flex Modulus $MN/m^2 \times 10^{-4}$	Transverse Tensile, MN/m^2	Composite Wt. Loss %	Fiber Wt. Loss %
298/0 hr.	68.3 70.3 66.2				14.0 14.1 14.4	13.4 13.2 13.6	11.8 11.5 10.8		
533/0 hr.	46.2 42.7 46.4				11.1 11.3 12.6	13.3 12.8 13.0	6.5		
588/0 hr.									
533/200 hr.	42.5 45.6 49.9	53.1 61.4 58.6	43.0 42.0 45.3	66.9 60.7 60.0	10.5 10.4 5.6	11.7 11.9 6.35	7.1 5.0 8.5	.54 .34 .77	-
588/200 hr.									4
533/500 hr.	30.6 28.4 31.2	38.6 32.4 31.7	42.5 40.3 41.4	62.7 54.5 51.7	8.49 8.86 8.16	8.76 8.90 8.96	7.6 7.8	.99 1.25 1.33	-
588/500 hr.									24
533/1000 hr.	19.3 19.8 18.1	22.5 20.2 15.8	45.8 42.1 45.5	60.0 60.4 58.4	3.37 3.07 2.70	3.72 3.79 3.31	2.2 2.6	10.7 10.2 8.3	4
588/1000 hr.									60

REFERENCES

1. Herrick, J.W., et al, AFML-TR-66-178, July 1966.

2. Bacon, R., Palozzi, A., and Slosarik, S., 21st Conf., Soc. Plastics Inc., 8E-1, Feb. 1966.

3. Wong, Robert, et al, "Thermally Stable Finishes for Glass Fiber Reinforced Polyaromatic Resin Laminates", Owens-Corning Fiberglas Corp., Technical Report AFML-TR-65, 316, Part III, March 1968.

4. Vaughn, D.J., "A New Concept in Coupling Agents for Glass Reinforced Epoxy Laminates", Insulation Circuits, 19, No. 3, pg. 20, March 1973.

5. Serafini, T. T., Delvigs, P. and Lightsey, G. R., "Thermally Stable Polyimides from Solutions of Monomeric Reactants", Journal of Applied Polymer Science, 16, 905 (1972), and NASA TN D-6611, January 1972.

6. Serafini, T.T., Delvigs, P. and Vannucci, R.D., "In-Situ Polymerization of Monomers for High Performance Polyphenylquinoxaline Graphite Fiber Composites", Journal of Applied Polymer Science, 17, 3235 (1973).

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

8. Delvigs, P., Serafini, T.T. and Lightsey, G., "Addition-Type Polyimides from Solutions of Monomeric Reactants", NASA TN D-6877, August 1972.

9. Adams, R. et al, Organic Reactions, IV , p. 22 and 47 (1948).

10. Walton, H.M., J. Org. Chem. 22, 308 (1957).

11. Hergenrother, P.M., AFML-TR-73-68, May 1973.

12. Mullin, J.V. and Mazzio, V.F., "Basic Failure Mechanisms in Advanced Composites", Final Report, NASA Contract NASw-2093, October 1971.

13. Larson, J.V., Smith, T.G., and Erickson, P.W., "Carbon Fiber Surface Treatments", NOL-TR-71-165, p25, 29 October 1971.

14. Johnson, D.J. and Tyson, C.N., British Journal of Applied Physics (J.Phys.D.), 2, 787 (1969).

15. Ruland, W., J. Polymer Science, 7, No. 28, Part C, 143 (1969).

16. Thorne, D.J. and Prince, A.J., Fiber Sci. & Tech. 4, 9 (1971).

17. Mimeault, V.J. and McKee, D.W., 10th Carbon Conf., Bethlehem, Pa., FC-25, (1971).

18. McKee, D.W., "Carbon and Graphite Science", General Electric Co. Technical Information Series, Report No. 72CRD319, Nov. 1972.

19. Hanson, M.P. and Serafini, T.T., "Effects of Thermal and Environmental Exposure on the Mechanical Properties of Graphite/ Polyimide Composites", Nat. SAMPE Tech. Conf., p. 31 (1971).

20. Parker, J.A. and Winkler, E.L., "The Effects of Molecular Structure on the Thermo-chemical Properties of Phenolics and Related Polymers", NASA TR-R-276, November 1967.

21. Barry, W.T., U.S. Patent 3,177,175, April 6, 1965.

22. Chemical and Engineering News, 48, 12 (1969).

23. Arthur, J.R., Trans. Faraday Soc. 47, 164 (1951).

24. Hawtin, P. and Gibson, J.A., Conf. on Industrial Carbon and Graphite, Society of Chemical Industry, London (1970).

25. McKee, D.W., Savage, R.H. and Gunnoe, G., Wear, to be published.

26. McKee, D.W., "Effect of Adsorbed Phosphorus Oxychloride on the Oxidation Behavior of Graphite", GE Report No. 72CRD076, March 1972.

27. Duffy, J.V., "Carbonized Polymer Coatings as Surface Treatments for Carbon Fibers", NOL TR73-153, August 1973.