PROCESSABLE HIGH-TEMPERATURE-RESISTANT
ADDITION-TYPE POLYIMIDE LAMINATING RESINS

by Tito T. Serafini and Peter Delvigs

Lewis Research Center
Cleveland, Ohio 44135

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**Authors**: Tito T. Serafini and Peter Delvigs

**Performing Organization Name and Address**: Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio 44135

**Sponsoring Agency Name and Address**: National Aeronautics and Space Administration
Washington, D. C. 20546

**Abstract**: This report reviews basic studies that were performed using model compounds to elucidate the polymerization mechanism of the so-called addition-type (A-type) polyimides. The fabrication and properties of polyimide/graphite fiber composites using A-type polyimide prepolymer as the matrix are also reviewed. An alternate method for preparing processable A-type polyimides by means of in situ polymerization of monomer reactants (PMR) on the fiber reinforcement is described. The elevated temperature properties of A-type PMR/graphite fiber composites are also presented.

**Key Words**: Monomer reactants, Thermally stable polymers, Polyimides, Composites

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SUMMARY

An important finding that resulted from research that was conducted to develop improved ablative resins was the discovery of a novel approach to synthesize processable high-temperature-resistant polymers. Low-molecular-weight polyimide prepolymers end-capped with norbornene groups were polymerized into thermo-oxidatively stable modified polyimides without the evolution of void producing volatile materials.

This report reviews basic studies that were performed using model compounds to elucidate the polymerization mechanism of the so-called addition-type (A-type) polyimides. The fabrication and properties of polyimide/graphite fiber composites using A-type polyimide prepolymers as the matrix are also reviewed. An alternate method for preparing processable A-type polyimides by means of in situ polymerization of monomer reactants (PMR) on the fiber reinforcement is described. The elevated temperature properties of A-type PMR/graphite fiber composites are also presented.

INTRODUCTION

In order to synthesize polymers capable of withstanding temperatures of about 315°C (600°F) for extended periods of time, it is necessary to incorporate thermo-oxidatively stable aromatic and/or heterocyclic structural units in the polymer molecular structure. Until recently, all thermally stable polymers were synthesized by condensation reactions. These polymers can be referred to as C-type polymers. There are a number of disadvantages associated with the use of C-type polymers as matrix resins for fiber reinforced composites. The primary disadvantage is conversion of the polymer into an intractable state prior to the complete elimination of void-producing volatile materials.

Under NASA sponsorship, TRW, Inc., developed an approach to prepare processable
thermally stable polyimides, known as A-type polyimides, which cure by an addition reaction (ref. 1). This approach utilizes low molecular weight amide-acid prepolymer and capped with reactive norbornene groups that polymerize into thermo-oxidatively stable polyimides without the evolution of byproducts. A method was developed in our laboratory to fabricate A-type polyimide/fiber composites using a technique of in situ polymerization of monomers (ref. 2).

This report reviews composites fabrication and characterization studies that were conducted using the prepolymer or in situ polymerized A-type polyimides.

**DISCUSSION**

Studies performed under NASA sponsorship to develop improved ablative resins were reported by Burns, Lubowitz, and Jones (ref. 1). These investigators concluded that the polymers best able to withstand the combustion environment of fluorine containing propellants were polymers whose molecular structure contained a multiplicity of aromatic groups. Their studies with model compounds such as those shown in figure 1 to determine the temperatures required for thermally induced aromatization led to the discovery of what are known today as addition-type (A-type) polyimides. It can be seen in figure 1 that the group II bis-imide capped with the partially unsaturated bridged structure gave a higher weight retention than either group I (completely aromatic) or

![Figure 1: Thermograms of model bisimides (ref. 1). Environment, nitrogen; scanning rate, 3°C per minute.](image-url)
group III (partially unsaturated) model compounds. The inflections in the thermogravi-
metric analysis (TGA) curve between 200° and 300° C for the group II model compounds,
compared with the smooth curves for model compounds in groups I and III, led them to
conclude that macromolecules were formed during the heating of the group II model
compounds. They referred to the polymerization process as pyrolytic polymerization.
They immediately realized the significance of this finding and their continued research
culminated in the development of the A-type polyimide known as P13N. This processable
polyimide met with considerable acceptance by the plastics industry. The structures of
the amide-acid and imidized prepolymers of P13N are shown in figure 2. P13N is avail-
avable from the Ciba-Geigy Corporation which acquired license to the material from TRW,
Inc.

Under subsequent NASA sponsored programs (refs. 3 and 4) studies were performed
to develop A-type polyimides having improved thermo-oxidative stability (TOS) at 315° C
(600° F) for use as laminating resins. Some studies were also performed during these
programs to elucidate the mechanisms of the reactions leading to the formation of
macromolecules. Pyrolysis studies were conducted with the model compound I,
N-phenyl-5-norbornene-2, 3-dicarboximide (fig. 3) under vacuum, pressure, or pres-
sure and catalyst environments. It was concluded that essentially the same polymer
structure results from pyrolysis in any of the environments (ref. 4). It should be
pointed out that low-molecular-weight oligomers, instead of high molecular weight poly-
mers, resulted from the pyrolysis of the model compound. The postulated reaction
mechanism is shown in figure 3. The first step involves a reverse Diels-Alder reaction,
which leads to the formation of cyclopentadiene and N-phenylmaleimide, which imme-
diately co-react to form adduct II. It was further postulated that the adduct initiates
homopolymerization of the norbornene species I. The various environments only seem
to affect the degree of polymerization. Thermogravimetric analyses of residues pro-
duced at pyrolysis temperatures in the range of 271° to 350° C indicated the optimum
pyrolytic polymerization temperature to be 316° C.

Figure 4 shows the results from isothermal-gravimetric analysis (ITGA) in air at
315° C (600° F) of various A-type polyimides (ref. 3). The label given on each curve
identifies the reactants that were used to synthesize the prepolymers, which were sub-
sequently cured to cross-linked polyimides. The stoichiometry of the reactants was
selected to prepare prepolymers having an average formulated molecular weight (FMW)
of 1300. It is clear from the results presented in figure 4 that the use of
4,4'-oxydianiline (ODA) with either 3,3',4,4'-benzophenonetetracarboxylic dianhydride
(BTDA) or pyromellitic dianhydride (PMDA) resulted in A-type polyimides exhibiting
lower TOS than the use of 4,4'-methylenedianiline (MDA). The most significant finding
was that the polymers made from NA/MDA/PMDA prepolymer exhibited higher TOS
than any of the other A-type polyimides including P13N (curve labeled NA/MDA/BTDA
in fig. 4).
Figure 2. - P13N prepolymers.

Figure 3. - Pyrolytic polymerization reaction mechanism (ref. 4).

Figure 4. - Weight loss of A-type polyimides (ref. 3). Environment, air at 315°C (600°F); formulated molecular weight, 1300.
Composite fabrication studies with the NA/MDA/PMDA prepolymer showed that it was necessary to adjust the stoichiometry of the reactants to yield prepolymer having an average FMW of 1000. This prepolymer became known as P10P. The reduction in the FMW was necessary for adequate resin flow. Properties of composites made from the P10P prepolymer and Hercules HTS graphite fibers are shown in figure 5 as a function of exposure time in air at 260° and 315° C (500° and 600° F) (ref. 5). The mechanical property results presented in figure 5 clearly show excellent retention of properties at 260° C (500° F) for 1000 hours. In contrast, at 315° C (600° F) after 600 hours of exposure the composites retained approximately 30 percent of their room temperature values. It was suggested (ref. 5) that some of the composite property degradation at 315° C (600° F) could be attributed to oxidative degradation of the HTS graphite fiber.

![Diagram](https://example.com/diagram.png)

Figure 5. Properties of HTS/P10P composites as function of time at temperature (ref. 5).
<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>Monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid</td>
<td>NE</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>Dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid</td>
<td>BTDE</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>2, 5-dicarbomethoxyterephthalic acid</td>
<td>PMDE</td>
</tr>
</tbody>
</table>

Figure 6. - Viscosity changes of P10P amide acid prepolymer solution and monomer solution A (ref. 2). 20 weight percent solids in DMF at 25°C.
To prepare A-type polyimides, another approach was developed in our laboratories (ref. 2). Our approach eliminates the need for prepolymer synthesis and circumvents some of the shortcomings of A-type amide-acid prepolymers. The method involves the use of ester-acids rather than anhydrides, thereby preventing the formation of prepolymers at room temperature. A solution containing a diamine and the ester-acids is used to impregnate the reinforcing fibers. In situ polymerization of the monomer reactants (PMR) occurs upon heating the impregnated fibers. Table I shows the structures of the various ester-acids used in the study reported in reference 2. Figure 6 shows the variation of solution viscosity with time for monomer and prepolymer solutions. Monomer solution A (fig. 6) has the same stoichiometry as the amide-acid prepolymer P10P. Figure 6 shows the following: (1) Monomer solutions exhibit considerably less viscosity variation than prepolymer solutions, and (2) monomer solutions have a much lower viscosity. Their lower viscosity enhances fiber wetting and also permits the use of solutions having higher solids contents. In contrast to amide-acid prepolymers (which require the use of high boiling aprotic solvents, such as N,N-dimethylformamide), low boiling alcohols, that is, methanol, can be used as solvents for monomer solutions.

The variation of composite interlaminar shear strength with exposure time in air at 315°C (600°F) for HTS graphite composites made from either a monomer or prepolymer solution is shown in figure 7. It can be seen that the interlaminar shear strength retention of the PMR/HTS fiber composites was essentially identical to the interlaminar shear strength retention of the P10P/HTS fiber composites. Comparison of other properties, such as flexural strength, established the utility of the PMR approach. In fact, a composite made from a NE/MDA/BTDE solution, in which the stoichiometry had been selected to yield a prepolymer having an average FMW of 1500, exhibited a 9.5-percent
weight loss after 600 hours in air at 315° C (600°F) (ref. 2). Under identical conditions the P10P/HTS composite weight loss was approximately 18 percent.

Studies conducted to establish the validity of the aforesaid finding and to improve the TOS of PMR A-type polyimides are reported in reference 6. In the earlier work using the PMR approach, the diamines used in the prepreg solutions were either MDA or TDA (ref. 2). Six additional diamines were used in a composite screening study reported in reference 6. Their structures are shown in table II.

**TABLE II. - STRUCTURES OF DIAMINES**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂N-CH₂-CH₂-NH₂</td>
<td>4, 4'-methylenedianiline</td>
<td>MDA</td>
</tr>
<tr>
<td>H₂N-CH₂-O-NH₂</td>
<td>4, 4'-oxydianiline</td>
<td>ODA</td>
</tr>
<tr>
<td>H₂N-CH₂-S-NH₂</td>
<td>4, 4'-thiodianiline</td>
<td>TDA</td>
</tr>
<tr>
<td>H₂N-CH₂-SO₂-NH₂</td>
<td>4, 4'-sulfonyldianiline</td>
<td>SDA</td>
</tr>
<tr>
<td>H₂N-CH₂-CH₂-NH₂</td>
<td>4, 4'diaminostilbene</td>
<td>DAS</td>
</tr>
<tr>
<td>H₂N-CH₂-NH₂</td>
<td>p-phenylenediamine</td>
<td>PPDA</td>
</tr>
<tr>
<td>H₂N-CH₂-NH₂</td>
<td>m-phenylenediamine</td>
<td>MPDA</td>
</tr>
</tbody>
</table>
The chemical composition and some properties of 11 different composites are summarized in table III. The stoichiometry of the reactants was governed by the desired number of imide rings or by the desired percent of alicyclic content. The formulated molecular weight is considered to be the average molecular weight of the imidized prepolymer that could have been formed if amide-acid prepolymer solutions had been synthesized. For any given monomer combination, the molar ratio of 5-norbornene-2, 3-dicarboxylic acid monomethyl ester/diamine/tetracarboxylic acid dimethyl ester was 2/(n + 1)/n. The composite processing conditions used throughout this investigation were essentially those that had been optimized for amide-acid prepolymer solutions (ref. 3).

Samples 1 to 5 are chemically similar to the commercially available P13N resin. All of them, however, have a lower alicyclic content than P13N. Samples 1 to 3 possessed a combination of unusually high thermo-oxidative stability and high initial interlaminar shear at room temperature. The results from a more detailed study of their mechanical properties after exposure at 315° C (600° F) will be described in a subsequent section of this paper.

Sample 6 has a composition equivalent to that of P10P prepolymer. Its properties

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Monomer solution composition</th>
<th>Average number of repeat units, n</th>
<th>Formulated molecular weight, FMW</th>
<th>Laminate properties</th>
<th>Composite weight loss, percent&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interlaminar shear at 24° C (75° F)</td>
<td>Interlaminar shear at 315° C (600° F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>ksi</td>
</tr>
<tr>
<td>1</td>
<td>NE/MDA/BTDE</td>
<td>2.087</td>
<td>1500</td>
<td>105.5×10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>15.3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2.603</td>
<td>1750</td>
<td>99.3</td>
<td>14.4</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>2.913</td>
<td>1900</td>
<td>103.4</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>3.120</td>
<td>2000</td>
<td>67.6</td>
<td>9.8</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>5.186</td>
<td>3000</td>
<td>56.5</td>
<td>8.2</td>
</tr>
<tr>
<td>6</td>
<td>NE/MDA/PMDE</td>
<td>1.342</td>
<td>1000</td>
<td>74.5</td>
<td>10.8</td>
</tr>
<tr>
<td>7</td>
<td>NE/MDA/PMDE</td>
<td>1.868</td>
<td>1200</td>
<td>84.8</td>
<td>12.3</td>
</tr>
<tr>
<td>8</td>
<td>NE/MDA/PMDE</td>
<td>2.658</td>
<td>1500</td>
<td>42.1</td>
<td>6.1</td>
</tr>
<tr>
<td>9</td>
<td>NE/MDA/(1BTDE:1PMDE)</td>
<td>2.338</td>
<td>1500</td>
<td>98.6</td>
<td>14.3</td>
</tr>
<tr>
<td>10</td>
<td>NE/MDA/(1BTDE:1PMDE)</td>
<td>2.917</td>
<td>1750</td>
<td>93.8</td>
<td>13.6</td>
</tr>
<tr>
<td>11</td>
<td>NE/MDA/(1BTDE:1PMDE)</td>
<td>3.264</td>
<td>1900</td>
<td>86.9</td>
<td>12.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>After 600 hr in air at 315° C (600° F).
were shown to be virtually identical with those of composites made from P10P. Samples 7 and 8 have the same chemical composition as sample 6, but differ in stoichiometry.

The monomer combination used in samples 9 to 11 was selected to investigate the effect of increasing the number of imide linkages over that in the corresponding samples 1 to 3 while maintaining a constant alicyclic content. For example, sample 9 has the same alicyclic content as sample 1, but a higher number of imide linkages. The higher number of imide linkages is achieved by partial substitution of PMDE for BTDE. Theoretically this should give a correspondingly higher thermo-oxidative stability. Actually, the results indicate that the thermo-oxidative stabilities of samples 9 to 11 are approximately equivalent to those of samples 1 to 3.

Results from the screening study with diamines other than MDA showed that the incorporation of these diamines did not improve composite properties. In some instances, for example, with PPDA, BZD, and DAS, the composites were poorly consolidated and could not be tested.

Based on the results of the screening study and detailed investigation of samples 1 to 3, 7, and 9, the monomer system that displayed the best overall balance of processability and thermomechanical properties was NE/MDA/BTDE in which \( n \) has a value of 2.087 (sample 1, FMW = 1500). Some results of the studies conducted with monomer systems having FMW's of 1500, 1750, 1900, and 1000 (samples 1 to 3, and 6, table I) are presented in figure 8. The range of interlaminar shear strength values is 95 to 123 newtons per square meter (13 800 to 17 800 psi). These values are somewhat higher than those previously reported (ref. 5) for A-type polyimide/HTS fiber composites. There is a considerable drop in the interlaminar shear strength when the composites are tested at 315° C (600° F), to as low as 34 newtons per square meter (5000 psi). There was a greater decrease for samples 1 to 3 than for sample 6. The interlaminar shear strength decrease for sample 6 is nearly identical to that reported by Hanson and Serafini (ref. 6).

![Figure 8. Interlaminar shear strength of polyimide/HTS graphite fiber composites (ref. 6).](image-url)
It appears that composite samples 1 to 3 underwent a postcure on exposure in air at 315°C (600°F), since the interlaminar shear strength increased during exposure, whereas that of sample 6 decreased with time. The important fact to note is that the interlaminar shear strength of samples 1 to 3 remained nearly constant from 100 to 600 hours. The strength after 600 hours for samples 1 to 3 averaged approximately 45 newtons per square meter (6500 psi). The data for samples 1 to 3 represent the best interlaminar shear retention for A-type polyimide/HTS fiber composites reported to date. The interlaminar shear strength of sample 1 increased to 48 newtons per square meter (7000 psi) after 200 hours of exposure and remained constant up to 600 hours of exposure.

Photomicrographs of a cross section of composite sample 1, before and after exposure, are shown in figure 9. There is no evidence of voids in the composite as a result of fabrication. After exposure at 315°C (600°F) for 600 hours, the composite shows an extremely small number of voids. This indicates that the original void-free composite was very resistant to the oxidative degradation that might occur by a diffusion mechanism. Any degradation that did occur, took place on the surface of the composite.

Figure 9. - Polyimide/HTS graphite fiber composites before and after exposure in air at 315°C (600°F) for 600 hours (ref. 6).
The absence of internal voids after exposure also indicates that the composite is very resistant to thermal decomposition.

Under NASA contract NAS3-15829, TRW, Inc., is using the PMR approach to develop high-temperature-resistant polyimide/graphite fiber air breathing engine components, such as blades and vanes. The monomer system being investigated is NE/MDA/BTDE at FMW's in the range of 1500 to 1900. Figure 10 shows the average weight loss of HMS graphite fiber composites exposed at 315°C (600°F) in air. Also shown in the figure is the weight loss of composites fabricated with HTS fiber (ref. 6). It can be seen that the HMS composites exhibited excellent weight retention (~96 percent). The greater weight loss of the HTS composite can be attributed to the lower thermo-oxidative stability of the HTS fiber (ref. 5). The point that can be made is that the investigators were able to fabricate thermo-oxidatively stable composites using the in situ PMR approach with little or no difficulty.

Figure 11 is a flow chart of the PMR approach for the fabrication of high-performance-resin/fiber composites. We have been able to use the PMR approach for the fabrication of polyphenylquinoxaline/graphite fiber composites. These studies will be described in a forthcoming publication. The PMR approach as outlined in figure 11 is considerably less complex than composites fabrication processes that use conventional prepreg fabrication techniques. In addition to the advantages discussed previously, such as low viscosity, high solids content solutions, etc., the PMR approach eliminates the problems associated with packaging, shipping, and storage of prepreg. The PMR approach also should ultimately lead to overall cost savings.

We view the PMR approach as one that should permit the use of a number of polymers that have demonstrated outstanding high-temperature TOS but could not be used as matrix resins because of the intractability inherent in their polymer structure.
CONCLUSIONS

Modification of the molecular structure of aromatic polyimide precursors by incorporating norbornene end groups is an excellent approach to achieve processable thermally stable polyimides for use as matrix resins in fiber reinforced composites. Preparation of A-type polyimide/fiber composites using a technique of in situ polymerization of monomer reactants (PMR) is a powerful approach that should be applicable to a variety of high-temperature polymers. The PMR approach offers a number of advantages to the composites fabricator, such as the use of low boiling, relatively nontoxic solvents, and simplified materials handling logistics.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 26, 1973,
501-21.

REFERENCES


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—National Aeronautics and Space Act of 1958

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