Low-Cost Production of Composite Bushings for Jet Engine Applications

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PROJECT SUMMARY

Although advanced composites currently meet the light-weight design requirements for existing engine applications, the current economic climate of the aerospace community demands low cost composite components that are reliable. Variable stator vane bushings represent one such composite application that has been targeted as a "high-cost" component. Although the composite bushings are small in size, they are utilized in every military and commercial aircraft engine.

The objectives of this research program were to reduce the manufacturing costs of variable stator vane bushings by 1) eliminating the expensive carbon fiber braiding operation, 2) replacing the batch mode impregnation, B-stage, and cutting operations with a continuous process, and 3) reducing the molding cycle and machining operations by utilizing injection molding to achieve near-net shapes. Implementation of this plan would significantly impact both the starting raw material costs and the labor hours which are the two major cost reductions needed for manufacturing low cost variable stator vane bushings.

Maverick initiated the research program by synthesizing two modified versions of the current NASA formulation for low-toxicity AMB-21 polyimide solution. These systems, AMB-17XLD and AMB-TPD were designed to offer enhanced glass transition temperature (Tg) and thermal stability when compared to AMB-21.

New Hampshire Ball Bearing was successful in fabricating both AMB-17XLD and AMB-TPD braided bushings by utilizing a cure cycle that was similar to PMR-15. Both systems molded beautifully with low internal porosity and minimal surface blemishes. The composite bushings achieved high glass transition temperature after post-cure (+300°C) and comparable weight loss to the PMR-15 bushings. AMB-17XLD bushings made with "batch-mode" molding compound (at 0.5 in. fiber length) achieved a +300 lb.-force flange break strength which was superior to the continuous braided-fiber reinforced bushing. Based on these results, NHBB expressed an interest in continuing the development of non-MDA resin technology for bushing applications not to exceed 300°C.

Chemical modification to the original AMB-21 formulation was successfully carried out by utilizing a "novel" chemistry approach which involved a fairly unreactive diamine (2,6-diaminopyridine, or DAP). Replacing BAPP with different stoichiometric amounts of DAP was similar to adding an endcap to AMB-21 for controlling molecular weight. This was reflected in the Brookfield viscosity measurements of the initial poly(amic-acid) solutions.
Two thermoplastic polyimide resins (without and with DAP) were synthesized in order to generate injection molding compound powders. Excellent processing results were obtained at injection temperatures of 343°C for the control (without DAP) and 304°C for the polyimide powder containing DAP. Micro-tensile specimens were produced from each resin type and the Tg measurements (by TMA) for these samples were equivalent to AURUM®. Thermal Gravimetric Analysis (TGA) conducted at 10°C/min showed that the non-MDA AMB-type polyimide thermoplastics had comparable weight loss to PMR-15 up to 500°C.

INTRODUCTION

1. Identification of the Problem and Opportunity

The weight of aerospace structures can be significantly reduced by the application of high-performance polymeric composites. By replacing metallic components with composite materials, a weight savings between 25 and 50 percent can be realized. The advent of high modulus fibers and thermally stable polymers has made possible the introduction of composites into the higher temperature regimes that are associated with aircraft engines.

Although advanced composites currently meet the light-weight design requirements for existing engine applications, the current economic climate of the aerospace community demands low cost composite components that are reliable. Variable stator vane bushings represent one such composite application that has been targeted as a "high-cost" component. Although the composite bushings are small in size, they are utilized in every military and commercial aircraft engine.

The goal of this research program was to significantly reduce the retail cost of composite variable stator vane bushings. A two pronged approach involving both materials and process engineering was utilized in an attempt to impact production cost: 1) development of a continuous process for producing high-temperature molding compound for compression molding, and 2) compounding oligomeric polyimide powders for injection molding applications.

2. Material Issues

For composite applications in the range of 250°C to about 325°C the resin system of choice has generally been PMR-15. In fact, the production and use of PMR-15 has grown during the past twenty years from laboratory quantities to an annual industry usage of approximately 50,000 pounds, mostly in the aircraft industry where the high strength, modulus, and thermal stability of the composite is highly valued.

However, PMR-15 contains 4,4'-methylenedianiline (MDA), a known animal carcinogen, a suspected human carcinogen, and a known kidney and liver toxin (1). When thousands of pounds of PMR-15 prepreg are being manufactured, or when hundreds of pounds of this material are being laid up into composite structures, exposure to MDA becomes a serious health hazard. Thus it has become necessary for the Occupational Safety and Health Administration (OSHA) to issue and enforce very strict regulations regarding worker exposure to MDA. These regulations have already significantly increased the manufacturing costs for suppliers and fabricators of PMR-15.
Due to these environmental issues, scientists at NASA Lewis Research Center initiated programs to synthesize and evaluate low-toxicity, high-temperature polyimide systems to replace PMR-15 and its highly toxic diamine, MDA (2). Their efforts have led to several non-MDA formulations which offer potential to replace PMR-15 (3, 4). For this investigation, AMB-21 was chosen as the low-cost, non-toxic PMR-15 replacement.

3. Background

GE Aircraft Engines (GEAE) is one of the largest users of composite variable stator vane bushings in the world. Other aerospace companies who also procure these composite components include Allison, Pratt & Whitney, Rolls Royce, and SNECMA. Over the years, these engine companies have established an excellent supplier base which has fostered competition; however, the retail component price still remains expensive. Their current objectives are to reduce component costs and move towards environmentally friendly composite materials.

The high bushing cost is due to both the materials of construction as well as the extensive manual labor that is necessary during production (Figure 1). In order to manufacture composite variable stator vane bushings, the Panex carbon fiber reinforcement is first braided into a continuous tube or sock by a commercial braiding house (e.g. Atkins & Pearce). The braid is then pre-impregnated with a polyimide resin either under pressure or vacuum, and B-staged (or imidized) in an air re-circulating oven. The hardened preform is then cut to length and placed into a matched metal die tool. Several bushing tools are then loaded into a carriage and compression molded at high temperature and pressure. The cure cycle time is approximately one hour and the post cure cycle can last up to twenty four hours. After molding, each bushing is machined to print and inspected for quality before shipment to the customer.

Expensive materials and high manual labor contribute to the increased cost of composite bushings.

Figure 1: Current Bushing Fabrication Process
4. Objectives

The objectives of this research program were to reduce the manufacturing costs of variable stator vane bushings by 1) eliminating the expensive carbon fiber braiding operation, 2) replacing the batch mode impregnation, B-stage, and cutting operations with a continuous process, or 3) reducing the molding cycle and machining operations by utilizing injection molding to achieve near-net shapes. Implementation of this plan would significantly impact both the starting raw material costs and the labor hours which are the two major cost reductions needed for manufacturing low cost variable stator vane bushings.

5. Work Tasks

The overall goal of this research was to develop low-cost processing technologies for the manufacture of aircraft engine bushings. The specific work tasks to be accomplished in the course of this study included the following:

Task 1: AMB polyimide molding compound and process development:

- Using AMB-21 as the base polymer, conduct studies to develop a polyimide/graphite molding compound for use in compression molding of aircraft engine stator vane bushings.
- Conduct studies to develop a continuous process for producing chopped fiber molding compound.
- Fabricate and test bushings for porosity, glass transition temperature (Tg), thermo-oxidative stability (TOS), and flange break.

Task 2: AMB polyimide injection molding compound and process development:

- Using AMB-21 as the base polymer, conduct studies to develop a resin amenable to an injection molding process.
- Conduct processing studies to develop a bulk compound for injection molding of components.
- Using the bulk compound and the injection process, fabricate test bushings/components for physical and mechanical property evaluation.

DISCUSSION

1. Chopped Molding Compound

Maverick Corporation has been working with U. S. Composites in Albany, NY to develop a continuous process for producing chopped fiber molding compound. A schematic of the process can be found in Figure 2. Essentially, the carbon fiber bobbin is unwound on to a drive motor which controls the line speed of the process. The fiber then passes through a proprietary resin bushing which impregnates the fiber tow with polyimide solution. The impregnated tow then goes through a tube furnace which volatilizes the solvent and imidizes the resin onto the carbon
fiber. The pre-imidized tow then proceeds to a winder followed by a rotating chopper which produces the final molding compound.

A continuous molding compound line would provide inexpensive starting material for compression molding variable stator vane bushings.

Figure 2. Schematic of Continuous Molding Compound Line.

In order to conduct research studies without purchasing major capital equipment, the proposed molding compound line shown in Figure 2 was modified to run in "batch" mode (Figure 3). In this operation, the pre-imidized tow was wound on a bobbin, and then placed in an air recirculating oven in order to complete the imidization cycle. Once "B-staged", the tow was chopped to desired lengths (e.g. 1/8, 3/8, or 1/2 in.) to produce molding compound. A systematic study was conducted by U. S. Composites in order to determine line speed and tension.

A "batch" mode operation provided an inexpensive method for conducting research studies.

Figure 3. Schematic of Batch Molding Compound Line.

Once the molding compound was manufactured, generic bushings were compression molded at New Hampshire Ball Bearing (NHBB) by utilizing existing production tooling. Preliminary molding cycle experiments were conducted on braided-reinforced bushings in order to define the process parameters that would be needed for "molding compound" parts.
It should be noted that several technical challenges must be overcome if molding compound bushings are to be successful. First, the flange break strength requirement for variable stator vane bushings is approximately a 120 lb.-force load. In the current braided bushing design, the flange break strength exceeds 220 lb.-force.

For molding compound components, the fiber length becomes the key issue. The longer length molding compound (0.5 in.) has a better chance of meeting this strength requirement than the shorter length (0.125 in.) material. However, shorter length systems are easier to mold into high-quality parts. The trade-off becomes one of strength versus processability.

Maverick will manufacture bushings from molding compounds that have different fiber lengths (e.g., 1/8, 3/8, or 1/2 in.) and NHBB will test for flange break strength. The possibility exists that a combination or mixture of several fiber lengths may be needed to comply with the flange break strength requirements.

An additional point to be concerned with is thermal oxidative stability. A bushing made from molding compound may have higher weight loss than the traditional high-cost braided bushings. This is due primarily to the relatively high fiber-matrix interface surface area that would be exposed after machining the molding compound part.

**Experimental**

Maverick initiated the research program by synthesizing two modified versions of the current NASA formulation for AMB-21 polyimide solution. (The basic monomers utilized in AMB-21 can be found in Figure 4.) These systems, AMB-17XLD and AMB-TPD were designed to offer enhanced glass transition temperature (T_g) and thermal stability compared to the AMB-21 baseline.

Maverick's AMB-17XLD formulation represents 40 mole % replacement of BAPP with 30 mole % p-phenylenediamine and 10 mole % of 2,6-diaminopyridine (DAP), where as the AMB-TPD formulation represents 30 mole % replacement of BAPP with 15 mole % p-phenylenediamine and 15 mole % DAP. The solvent system for these ester solutions was changed from 100% methanol to a mixture of methanol/n-methylpyrrolidinone in order to be consistent with current bushing production cure cycles.

U.S. Composites Corporation was contracted to manufacture chopped molding compound from both the AMB-17XLD and the AMB-TPD polyimide systems. U.S. Composites "impregnated" the carbon fiber tow on a continuous basis; however, the imidization step was conducted in batch mode (see Figure 3). The pre-imidized fiber tow was cut into various lengths (0.125 - 0.50 in.) and then will be evaluated for processability by New Hampshire Ball Bearing (NHBB), Laconia, NH.

NHBB is currently a GE Aircraft Engines supplier for variable stator vane bushings. The reinforcement in the NHBB/GEAE design utilizes a braided carbon fiber preform which represents the current state-of-the-art (rather than chopped fiber molding compound). Maverick requested that NHBB evaluate the AMB-17XLD and AMB-TPD resin systems using braided
fiber construction. The one advantage of using NHBB for this program is that they will gain experience in working with molding compounds, and this will allow NHBB to easily transition the research into production.

*AMB-21 was chosen as the base polyimide resin due to low-cost and low-toxicity.*

![Monomers utilized in the formulation of AMB-21 polyimide resin.](image)

The preliminary fabrication trials conducted by NHBB consisted of molding both resin systems with their production cure cycle for PMR-15. The AMB-17XLD molded beautifully with low internal porosity; however, the AMB-TPD produced bushings with both voids and surface blemishes. Maverick worked closely with GE Aircraft Engines and NASA-Lewis in developing a "robust" compression molding cycle for both materials. Both rheology (RDS) and thermal gravimetric analysis (TGA) data were used to recommend alternative cure cycles.

NHBB was successful in fabricating both AMB-17XLD and AMB-TPD braided bushings by utilizing the "improved" cure cycle. Both systems molded beautifully with low internal porosity and minimal surface blemishes. The composite bushings achieved high glass transition temperature after post-cure (+300°C); however, it should be noted that the 329°C (625°F) post-cure temperature utilized by NHBB was too severe since the outside finish of the bushing turned from "glossy" to "dull." A 316°C (600°F) post-cure (or slower post-cure) was recommended to NHBB for future work. NHBB also agreed to run accelerated thermal oxidative stability testing on both systems in order to compare results to PMR-15 bushings.

In addition to braided bushing fabrication, NHBB proceeded with the "fiber-length" molding trials for the AMB-TPD and AMB-17XLD resin systems. Chopped fiber molding compound from each resin system were evaluated at two different fiber lengths (approximately 1/8 and 1/2
After conducting several molding trials with both lengths, all of the resulting composite bushings were found to be "fuzzy" and severely resin starved. In addition, resin flash was not detected within the tools when they were disassembled.

Although the molding compounds were thought to be a minimum of 50% resin content, it was found that the resin content range, determined by acid digestion, of the molding compounds utilized in this study was only 30-32%. This unexpected result was well below the original 50% objective. It should be noted that during the continuous production of the molding compound, different fiber line speeds were evaluated. Two medium range speeds were selected which offered a balance between having good resin pick-up (visually) vs. the economics of running the line at an extremely slow speed. In either case, both of the speeds that were selected resulted in unusable molding compounds with low resin content.

During the original development studies to produce the molding compounds, various attempts were made to use high monomer solids in the solution bath while maintaining a constant line speed. In this manner, high resin content molding compounds should be achievable. However, when the solution concentration was elevated over 60% monomer solids, the acetone/methanol solvent evaporated much more quickly, and the resin would then form a "skin" which was both sticky and hard to handle. Basically, in a relatively short period of time, the resin became increasingly unworkable, especially with respect to a continuous impregnation process.

In order to obtain a small amount of "useful" molding compound, additional AMB-17XLD resin was synthesized at 60% monomer solids and shipped to NHBB. They then vacuum impregnated the resin into carbon fiber braid and "B-staged" the material in an air re-circulating oven at 210°C. The material was then cut to approximately 0.5 inch fiber lengths and molded into bushings. By using molding compound with high solids content, all parts molded extremely well. These bushings were subjected to both glass transition and thermal oxidative stability testing and compared with PMR-15 data.

2. Polyimide Molding Powders

Maverick Corporation recently obtained an exclusive license on patented technology for aiding in the processing of high-temperature polyimides. It was felt that this process technology could enhance the melt flow characteristics of AMB-21 to the point where pre-imidized oligomers could be injection molded. Maverick Corporation utilized the injection molding facilities of Performance Plastics Inc. (Cincinnati, Ohio) in order to prove technical feasibility of the concept and produce prototype parts for component tests.

Chemical modification to the original AMB-21 formulation was necessary to complete this portion of the project. The "novel" chemistry approach involved a fairly unreactive diamine (2,6-diaminopyridine, or DAP). The nitrogen atom in the heterocyclic ring of DAP is extremely electron withdrawing, and this causes the amine groups to have low reactivity. When one of the two amine groups of DAP reacts with an anhydride (or the alkyl ester) to form either the amide or imide bond (which is also electron withdrawing), the unreacted amine group of DAP becomes deactivated. In fact, this "free" amine group remains unreactive until the processing temperature reaches 220°C.
Essentially, at lower processing temperatures (< 220°C), DAP behaves like a mono-functional monomer (e.g. aniline). This means that replacing BAPP with different stoichiometric amounts of DAP would be similar to adding an endcap to AMB-21 for controlling molecular weight. As long as the processing temperature remains below 220°C, DAP will remain a mono-functional endcap in the AMB-21 formulation. Ultimately, this would result in low molecular weight oligomeric species.

These low molecular weight polyimide oligomers should have increased melt flow, and this would be desirable for injection molding. Once the imide oligomers are compounded into powder and quickly molded into a component, the parts could be slowly heated above 220°C in an air re-circulating oven in order to complete the reaction and to finish building high molecular weight polymer. It should be noted that the "DAP" processing technology can also be used in "PMR" (or alkyl ester) formulations to achieve enhanced resin flow in large composite structures that are fabricated by either autoclave, compression, or resin transfer molding.

Experimental

Several technology review meetings were held between GE Aircraft Engines, Maverick Corp., NASA-Lewis, and Performance Plastics to discuss the feasibility of injection molding near-net-shape polyimide stator vane bushings. It was unanimously decided to conduct all initial resin processing studies with a resin transfer press rather than an actual injection molding machine. This is because the "shot" size of the transfer press is on the order of grams (5-10 g) whereas an injection molding machine requires 5 to 10 pounds of polymer for one molding trial. Performance Plastics was sub-contracted to conduct all thermoplastic processing evaluations on their Dake transfer press (Figure 5) which was retrofitted for high-temperature operation.

Towards the middle of the program, Performance Plastics and Maverick mutually decided to machine tooling for the Dake press which would allow transfer molding of tensile coupons (Figure 5) rather than stator vane bushings. With this type of tool, different resin formulations could be tested for tensile strength. These values could then be compared to literature values for other low-temperature injection moldable resin systems that were commercially available (e.g. AURUM®, PEEK®, TORLON®, or ULTEM®). In addition, it was decided to mold a "standard" production material (such as AURUM®) in the Dake press in order to prove out the tooling. Several "good" tensile coupons were injected with AURUM®, and the tool and Dake press were working as designed.

Two thermoplastic polyimide resins were synthesized in order to generate injection molding compound powders. The first system was formulated to have a 1.01:1 molar ratio of 3,3',4,4'-benzophenonetetracarboxylycianhydride (BTDA) and 2,2-bis(4-(4-aminophenoxyl)phenyl) propane (BAPP). The reaction mixture contained 15 weight percent monomers in 1-methyl-2-pyrroolidinone (NMP) solvent. High molecular weight polymer was produced almost immediately, resulting in extremely high solution viscosity.
Micro-tensile specimens were molded using a resin transfer press rather than an actual injection molding machine.

![Diagram of transfer press and micro-tensile specimen](image)

Figure 5. Schematic of “Dake” transfer press and micro-tensile specimen.

The solution was then diluted to 13 weight percent with NMP to promote better mixing. The total reaction time was 2 hours, and the final reaction temperature was held at 57°C. The solution viscosity was then measured with a Brookfield viscometer using Spindle #6, at 10 rpm. Even after diluting the solution to 13 weight percent, the viscosity was measured to be 45,900 cp. at 25°C.

Of course, by having high solution viscosity, reaction conditions were sufficient to produce high molecular weight poly(amic-acid), and therefore the resulting polyimide would be expected to have good physical properties. However, high solution viscosity can be detrimental during the precipitation of the polymer solutions, especially when attempting to obtain molding powder.

The novel chemistry approach in formulating the second polyimide involved the fairly unreactive diamine 2,6-diaminopyridine, or DAP. This system was formulated to have a 1.01:1.0 ratio of BTDA:diamine, except this time the two diamines consisted of 85 mole % BAPP with 15 mole % DAP. As before, the reaction mixture contained 15 weight percent monomer solids in NMP solution. The reaction conditions were 2 hours at a final temperature of 40°C. High viscosity poly(amic-acid) solution resulted, but dilution was not necessary.

The Brookfield viscosity of the DAP-containing poly(amic-acid) solution measured 600 cp. at 25°C using spindle # 5 at 10 rpm. The lower viscosity solution means that DAP *did* act as an end-cap, resulting in a solution that should be easier to precipitate. Since DAP was present, an
endcap was not needed to control the polymer molecular weight. The overall goal was to find a high molecular weight polyimide oligomer (i.e. the lowest DAP content) that would still melt flow at processing temperatures around 220°C. This would be desirable for minimizing the volatiles that would be evolved from the imidization reactions that would occur during the final post-cure cycle.

In general, there are several ways to "imidize" poly(amic-acid) solutions: 1) precipitation of the poly(amic-acid) solution in a non-solvent followed by thermal imidization in an oven, 2) thermal imidization in an oven, 3) chemical imidization with acetic anhydride and a tertiary amine, and 4) thermal imidization in solution using a reactor with a Dean & Stark trap. The first method is preferred for generating high-surface area molding powders. The other techniques are well suited for generating polyimide films, fibers, or coatings.

In the past, Maverick has had experience and success in precipitating rigid chain poly(amic-acid) solutions in acetone [e.g. systems with 1,2,4,5-benzenetetracarboxilic dianhydride (PMDA)]. The technique involves pouring the poly(amic-acid) solution into a mixing blender full of acetone solvent. The extreme shear mixing within the blender favors the formation of a fine powder which is then filtered, washed, and imidized in an oven.

This technique was tried with the high-viscosity solution, as well as the DAP-containing (lower viscosity) solution. At 13 weight percent solids, the precipitation method described above produced "globs" of material. By diluting either solution to 6.5 weight percent, fibers and strings were obtained. Further dilution resulted in non-continuous fibers or strings, and it wasn't until 1-2 weight percent solids that a fine powder was obtained. These results were unexpected, and a dilution of this magnitude would not be economically feasible in production.

The next isolation technique Maverick attempted was slow thermal imidization in an oven. 500 grams of each solution were placed in aluminum weighing pans and heated in an oven using a "step-wise" B-stage cycle. The final hold temperature was 208°C for approximately 2 hours. Both samples produced tough, hard films. Maverick anticipated this result for the thermoplastic system, but had hoped that the DAP-containing poly(amic-acid) solution would produce a powder rather than a film.

Chemical imidization using acetic anhydride and isoquinoline was the next isolation technique to be studied. A matrix of acetic anhydride/isoquinoline solutions were made ranging from 2:1 molar ratio to the reverse at 1:2. Known amounts of the imidizing solution were added to specific weights of the poly(amic-acid) solutions. Since none of the mixtures would imidize at room temperature, they were warmed slightly on a hot plate. Unfortunately all solutions resulted in "gels" during chemical imidization.

In developing injection moldable powders, isolating the poly(amic-acid) was unexpectedly difficult. Maverick believes the problem was two-fold. The BTDA/BAPP chemical composition resulted in a "flexible" polymer chain backbone, not a rigid system. This in combination with the fact that NMP is an excellent solvent has essentially made the preferred method of precipitation next to impossible as well as uneconomical.
However, both poly(amic-acid) solutions were placed in a reactor and thermally imidized for 2 hours in solution at 180°C. Upon cooling, the solutions "gelled" and the imide product was isolated by grinding the gels in a blender filled with water, followed by vacuum filtration and drying in an oven for 14 hours at 150°C. The filter cakes were ground in a small milling machine, and the resulting powders were yellowish in color and extremely fine. DSC data of these powders revealed sharp melting points at about 285°C, which would be suitable for injection processing. These powders were forwarded to Performance Plastics in order to conduct transfer molding studies in the Dake press.

RESULTS

1. Chopped Molding Compound

New Hampshire Ball Bearing (NHBB) was contracted by Maverick to evaluate the AMB-17XLD and AMB-TPD polyimide resin systems by utilizing braided carbon fiber preforms. Preliminary test data for several of the experimental variable stator vane bushings were collected and compared to PMR-15 and PMRII-50 in Table I shown below:

Table I: Physical and Mechanical Test Data on Selected Braided-Reinforced Bushings.

<table>
<thead>
<tr>
<th>RESIN:</th>
<th>AMB-TPD</th>
<th>AMB-17XLD</th>
<th>PMR-15</th>
<th>PMRII-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>DENSITY (g/cc)</td>
<td>1.34</td>
<td>1.45</td>
<td>1.53</td>
<td>1.57</td>
</tr>
<tr>
<td>VOID CONTENT (Visual)</td>
<td>HIGH</td>
<td>LOW</td>
<td>LOW</td>
<td>LOW</td>
</tr>
<tr>
<td>T_g by TMA (°C)</td>
<td>251/304</td>
<td>335</td>
<td>325-360</td>
<td>345-365</td>
</tr>
<tr>
<td>WEIGHT LOSSa (%)</td>
<td>15.8</td>
<td>28.7</td>
<td>20.1</td>
<td>3.4</td>
</tr>
</tbody>
</table>

aWeight Loss Conditions: 357°C for 24 hours under 85 psia air pressure with four changes/hour.

Several points can be made from the comparative results shown in Table I. First, the current cure cycle for AMB-TPD has not yet been optimized since "high" void content and "low" composite density were measured for these bushings. However, even with high voids, the AMB-TPD resin system exhibited excellent thermal stability with a weight loss of only 15.8 % (vs. 20.1% for PMR-15). Unfortunately, the glass transition temperature for AMB-TPD was found to be lower than expected (251°C) even with a 330°C post-cure.
Conversely, the AMB-17XLD resin system produced bushings with low voids and adequate composite density proving that the current molding cycle was acceptable. The glass transition was found to be equivalent to PMR-15, but the weight loss results were somewhat higher than anticipated (28.7% vs. 20.1% for PMR-15). It appears that a resin formulated between these two systems might represent a PMR-15 replacement for bushing applications.

In molding the AMB-TPD resin system, NHBB noted that the parts distorted dimensionally during the 330°C post-cure. This is reasonable since the glass transition temperature for AMB-TPD was determined to be only 251°C after post-cure. It was thought that a longer, slower post-cure with a 316°C final temperature would be more appropriate for the AMB-TPD resin system.

Therefore, an additional lot of braided-fiber bushings were molded and subjected to the new post-cure keeping the original molding cycle constant. The measured glass transition temperature after this new post-cure was on average 304°C, which represents a 21% increase. It appears that the 330°C post-cure was definitely excessive for the AMB-TPD system.

In order to obtain a small amount of "useful" data on AMB-17XLD molding compound, additional resin was synthesized, vacuum impregnated into carbon fiber braid, and "B-staged" in an air re-circulating oven at 210°C. The pre-imidized material was then cut to approximately 0.5 inch fiber lengths and molded into bushings by NHBB. These bushings were subjected to both glass transition and thermal oxidative stability testing and compared with PMR-15 data as shown in Table II.

Table II: Weight Loss and Glass Transition Results of Composite Bushings.

<table>
<thead>
<tr>
<th>RESIN:</th>
<th>AMB-17XLD</th>
<th>AMB-17XLD (CHOPPED FIBER)</th>
<th>PMR-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg by TMA (°C)</td>
<td>367</td>
<td>313</td>
<td>398</td>
</tr>
<tr>
<td>WEIGHT LOSSa (%)</td>
<td>8.8</td>
<td>9.1</td>
<td>7.2</td>
</tr>
</tbody>
</table>

aWeight Loss Conditions: 316°C for 24 hours under 85 psia air pressure with four changes/hour.

The data in Table II reveal that the AMB-17XLD resin system was considerably more thermally stable at 316°C (weight loss = 8.8%) vs. 357°C (weight loss = 28.7%). The system also appears to be more equivalent to PMR-15 (weight loss = 7.2%) with respect to thermo-oxidative stability at the 316°C test temperature. Although the 0.5 in. "chopped" molding compound bushing had good thermal stability (weight loss = 9.1%), the Tg of the material was slightly depressed.
(313°C) compared to the braided-fiber reinforced specimen (367°C). Conversely, the Tg of the PMR-15 bushing was found to be extremely high (398°C). These results could be an artifact of an abnormal post-cure cycle.

Both the “braided” and the “chopped” AMB-17XLD bushings were visually inspected by NHBB and determined to be fabricated with low porosity. Both were machined to size and subjected to a flange break test. The “batch-mode” molding compound stator vane bushing produced a flange break strength of +300 lb.-force compared to the 200-250 lb.-force break strength measured for the continuous braided-fiber bushing. This was an unexpected but encouraging result.

The only explanation that can be offered at this point might be that when the continuous braided preform is forced to form the flange during molding, it actually might become crushed (or break apart) during the pressure application. The “chopped” fiber, being short and more pliable, would not have this problem, and therefore, would result in a bushing with superior flange strength. Although the “chopped” fiber bushings exhibited a somewhat low Tg, both the weight loss values and the flange break strength appear in order for applications that would not exceed 300°C.

2. Polyimide Molding Powders

DSC data of the two polyimide powders (with and without DAP) revealed sharp melting points approximately at 285°C. This temperature represented a good place to start for the transfer press processing studies, however, neither powder flowed at a 285°C injection temperature. After several days of processing cycles, the best results were obtained at injection temperatures of 343°C for the control (without DAP) and 304°C for the polyimide powder containing DAP. Several micro-tensile specimens were produced from each resin type and the Tg measurements (by TMA) for these samples as well as AURUM® can be found in Table III. After the initial “as-molded” Tg was determined, a 316°C post-cure cycle was employed to determine whether the Tg could be advanced to a higher level.

Table III: Glass Transition Results of Thermoplastic Micro-Tensile Specimens.

<table>
<thead>
<tr>
<th>RESIN:</th>
<th>CONTROL</th>
<th>WITH DAP</th>
<th>AURUM®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg (No P.C.) (°C)</td>
<td>229</td>
<td>218</td>
<td>209</td>
</tr>
<tr>
<td>Tg (316°C P.C.) (°C)</td>
<td>250</td>
<td>240</td>
<td>247</td>
</tr>
</tbody>
</table>

The data in Table III reveal that the AMB-type polyimide resin systems were comparable to AURUM® with respect to Tg; however, Maverick was looking for a much higher-temperature material than what would be currently available commercially. Although not shown, Thermal Gravimetric Analysis (TGA) was conducted at 10°C/min on these specimens along with a
sample of PMR-15. The results showed that the BTDA/BAPP polyimide thermoplastics had comparable weight loss up to 500°C; however, due to the disappointing Tg values, additional physical or mechanical testing was not conducted on these micro-tensile specimens.

CONCLUSIONS

1. Chopped Molding Compound

The "modified" AMB-type resin systems were extremely close to PMR-15 for bushing applications. These non-MDA materials exhibited similar Tg values, comparable thermal oxidative stability at 316°C, and equivalent processing characteristics to PMR-15, but without the toxicity. The "batch-mode" molding compound (at 0.5 in. fiber length) was successfully molded into low-void bushings. These bushings achieved a +300 lb.-force flange break strength which was superior to the continuous braided-fiber reinforced bushing. Based on these results, NHBB expressed an interest in continuing the development of this non-MDA resin technology for bushing applications not to exceed 300°C.

One of the principle drivers of this research program was to reduce the manufacturing costs of variable stator vane bushings by eliminating the expensive carbon fiber braiding operation, and by replacing the batch mode impregnation, B-stage, and cutting operations with a continuous process. Successful implementation of this technology would significantly impact the starting raw material costs and the labor hours associated with bushing fabrication. It was felt that these two major process improvements were needed for manufacturing low cost variable stator vane bushings.

Unfortunately, a continuous process for economically producing chopped fiber molding compound was not successful. Even though different processing parameters were investigated during the continuous production of molding compound, it was found that the resin content range, determined by acid digestion, for all of the molding compounds manufactured in this study was only 30-32%. This unexpected result was well below the original 50% objective. These molding compounds were found to be unusable, producing bushings that were "fuzzy" and severely resin starved.

As stated earlier, the molding compound (at 0.5 in. fiber length) made in a "batch-mode" was successfully molded into low-void bushings and this would eliminate the expense (or cost) of braiding the carbon fiber (since pre-chopped fiber can be purchased direct from the carbon fiber manufacturer). However, another disadvantage of chopped fiber molding compound was discovered during the program.

Molding compound generally has a "bulk" factor associated with it during fabrication of components. This means that material must be filled to the top of the bushing tool and then compressed down in the press. This procedure must be repeated several times (with the current bushing tool design) until enough molding compound is in the mold to sufficiently yield an acceptable part. This process took NHBB at least 20 minutes additional time to load only a four mold bushing carriage. In production, this increase in labor cost would far out weigh the savings in buying the carbon fiber braided preform.
In order to be successful from a manufacturing standpoint, NHBB feels that the bushing tools presently used for the production of braided fiber bushings would have to be re-designed in order to take into account the "bulk" factor of the molding compound. They also recommended that molding compound applications would be more amenable to the fabrication of flat shapes such as washers. Although the research program did not uncover significant cost reductions towards the manufacture of variable stator vane bushings, NHBB has still expressed an interest in continuing the development of non-MDA resin technology for applications around 300°C.

2. Polyimide Molding Powders

Chemical modification to the original AMB-21 formulation was successfully carried out by utilizing a "novel" chemistry approach which involved a fairly unreactive diamine (2,6-diaminopyridine, or DAP). Replacing BAPP with different stoichiometric amounts of DAP appeared to be similar to adding an endcap to AMB-21 for controlling molecular weight. This was reflected in the Brookfield viscosity measurements of the initial poly(amic-acid) solutions. Maverick’s DAP technology appears to be useful for obtaining low-viscosity, high-solid poly(amic-acid) solutions.

Two thermoplastic polyimide resins (without and with DAP) were synthesized in order to generate injection molding compound powders. The best processing results were obtained at injection temperatures of 343°C for the control (without DAP) and 304°C for the polyimide powder containing DAP. Micro-tensile specimens were produced from each resin type and the Tg measurements (by TMA) for these samples were equivalent to AURUM®. Thermal Gravimetric Analysis (TGA) conducted at 10°C/min showed that the non-MDA BTDA/BAPP polyimide thermoplastics had comparable weight loss to PMR-15 up to 500°C.

Unfortunately, due to the disappointing Tg values, tensile testing was not conducted on these materials. Additional work is needed to increase the Tg of these thermoplastics at least 50°C over the AURUM® polyimide. Chemical substitution of the BAPP diamine with p-phenylenediamine or the use of a compatible crosslinker represent just two reasonable approaches that could be tried in an attempt to increase the Tg to acceptable levels.

REFERENCES

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Low-Cost Production of Composite Bushings for Jet Engine Applications

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The objectives of this research program were to reduce the manufacturing costs of variable stator vane bushings by 1) eliminating the expensive carbon fiber braiding operation, 2) replacing the batch mode impregnation, B-stage, and cutting operations with a continuous process, and 3) reducing the molding cycle and machining operations with injection molding to achieve near-net shapes. Braided bushings were successfully fabricated with both AMB-17XLD and AMB-TPD resin systems. The composite bushings achieved high glass transition temperature after post-cure (+300°C) and comparable weight loss to the PMR-15 bushings. AMB-17XLD bushings made with "batch-mode" molding compound (at 0.5 in. fiber length) achieved a +300 lb.-force flange break strength which was superior to the continuous braided-fiber reinforced bushing. The non-MDA resin technology developed in this contract appears attractive for bushing applications that do not exceed a 300°C use temperature. Two thermoplastic polyimide resins were synthesized in order to generate injection molding compound powders. Excellent processing results were obtained at injection temperatures in excess of 300°C. Micro-tensile specimens were produced from each resin type and the Tg measurements (by TMA) for these samples were equivalent to AURUM®. Thermal Gravimetric Analysis (TGA) conducted at 10°C/min showed that the non-MDA AMB-type polyimide thermoplastics had comparable weight loss to PMR-15 up to 500°C.