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THERMALLY STABILE POLIMIDES FROM SOLUTIONS OF MONOMERIC REACTANTS

by T. T. Serafini, P. Delvigs, and G. R. Lightsey
Lewis Research Center
Cleveland, Ohio

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THERMALLY STABILE POLIMIDES FROM SOLUTIONS OF MONOMERIC REACTANTS

T. T. Serafini, P. Delvigs
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SYNOPSIS

A method to prepare thermally stable resin fiber reinforced composites using solutions of appropriate monomers is described. Solutions containing a dimethyl ester of an aryl tetracarboxylic acid, the monomethyl ester of nadic acid and an aryl diamine were used to impregnate graphite fibers. Composites fabricated from these prepregs exhibited excellent thermo-oxidative stability and retention of mechanical properties at 600°F. These results compare favorably to those obtained from composites made from amide-acid prepolymers capped with reactive alicyclic rings. Monomeric solutions provide excellent shelf-life and improved solubility compared to amide-acid prepolymer solutions.

INTRODUCTION

During the last decade polymer chemists have succeeded in synthesizing numerous polymers which, for organic materials, exhibit outstanding thermal stability. The key to synthesizing these so-called high temperature polymers has been to use highly stable structural units such as aromatic and/or heterocyclic rings. Unfortunately the structural units which confer thermal stability to high temperature polymers are also responsible for their inherent insolubility and infusibility, commonly referred to as intractability. The intractable nature of these polymers makes it very difficult - nearly impossible - to use them as matrix resins in advanced composites.

An approach of chemically modifying the structure of polyimide prepolymers as a means of improving the processability was reported by Delvigs, et al. (1) and Serafini (2). Although the chemically modified prepolymers were found to be more resistant to premature imidization, the long chain nature of the prepolymers prevented adequate resin flow during final processing. Lubowitz (3) and Burns, et al. (4) used the approach of preparing low molecular weight end-capped amide-acid (polyimide) prepolymers that polymerized into thermally stable polyimides without the evolution of by-products. A commercially available resin of this type is known as P13N. Another version, known as P10P, having considerably improved thermooxidative stability has been developed (5). From our in-house studies with P10P as a matrix resin we have observed that the P10P prepolymer solutions exhibit a very limited shelf life at room temperature as evidenced by precipitation and/or gel formation. Prior to the appearance of the precipitate or gel there is a steady decrease of solution viscosity. The significance of this has been discussed by Delvigs, et al. (1).

This report describes a new approach for the synthesis of processable polyimides. Graphite fiber reinforced composites are fabricated from fibers impregnated with solutions of appropriate monomers rather than from amide-acid prepolymer solutions. The mechanical properties and thermal stability characteristics of composites made from a selected solution of monomers are compared to the identical properties for composites made from P10P prepolymer solutions.

EXPERIMENTAL PROCEDURE

Monomers

The monomers used in this study are shown in figure 1. 4,4'-Methylenedianiline (I) and 4,4'-thiodianiline (II) were obtained from a commercial source and recrystallized from 2-propanol.

The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (III) was prepared according to the method of Walton (6).

2,5-Dicarbomethoxyterephthalic acid (IV) was prepared according to Bell and Jewell (7).

Dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (V) was synthesized by refluxing a suspension of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (64.4g, 2.00 x 10^{-1} mole) in dry methanol (60 ml) until the solid had dissolved (2 hr), then for an additional hour. Excess methanol was evaporated under reduced pressure at 50°C. The yellowish oil was dried in vacuum (10^{-3} torr) at room temperature for 24 hours to give 76.8g (99%) of the isomer mixture (V) as a crystalline solid.

Prepreg solutions

P10P amide-acid prepolymer solution was prepared according to the method of Burns, et al. (5) at a solids content of 40% by weight.

Solutions of monomers were prepared by dissolving a mixture of the reactants in the mole ratios indicated (Table 1) in anhydrous N,N-dimethylformamide (DMF) at room temperature. The solutions were prepared at a solids content of 60% by weight.

Viscosity Determination

Freshly prepared solutions in DMF with a solids content of 20% by weight were introduced into calibrated Ubbelohde viscometers. Periodic viscosity measurements were taken. The solutions were stored at 25°C in the capped viscometers for the duration of the experiment.

Composite Fabrication and Testing

Prepreg tapes were made by drum-winding and impregnating Hercules HTS graphite fiber with the various solutions of monomeric reactants and with P10P prepolymer solution in such proportions so that the prepreg contained 40% resin and 60% fiber by weight. The prepreg was heated for one hour at 130°F and then ten minutes at 250°F to reduce the solvent content to 5-10% by weight. The tape at this point was flexible, but not tacky.

Unidirectional composites were molded by the method of Burns, et al. (5). All laminates were six plys thick, ½ inch wide and 4 7/8 inch long. No attempt was made to optimize the fabrication procedure.

Test specimens were cut from the composites and the properties evaluated. Determinations of flexural strength and modulus were performed in accordance with ASTM D790. Shear strength was determined using the short beam flexural test procedure with a span-to-depth ratio of five. All 600° F tests were performed after a 15 minute soak at 600°F. The 600° F isothermal aging of the composites was conducted in a forced air oven, with an air change rate of 100 ml/min.

RESULTS AND DISCUSSION

Conventional condensation type aryl polyimides are synthesized by the reaction of an aryl dianhydride with an aryl diamine in a polar solvent. In the first step of the reaction a high molecular weight polyamide-acid prepolymer is formed. In the second step, water is eliminated by thermal and/or chemical means to form the cyclic polyimide. Composite processing difficulties encountered with condensation type polyimides are caused primarily by the volatilization of the reaction by-products formed during the second step of the reaction.

One of the major breakthroughs in the chemistry of high-temperature resins was the development of a novel class of polyimides which cure by an addition reaction (3,4). This approach utilizes low molecular weight amide-acid prepolymers end-capped with reactive alicyclic rings. The molecular structures of the amide-acid and imidized prepolymers of the version known as P10P are shown in figures 2a and 2b, respectively. Details concerning the synthesis, "B-staging", and final cure are given in reference 5. The version known as P13N has gained wide acceptance as a processable, thermally stable polyimide. P10P differs from P13N in the following two respects: (1) P10P has a formulated molecular weight of 1000 compared to 1300 for P13N, and (2) the dianhydride used in P10P is pyromellitic dianhydride (PMDA) rather than 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). As expected, the thermo-oxidative stability of P10P is superior to that of P13N (5).

A major shortcoming of P10P amide-acid prepolymer solutions is that they exhibit a very limited and variable shelf-life. We have observed gelation and/or precipitation to occur in solutions containing 40% solids within two days at room temperature. None of the monomeric solutions employed in this study have exhibited similar behavior. A monomeric solution containing 60% solids and stored at ambient conditions for six months appears to be unchanged.

The variation of solution viscosity for both an amide-acid prepolymer solution and a monomeric solution is shown in figure 3. The monomeric solution was formulated to approximate the composition of P10P. The gradual increase of viscosity for the monomeric solution (lower curve of figure 3) indicates that the monomers do undergo some pre-reaction in solution. The viscosity increase can be attributed to the formation of low molecular weight oligomers which do not appreciably alter the solution viscosity and shelf life. In contrast, the solution viscosity of the P10P prepolymer solution (upper curve of figure 3) markedly decreased. We hypothesize that hydrolytic degradation of the amide-acid prepolymer chains occurs continuously, resulting in the sharp decrease in solution viscosity. It is interesting to note that in order to make the viscosity measurements over a reasonable period of time, it was necessary to use relatively dilute (20% solids) solutions. Solutions having solids content in the range of 30-40% gelled and/or precipitated in a few days.

To evaluate the general applicability of the approach of using solutions of monomeric reactants to impregnate fiber reinforcements, six monomer solutions differing in chemical compositions and/or stoichiometry were prepared using the monomers shown in figure 1. The chemical composition, molar ratio of the reactants and some properties of graphite fiber composites are summarized in table 1. Sample A was formulated to have the chemical composition and stoichiometry of P10P. Samples C and D are chemically similar to P13N, however, their stoichiometry was adjusted to approximate prepolymers having formulated molecular weights of 1500 and 3000, respectively.

It should be pointed out that all of the data (weight loss, flexural strength and modulus and interlaminar shear strength) presented in this report were obtained from laminates fabricated according to a procedure which had been optimized for amide-acid prepolymer solutions rather than monomeric reactant solutions.

The room temperature and 600°F interlaminar shear strengths of composites made from the monomeric solution (Sample A) corresponding to P10P compare favorably to the values obtained from P10P prepolymers.

The variation in interlaminar shear strengths and weight loss resulted primarily from differences in the resin flow characteristics of the various monomer systems. In general, poor resin flow resulted from decreasing the molar ratio of the alicyclic end caps (III) in the monomeric solution.

The 600 hour, 600°F composite weight loss data for Samples A and B (18%) compare favorably with the 500 hour, 600°F weight loss (14%) for P10P/T50S graphite fiber composite (5), and with the data presented for P10P composites in Figure 4. The composite weight loss of Sample C was lower than anticipated. This could be due to enhanced resin flow resulting in a very low void content coupled with a lower alicyclic content. The superior thermal stability of the polyimide composite made with BTDA as the dianhydride moiety, compared to the PMDA moiety (weight loss Sample C $<$ weight loss Sample A) appears to be contradictory to the findings reported in reference 5. Apparently in the studies reported in reference 5, the greater thermal stability of the PMDA compared to BTDA overshadowed the higher alicyclic content of P10P (23% higher than for P13N). However, for Sample C the further reduction of alicyclic content (13% lower alicyclic content than for P13N) enhanced the thermal stability to a greater degree than the inclusion of PMDA in P10P. Currently resins having the chemical composition of Sample C are being evaluated to determine the optimum molar ratios of the reactants.

The physical and mechanical properties of composites made from amide-acid and monomeric solutions were compared over an extended period of time at 600°F. The results of the isothermal aging are shown in figure 4. The composite weight losses are essentially identical indicating that the thermooxidative stability is not lowered by the use of monomeric solutions.

Figure 5 illustrates the effect of thermal aging on the flexural strength. The flexural strength of the P10P composite was somewhat higher, due at least in part to a higher fiber content (54 V/% vs 52 V/% for Sample A). However, the change in flexural strength in going from room temperature to 600°F and during the isothermal aging was similar for both composite systems. The effect of temperature and isothermal aging on the flexural modulus of elasticity is shown in figure 6. After an exposure at 600°F for 15 minutes the 600°F modulus was lower than the room temperature modulus for unaged samples. It is interesting to note that the modulus decreased during the initial 150 hours whereas the flexural strength increased during this time interval.

The variation of interlaminar shear strength with time at 600°F is shown in figure 7. There was approximately a 40% decrease in the interlaminar shear strength in going from room temperature to 600°F. However, after the initial decrease, the interlaminar shear remained almost constant for more than 300 hours. The values were similar for the two composite systems, with the small differences attributed to variations in the resin content of the composites.

CONCLUSIONS

Based on the results of this investigation the following conclusions can be drawn:

1. Solutions of monomeric reactants for the synthesis of processable polyimides can be used for various combinations of appropriate monomers.

2. Solutions of monomeric reactants offer the following advantages over amide-acid prepolymer solutions:
    a. excellent shelf-life - as powder or as solutions
    b. increased solubility - solutions containing 60-70% solids by weight are readily obtainable
    c. low solution viscosity

3. The mechanical properties and thermal stability characteristics of graphite fiber reinforced composites made from solutions of monomeric reactants compare favorably to those of composites made from amide-acid prepolymer solutions.

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Table 1: Properties of Various Polyimide/graphite Fiber Composites Made from Monomeric Solutions

Sample	Monomeric Solution Composition[a]	Mole Ratio of Reactants	Interlaminar Shear[b] at 75°F (psi)	Interlaminar Shear[b] at 600°F (psi)	Composite Weight Loss[c] After 600 hrs. In Air at 600°F (%)
A	III/I/IV	2/2.34/1.34	10,800	6200	17.6
B	III/I/IV	2/4.32/3.32	------	4975	17.8
C	III/I/V	2/3.09/2.09	15,300	6000	9.5
D	III/I/V	2/6.19/5.19	------	5140	28.0
E	III/II/IV	2/3.49/2.49	8,400	----	22.6
F	III/II/V	2/3.97/2.97	-----	2315	20.6

a.
I : 4,4'-Methylenedianiline
II : 4,4'-Thiodianiline
III: Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid
IV : 2,5-Dicarbomethoxyterephthalic acid
V : Dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid

b. Average of two to four tests

c. Average from two composites

TABLE I

PROPERTIES OF VARIOUS POLYIMIDE/HTS GRAPHITE FIBER COMPOSITES MADE FROM MONOMERIC SOLUTIONS

SAMPLE	MONOMERIC SOLUTION COMPOSITION	MOLE RATIO OF REACTANTS	INTERLAMINAR SHEAR AT 75^0 F, PSI	INTERLAMINAR SHEAR AT 600^0 F, PSI	COMPOSITE WEIGHT LOSS AFTER 600 HR IN AIR AT 600^0 F
A	III/I/IV	2/2.34/1.34	10 800	6200	17.6
B	III/I/IV	2/4.32/3.32	------	4975	17.8
C	III/I/V	2/3.09/2.09	15 300	6000	9.5
D	III/I/V	2/6.19/5.19	------	5140	28.0
E	III/II/IV	2/3.49/2.49	8 400	----	22.6
F	III/II/V	2/3.97/2.97	------	2315	20.6

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FIGURE 1

MONOMERS USED FOR PREPARATION OF MONOMERIC SOLUTIONS

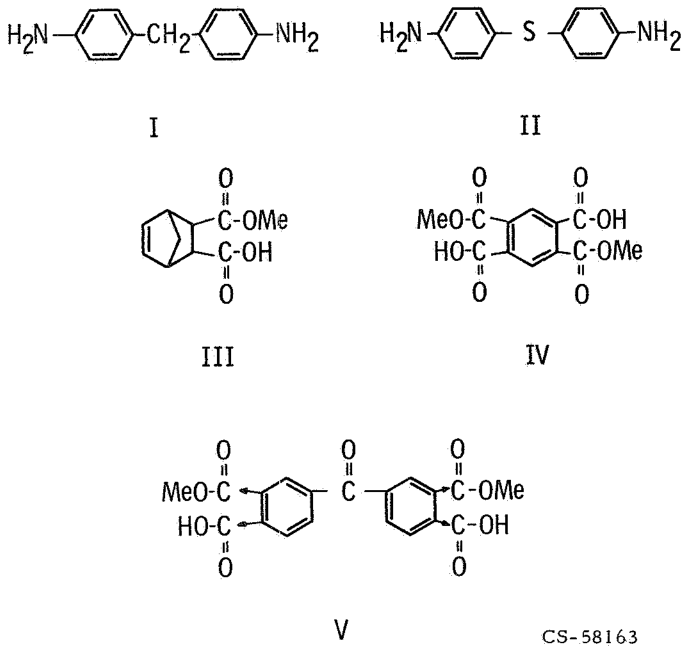

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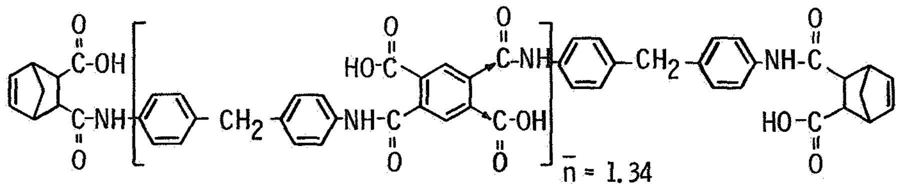
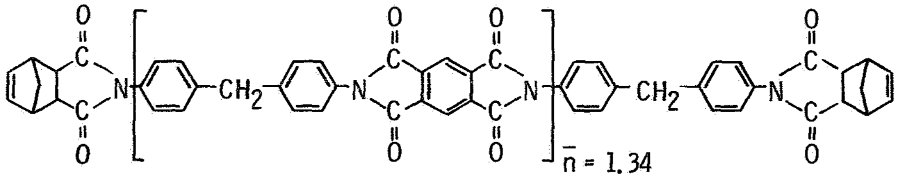
FIGURE 2

PIOP PREPOLYMERS



(A) AMIDE ACID PREPOLYMER.



(B) IMIDIZED PREPOLYMER. CS-58162

FIGURE 3

VISCOSITY CHANGES OF PIOP AMIDE ACID AND MONOMERIC SOLUTION A

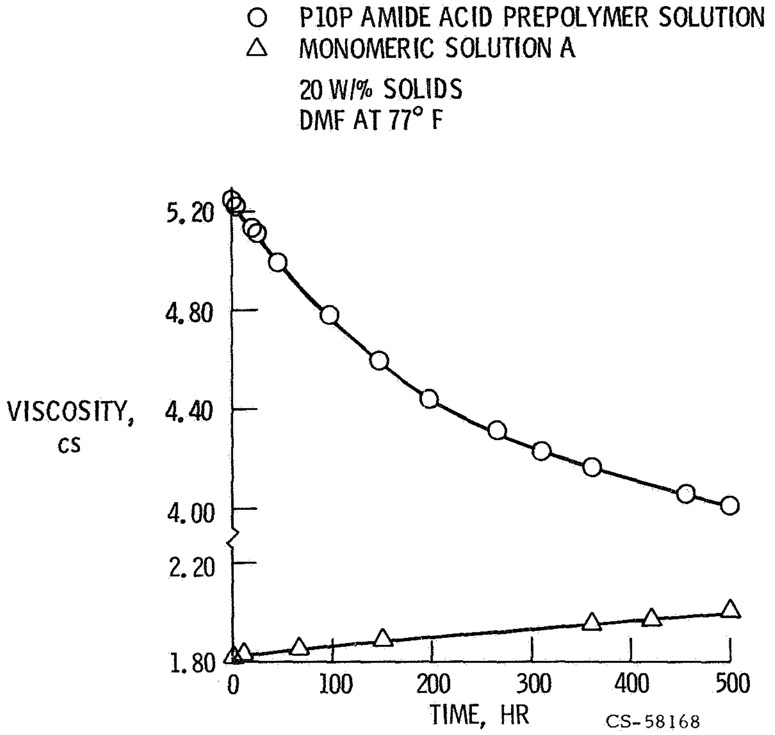


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FIGURE 4

PERCENT WEIGHT LOSS OF POLYIMIDE/HTS GRAPHITE FIBER COMPOSITES

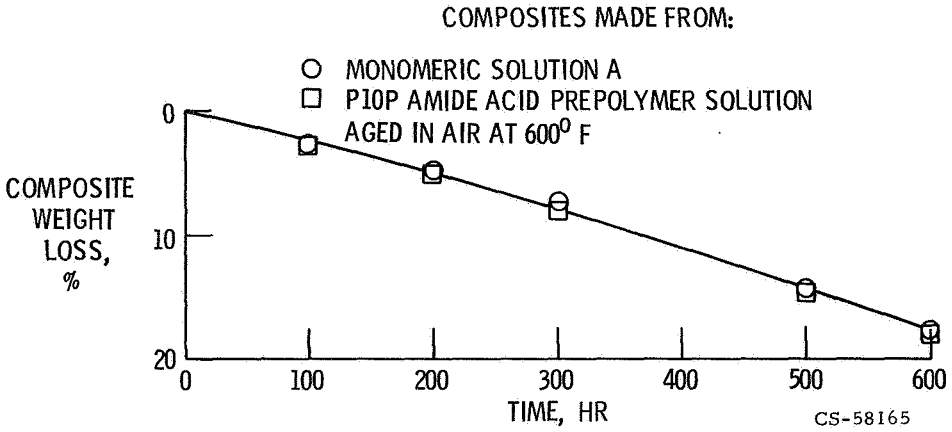


FIGURE 5

FLEXURAL STRENGTH OF POLYIMIDE/HTS GRAPHITE FIBER COMPOSITES

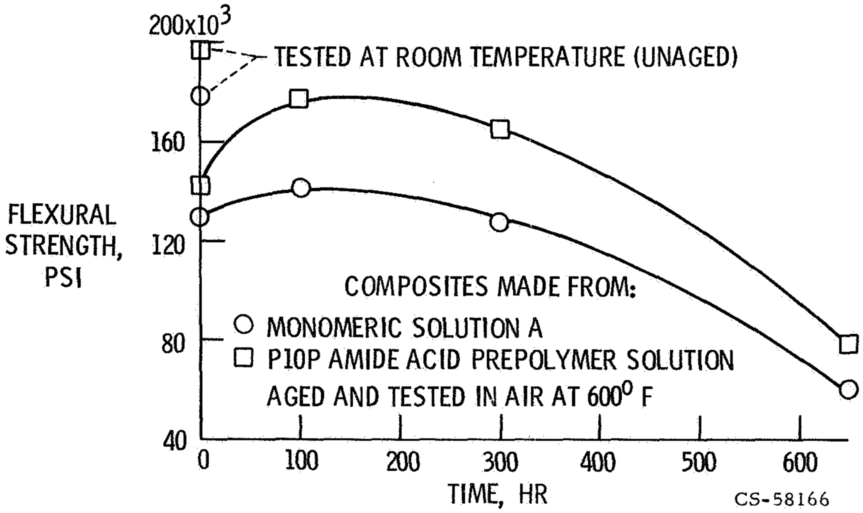


FIGURE 6

FLEXURAL MODULUS OF ELASTICITY OF POLYIMIDE/HTS GRAPHITE FIBER COMPOSITES

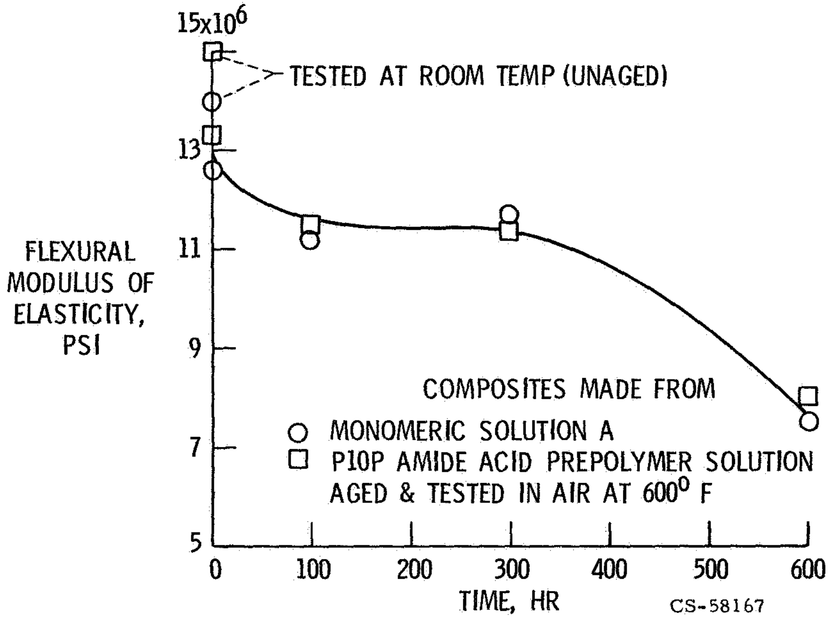
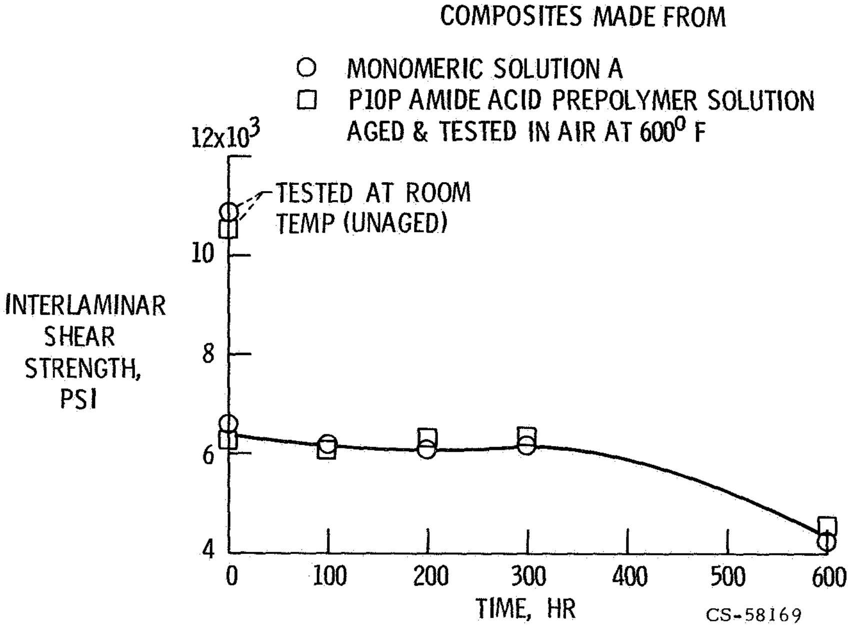


FIGURE 7

INTERLAMINAR SHEAR STRENGTH OF POLYIMIDE/HTS GRAPHITE COMPOSITES



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