RESIN TRANSFER MOLDING OF A POLYIMIDE (AMB-21)/CARBON FIBER COMPOSITE

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ABSTRACT

Polymer composites that maintain their properties at temperatures as high as 600°F are of increased interest for use in jet engine, rocket nozzle and high speed civil transport type applications. A composite material based on a polyimide matrix reinforced with carbon fibers is a serious candidate for those applications which are beyond temperature capability of commercial composites based on an epoxy matrix. A non-MDA based polyimide resin system under development at NASA - Lewis Research Center is utilized as the matrix. This resin, called AMB-21, has been especially formulated to improve the flow during fabrication by the Resin Transfer Molding (RTM) process. This paper details the description of the RTM mold design, the liquid matrix injection system, the procedure for injecting the matrix into the mold, the imidization of the matrix as well as the consolidation and cure schedule for producing composite panels. The quality of the molded composite panels was determined by various inspection techniques. A number of mechanical properties were determined experimentally and are reported here.

BACKGROUND

Polymeric composites in which temperature resistance up to 600°F is required, have in the past been fabricated using PMR-15 type polyimide prepregs primarily by autoclave consolidation techniques (L. Mir, reference 1). It has been reported that a more cost effective process would be to fabricate these composites by the Resin Transfer Molding (RTM) process. However, PMR-15 is not suitable for fabrication by the RTM process because the matrix never reaches a low enough viscosity for injection before cure begins. There is also the question of venting the gases which are generated in the imidization portion of the molding cycle. In addition, PMR-15 is based on a highly toxic MDA (methylenedianiline) which requires complex safety measures during the various steps of fabrication (R.D. Vannucci, reference 2). A heat resistant material which does not contain the MDA component would greatly reduce the cost required to isolate the MDA from the working environment. (R.D. Vannucci, reference 3)

The use of the RTM process to fabricate composite parts is very desirable because it provides the designer greater geometric flexibility as well as a potentially lower manufacturing cost process than possible utilizing prepreg and the autoclave processes (Kauffmann, reference 4). This is especially true for parts with a variable cross section and/or complex geometry. This research details an effort to fabricate panels by the RTM process utilizing a limited quantity of AMB-21 provided by NASA-Lewis Research Center. At this time it is not commercially available.

MATERIALS

Matrix

The matrix used for this research was a yellow powder supplied by NASA-Lewis Research Center as AMB-21. The material cures to become a polyimide. Figure 1, below, illustrates the molecular recipe of this material.

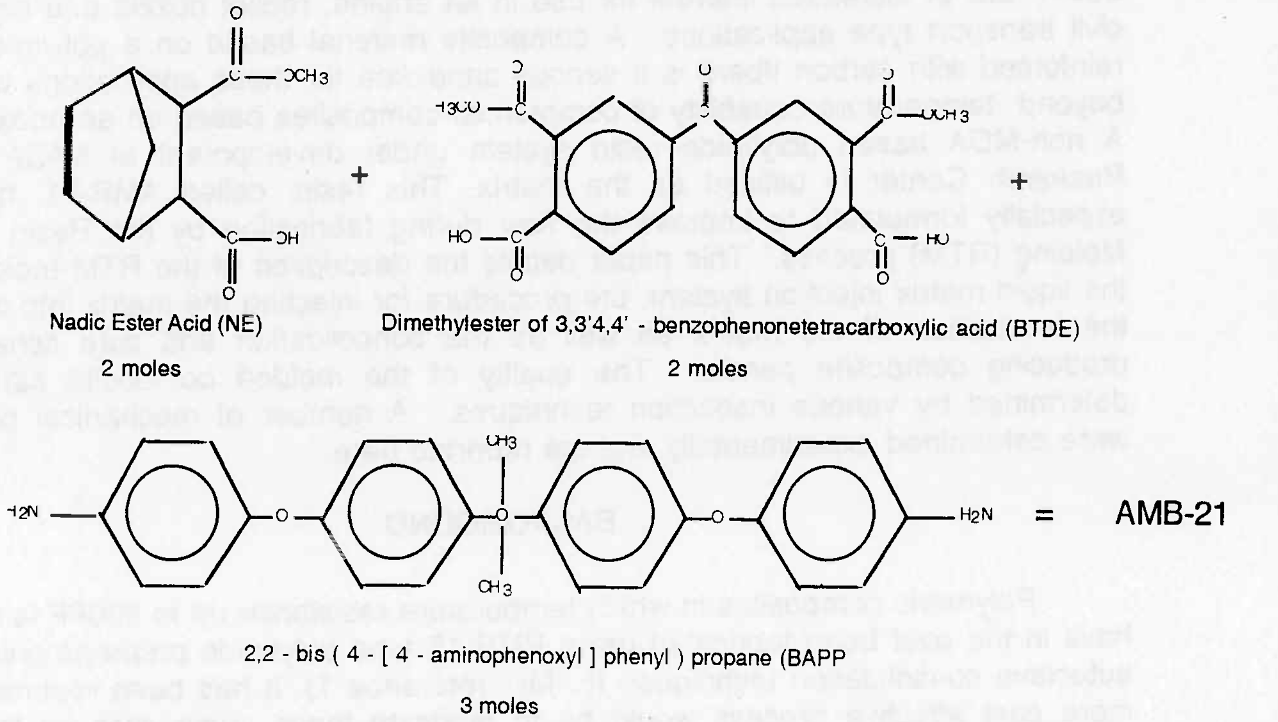

Figure 1, Recipe for AMB-21

Cured AMB-21 has a glass transition temperature (T_g) greater than 670^{O}F which is comparable to the state-of-the-art polyimide resins such as PMR-15 with a T_g at 637^{O}F (R.D. Vannucci, reference 3). Thermal stability of this magnitude makes the material a serious candidate for many high temperature applications.

The dry AMB-21 powder was dissolved in a solvent mixture prior to injection into the mold because the viscosity of the resin was too high to be injected into a mold even at elevated temperatures.

AMB21 = NE - BAPP - BTDE - BAPP - BTDE - BAPP - NE conjugated

Fiber

The fiber selected for this project was a polyacrylonitrile (PAN) based carbon fiber, MAGNAMITE AS4, from Hercules. It was a continuous fiber with a 550 ksi tensile strength, 1.53% strain and a 34 msi modulus. The fiber was supplied as a balanced plain weave cloth woven with 3k tow and surface treated to improve its handling and interlaminar shear properties. AS4, carbon fiber, has a good balance of mechanical properties.

PRELIMINARY PROCESS INVESTIGATIONS

Dissolving AMB-21

The initial trials with AMB-21 consisted of making solvent solutions using a mixture of methyl alcohol and tetrohydrofuran. The objective was to obtain a clear uniform solution with a viscosity of about 350 cps. This was thought to be a "high-side" viscosity for injecting into a RTM mold at room temperature. The final recipe for the solution was 30 grams of methyl alcohol, 10 grams of tetrohydrofuran and 66 grams of AMB-21. A uniform solution was obtained by adding the AMB-21 powder slowly to a beaker of mixed solvents on a heated magnetic stirring plate. Too much heat causes the solvent to evaporate too quickly, sometimes before a solution was achieved. Adding the powder too rapidly causes lumping which could stop the magnetic stirrer. By experimenting methodically, a repeatable process for obtaining the desired solution was obtained.

Making Prepreg

A simple prepreg was produced by brushing a solvent solution of the AMB-21 onto the carbon fiber cloth and allowing the solvents to evaporate. The prepreg looked like carbon cloth with yellow powder loosely attached to the fibers. Even with gentle handling, some of the AMB-21 fell off the prepreg .

Compression Molding Prepreg

The prepreg was cut into 4 X 4 inch squares and stacked into 8 and 16 plies. The stacks were put into a shallow pan. The pan with the prepreg was placed in the oven to evaporate the solvents and imidization products. The mold was held at 300^{o}F for one hour followed by one hour at 400^{o}F in a vacuum oven. The 300^{o}F step was to evaporate matrix solvents and the 400^{o}F step was to imidize the AMB-21. The impregnated preform was removed from the pan and placed in a preheated compression press between two sheets of Kapton film where it was cured for two hours at a temperature of 600^{o}F and a hydraulic pressure of 200 psi.

Using this basic technique four panels were fabricated. Two of the panels contained 8 plies of prepreg and the other two had 16 plies.

Panel Appearance

The eight-ply panels looked very good. The flash squeeze-out around the edges of composite was especially interesting as it was a clear dark brown matrix material essentially free of bubbles. Had the solvent removal process and/or the imidization cycle been incomplete, the squeeze-out should have been full of gas bubbles.

The 16-ply panels were not quite so good. There were bubbles in the squeeze-out indicating volatiles were still present during the 600^{o}F cure.

Remarks on Processing

Based on the results of the prepreg panel molding experiments, It was postulated that a RTM process could be developed for AMB-21 if it were possible:

- to drive off the solvents out of a mold with only vents,
- to provide a path for imidization products to be pulled through these same vents utilizing a vacuum and
- then to provide a consolidation pressure of 200 psi at 600^{o}F without removing the impregnated preform from the mold.

SIMULATED RESIN TRANSFER MOLDING OF AMB-21

RTM Mold Design

This mold was designed to determine if it was possible to vent the solvent and imidization products from a closed, but vented, RTM mold. The mold used for this study is illustrated in Figure 2. The design included a Pyrex faceplate for observing the mold filling process. The mold was capable of processing a panel 4.25 x 4.25 x 0.100 inches. The mold was designed to accommodate an eight-ply carbon fiber preform.

Mold Preparation

The mold as received from the machine shop was solvent cleaned to remove cutting oils and other contaminates. Two coats of Release All #100, Airtech International, Carson, CA were applied to all surfaces followed by an oven bake at 250^{o}F for two hours. The Release All #100 was a preventative measure taken to ensure that the composite did not adhere to the mold. A preform consisting of eight plies of cloth was placed in the mold. The plies were cut to closely fit the mold cavity. A strip of silicone elastomer sponge, as illustrated in figure 3, was added to both side edges of the mold to minimize the possibility of the matrix "race-tracking" around the edges of the preform. Silicone elastomer caulk was applied between the mold base plate and the Pyrex faceplate to provide a vacuum seal. The nine bolts holding the faceplate to the mold cavity component were tightened carefully to minimize stress on the Pyrex faceplate.

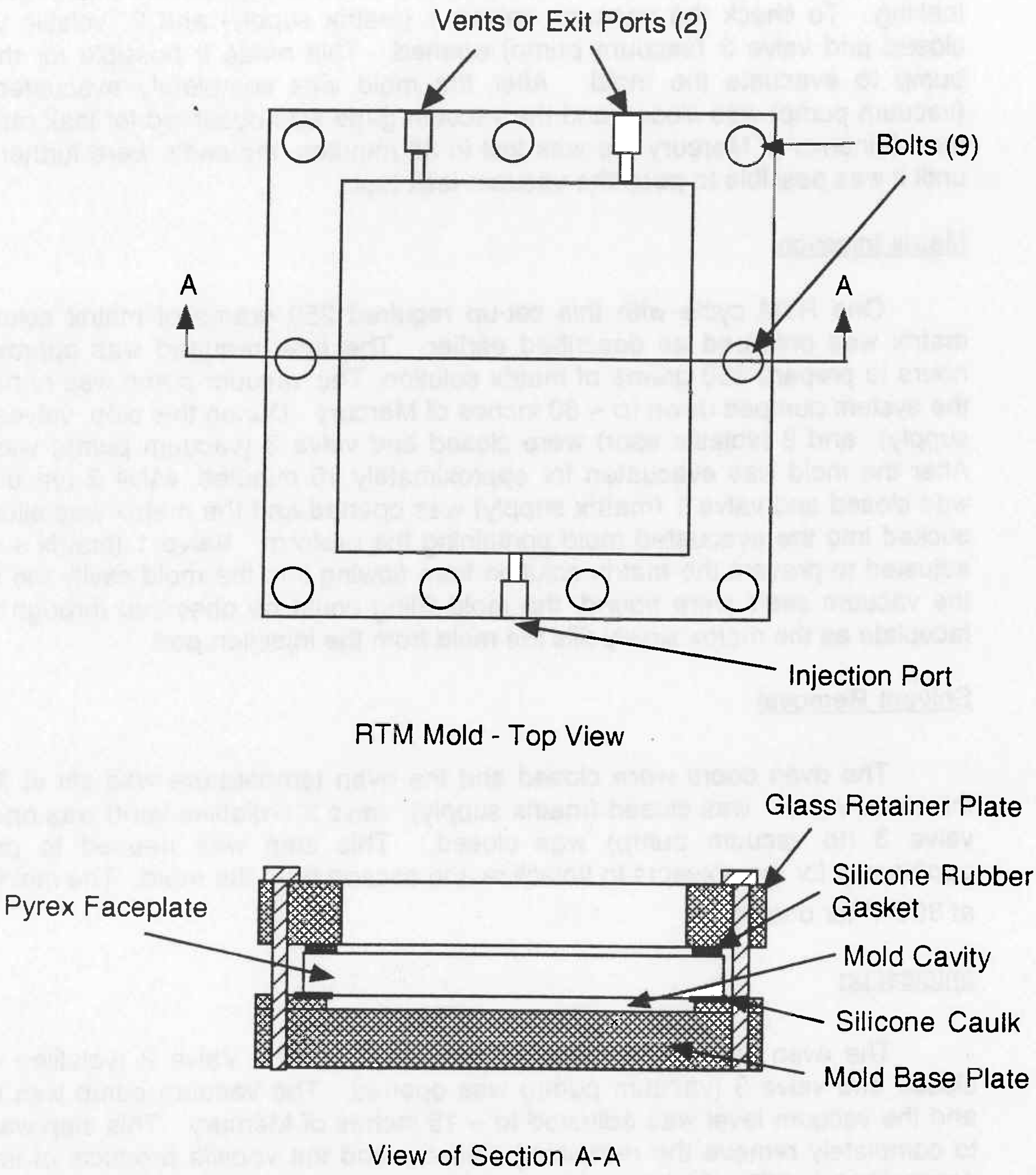

Figure 2, Mold for Evaluating Simulated RTM Process

Simulated RTM Set-up

The mold was mounted vertically in the oven with the Pyrex faceplate toward the oven door. The plumbing was assembled as shown in Figure 3. All of the plumbing joints were sealed to hold a vacuum and to prevent the matrix solution from leaking. To check the vacuum, valves 1 (matrix supply) and 2 (volatile vent) were closed and valve 3 (vacuum pump) opened. This made it possible for the vacuum pump to evacuate the mold. After the mold was completely evacuated, valve 3 (vacuum pump) was closed and the vacuum gage was observed for leak rate. If more than 5 inches of Mercury the was lost in 30 minutes, the seals were further improved until it was possible to pass the vacuum-leak test.

<u>Matrix Injection</u>

One RTM cycle with this set-up required 250 grams of matrix solution. The matrix was prepared as described earlier. The time required was approximately 2 hours to prepare 250 grams of matrix solution. The vacuum pump was turned on and the system pumped down to ~ 30 inches of Mercury. During this step, valves 1 (matrix supply) and 2 (volatile vent) were closed and valve 3 (vacuum pump) was opened. After the mold was evacuated for approximately 10 minutes, valve 3 (vacuum pump) was closed and valve 1 (matrix supply) was opened and the matrix was allowed to be sucked into the evacuated mold containing the preform. Valve 1 (matrix supply) was adjusted to prevent the matrix solution from flowing into the mold cavity too rapidly. If the vacuum seals were sound, the mold filling could be observed through the Pyrex faceplate as the matrix slowly fills the mold from the injection port.

<u>Solvent Removal</u>

The oven doors were closed and the oven temperature was set at 300^{O}F. At this time, valve 1 was closed (matrix supply), valve 2 (volatiles vent) was opened, and valve 3 (to vacuum pump) was closed. This step was needed to provide an opportunity for the solvents to volatilize and escape from the mold. The mold was held at 300^{O}F for one hour.

<u>Imidization</u>

The oven temperature was increased to 400^{O}F. Valve 2 (volatiles vent) was closed and valve 3 (vacuum pump) was opened. The vacuum pump was turned on and the vacuum level was adjusted to ~ 15 inches of Mercury. This step was needed to completely remove the remaining solvents and the volatile products of imidization. Approximately 17% of the weight, as water and alcohol, of the AMB-21 was lost during this step due to imidization. The 400^{O}F oven temperature and vacuum were maintained for one hour.

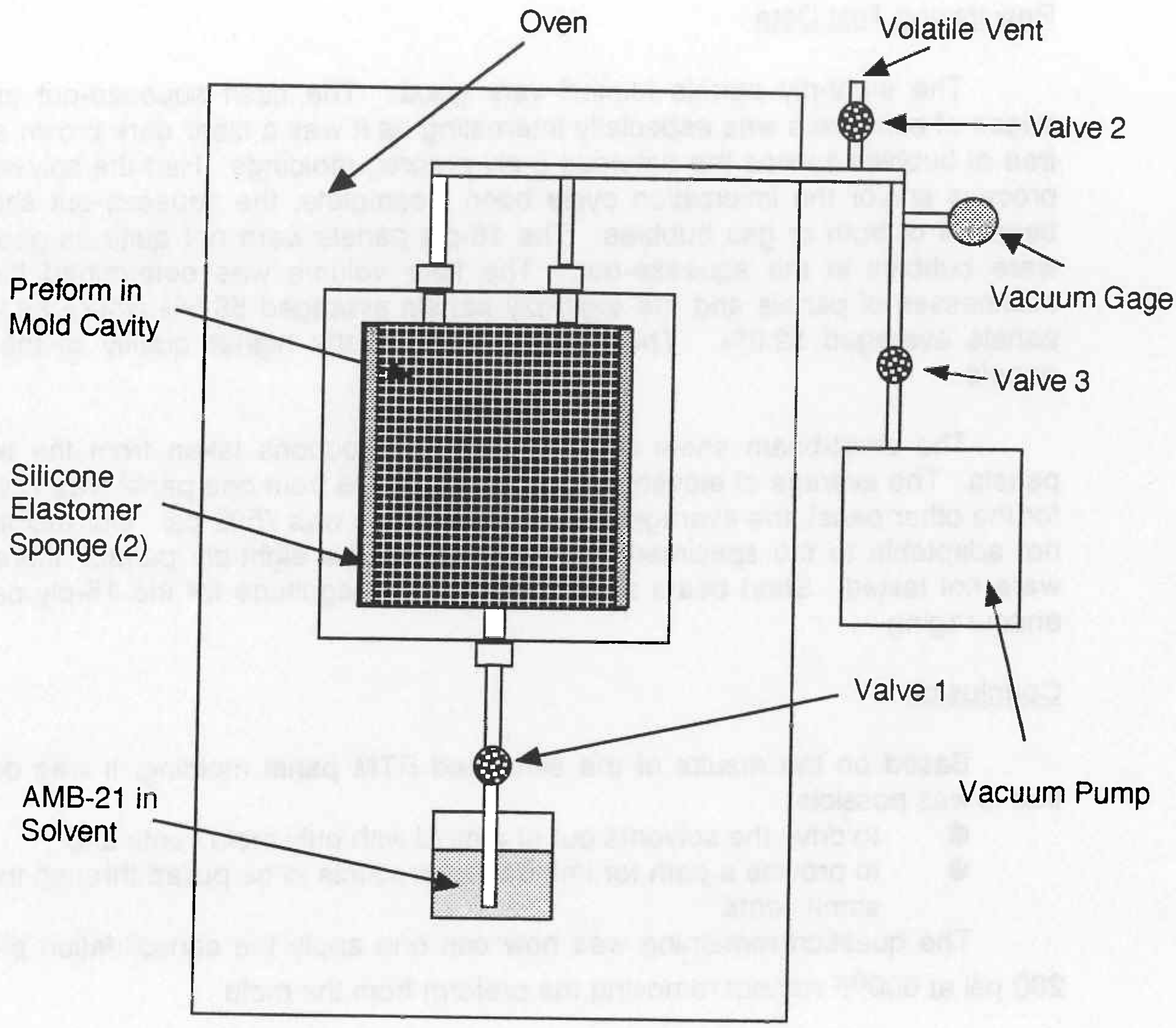

Figure 3. Set-up for Simulated RTM Process

Press Molding

After the mold cooled, the imidized prepreg preform was removed from the mold. It had the appearance of a rigid preform with a brown crusty coating. This preform was placed between two sheets of Kapton and into a preheated 600°F press. The preform was pressed at 200 psi for two hours. The composite remained under pressure until the press cooled. Two panels were press molded with eight plies and two with 16 plies. The 16-ply specimens were fabricated by stacking two eight-ply impregnated preforms.

Results and Test Data

The eight-ply panels looked very good. The flash squeeze-out around the edges of composite was especially interesting as it was a clear dark brown essentially free of bubbles as was the previous 8-ply prepreg moldings. Had the solvent removal process and/or the imidization cycle been incomplete, the squeeze-out should have been full of froth or gas bubbles. The 16-ply panels were not quite as good. There were bubbles in the squeeze-out. The fiber volume was determined for the two thicknesses of panels and the eight-ply panels averaged 56.5% where as the 16-ply panels averaged 52.0%. This further indicated the higher quality of the eight-ply panels.

The short-beam shear test were run on coupons taken from the two 16-ply panels. The average of eleven tests with specimens from one panel was 7368 psi and for the other panel, the average for eleven coupons was 7592 psi. Our test fixture was not adaptable to the specimen size required for the eight-ply panels, therefore they were not tested. Short beam shear data of this magnitude for the 16-ply panels was encouraging.

Conclusion

Based on the results of the simulated RTM panel molding, it was determined that is was possible:

- to drive the solvents out of a mold with only mold vents and
- to provide a path for imidization products to be pulled through these same vents.

The question remaining was how can one apply the consolidation pressure of 200 psi at 600^{O}F without removing the preform from the mold.

RESIN TRANSFER MOLDING (RTM) OF AMB-21

General

At this point in the research it was determined that only enough AMB-21 powder remained to mold four panels of sufficient size for determining mechanical properties.

The RTM process for AMB-21 can be broken into seven steps. They are 1) mold preparation 2) loading preform in the mold, 3) matrix preparation, 4) matrix injection, 5) solvent removal, 6) imidization and 7) consolidation and curing.

RTM Mold Design

The mold must be capable of functioning for multiple runs at 600^{O}F with a two hour cure cycle. This high temperature dictated a problem for the material selection for both the o-ring seal and the diaphragm. Normally silicone elastomer would have been selected for both applications but there was concern that the 600^{O}F exposure would be too great for silicones. Experts on silicone elastomers advised that 550^{o}F was the upper temperature limit for silicone elastomers. One supplier suggested a special heat resistant silicone elastomer for the diaphragm application but it was seriously degraded by a simple oven aging test at 600^{o}F. With some reluctance, metals were selected for both the o-ring seal and the diaphragm applications. Since the diaphragm would be joined to the mold cavity by oven brazing, it was felt that carbon steel would be required for both mold components in order to minimize prestressing the mold cavity plate-diaphragm assembly due to differences in thermal expansion coefficients. Stress calculations, based on the 200 psi inflation pressure, predicted a carbon steel diaphragm 0.0239 inches thick, which was available, would be appropriate for this application. Metallic o-rings made of silver plated aluminum were purchased for use as the mold seals.

It was decided to design a circular mold so that the deformation of the diaphragm would be uniform except at the attachment edges. A twelve inch diameter mold should yield a panel of uniform thickness for about 9 inches diameter. The mold was designed to be stood vertically during filling and the matrix solution would be injected near the bottom and would flow up and exit the mold near the top. This would encourage the mold to fill from the bottom and push the air out as the flow front advanced.

The mold was designed with a 0.125 inch deep cavity to accommodate a 16-ply preform. The o-ring groove and opposing top plate were finished to a high surface finish so that the metal o-ring would properly seal. Some additional details of the mold design are illustrated in figure 4.

<u>Mold Preparation</u>

Any residues remaining from the machining operations were removed with a cleaning solvent. A coat of Release All #100 mold release was applied to all mold surfaces and baked for two hours at 250^{o}F. After the mold was removed from the oven, the mold release was applied again and baked to insure the release of the molded panel after cure. The baking of the mold release is only required for the initial molding. To recycle the mold, only a single application of mold release at room temperature was necessary.

The metal o-ring and the o-ring groove were especially cleaned to insure a good fit with mating surfaces. To further improve the seal, a coat of silicone vacuum grease was applied to the o-ring.

The mold was now prepared for the loading of the preform. Further details of the mold are illustrated in figure 4 below :

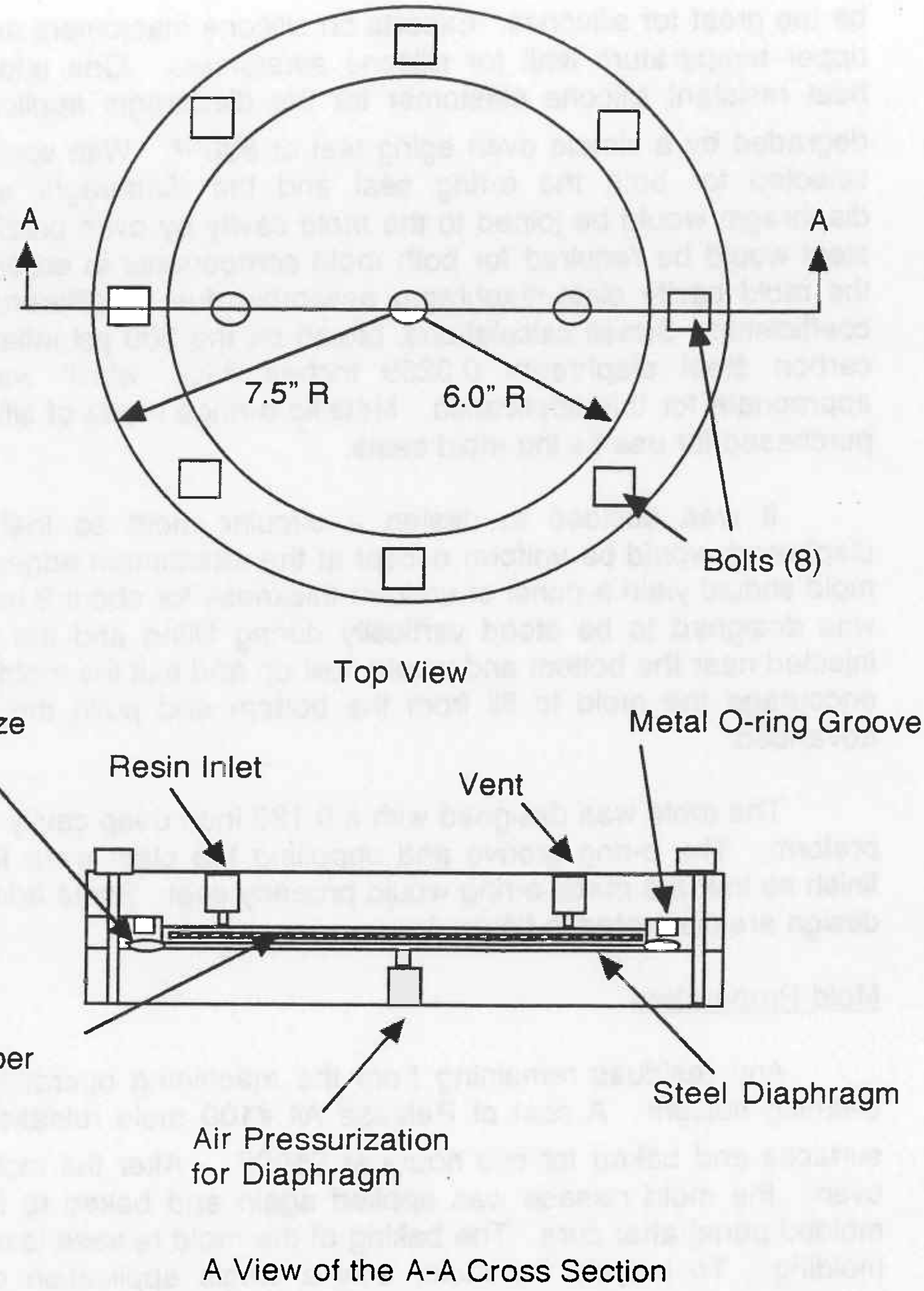

Figure 4, Top View and Cross sectional View of Diaphragm Mold

<u>Cutting and Stacking Preform</u>

The carbon fiber plain weave cloth was laid flat on a cutting table and cut in 11.5 inch circles using a metal template as a guide and a medical scalpel as the cutting instrument. A 12 inch diameter preform was not used to facilitate removing the cured panel from the mold. The preform required 16 plies of cloth to obtain a target composite thickness of about 0.125 inches. The plies were stacked symmetrically with respect to the mid-plane to balance the mechanical properties.

Loading the Preform into the Mold

Before the 11.5 inch diameter preform is loaded in the mold assembly the preform was inspected to verify the number of plies and stacking order were correct. After the preform was placed in the cavity a one-half inch strip of closed cell silicone elastomer foam was added to the edges of the preform where "race-tracking" was likely to occur because of imperfect preform-cavity fit. The use of foam strips to prevent "race-tracking" is discussed by Senibi and Morgan in references 5 and 5. The addition of the elastomer foam has eliminated the tendency for the matrix to preferentially flow along the edges of the preform. After the preform and foam strips are in position, the mold was closed with machine screws. The screws are finally tightened with a torque wrench to achieve uniform metal-to-metal contact around the edges of the mold. The closing gap was checked with 0.001 inch feeler stock to verify complete closure. If the mold does not completely close, it was disassembled and the closure procedure was repeated.

After the mold was fully assembled, it was vacuum tested to verify plumbing and o-ring seal were performing correctly. To do this, valves 1 (matrix supply) and 3 (gas supply) were closed and valve 2 (vacuum pump) opened. The mold was pumped down to ~ 30 inches of Mercury and allowed to stand with valve 2 (vacuum pump) closed and the vacuum pump off to see if the pressure level decays. If it holds without noticeable drop in pressure for two hours, it is considered satisfactory.

Matrix Preparation

About 500 grams of AMB-21 solution was required to fill the mold mold. The matrix solution was prepared immediately prior to injection as there was thought to be a shelf-life problem after the AMB-21 was dissolved. The following processing steps represent the planned process but as often occurs in research, important variations have developed. These variations are covered as the process for each of the four panels is described.

Matrix Injection

The set-up for the AMB-21 RTM process is illustrated in figure 5. The illustration shows the mold in the horizontal position which was used after the initial tool tryout run using epoxy in which the mold diaphragm was damaged. On the initial run it was permanently deformed because the depth of the mold cavity was machined incorrectly and the steel diaphragm yielded to fit the available cavity space at the 200 psi gas pressure. The mold cavity was machined to a depth of 0.230 instead of the 0.125 inches as designed. After the diaphragm was deformed, the matrix injection port was changed to the center of the preform as shown in figure 5. Whereas the deformation was undesirable, it did not however, render the mold useless. The injection port location was changed, the mold was filled with the mold positioned horizontally and the process continued.

The matrix solution was poured into the reservoir. The mold was evacuated. For the evacuation, valve 1 and 3 were closed and valve 2 was opened. The vacuum pump continued to pump the air from the mold for about 10 minutes after the ~ 30 inches of Mercury was reached. To inject the matrix solution, valve 2 was closed and valve 1 was opened as the peristaltic pump was started. The plan was to fill the mold cavity in about 45 minutes. The fill time varied for each of the four moldings.

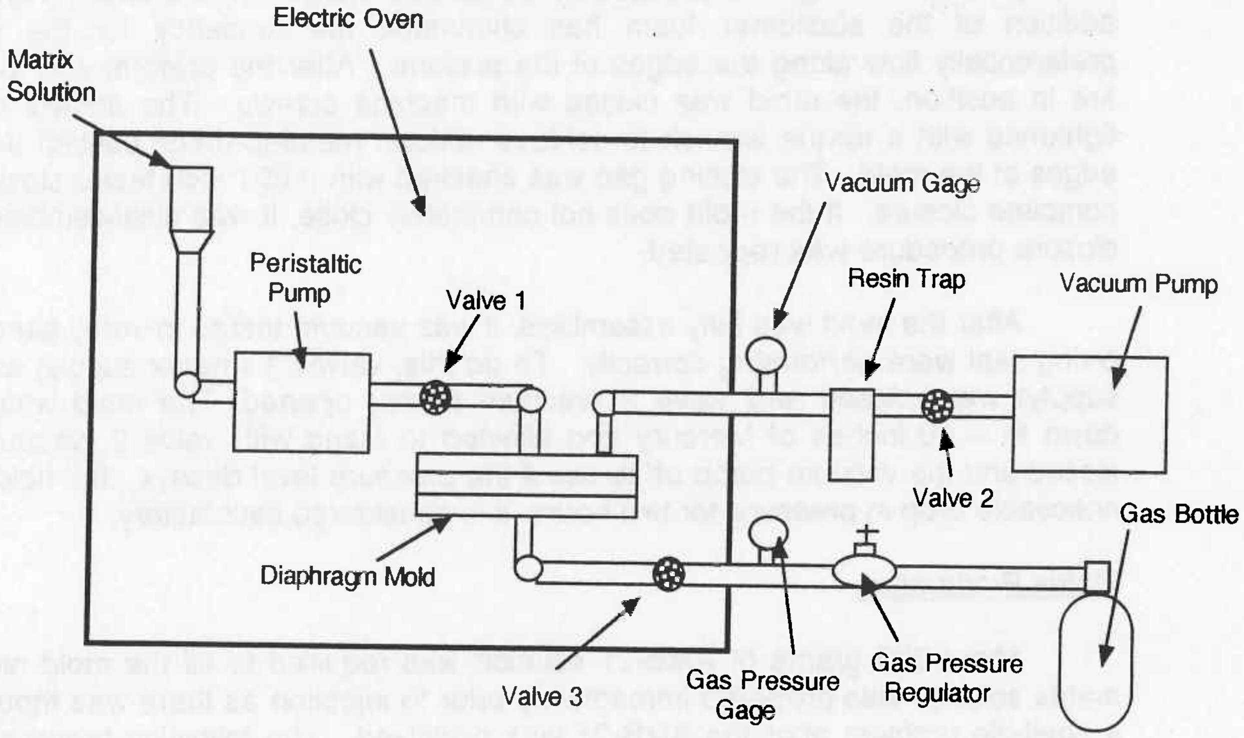

Figure 5, Set-up for AMB-21 RTM Process

After the mold was full, the matrix and vacuum lines were converted to stand-pipes as shown in figure 6. This provided the path for the solvents and imidization products to escape the mold.

Solvent Removal

The oven was turned on and set at a temperature of 300°F. At that temperature solvent evaporation took place as the matrix solution boiled in the stand-pipes. A 300°F temperature was maintained for one hour.

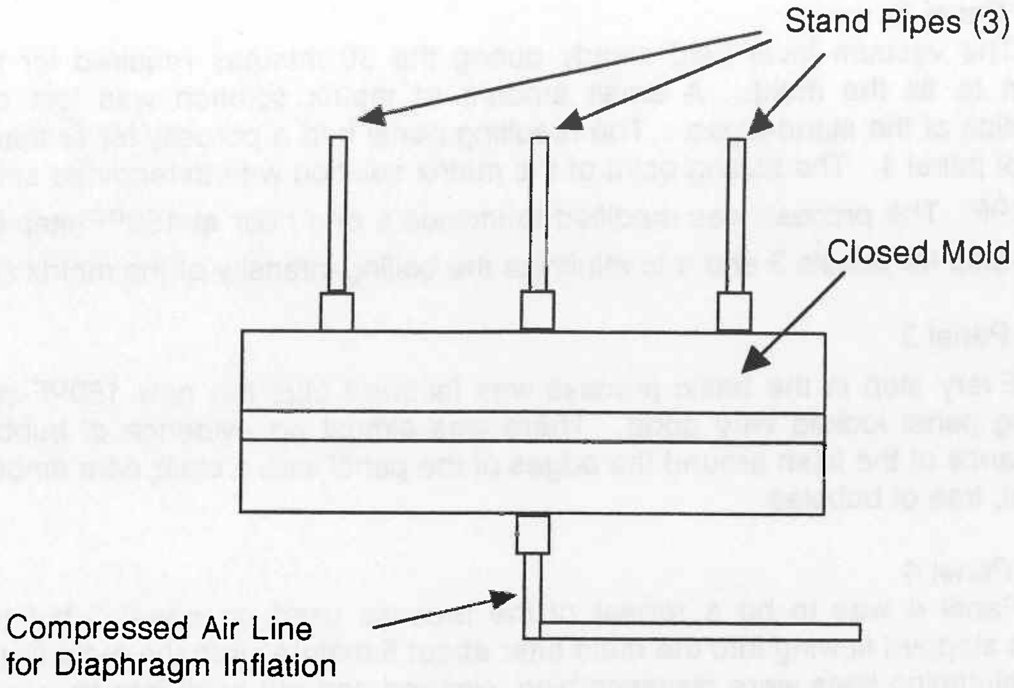

Figure 6, RTM Mold with Stand Pipes in Place

Imidization

For imidization, a vacuum was applied to the stand pipes and oven temperature was increased to 400^{O}F where it was held for one hour. During this period, the imidization products, water and alcohol, are evolved and evacuated out of the mold.

Consolidation and Cure

The oven temperature was increased to 600^{O}F and 200 psi gas pressure was applied to the diaphragm. This condition was maintained for two hours.

Specific Processing Results by Panel Number

Round Panel 1

The vacuum pressure began to drop at about 20 minutes into the process. The mold required 105 minutes to fill. During the 300^{O}F-solvent-removal step, back pressure build-up in the injection port caused the center stand-pipe to split and allowed a quantity of foamy matrix solution to escape from the mold. The mold was cleaned and the process continued without further deviation. The resulting cured panel had a matrix starved area about three inches in diameter in the center of the panel where the stand-pipe had split. The remainder of the panel contained low level porosity.

Round Panel 2

The vacuum level held steady during the 30 minutes required for the matrix solution to fill the mold. A small amount of matrix solution was lost during the installation of the stand-pipes. The resulting panel had a porosity lower than the best areas of panel 1. The boiling point of the matrix solution was determined and found to be 150°F. The process was modified to include a one hour at 150°F-step before the 300°F-step for panels 3 and 4 to minimize the boiling intensity of the matrix solution.

Round Panel 3

Every step in the basic process was followed plus the new 150°F-step. The resulting panel looked very good. There was almost no evidence of bubbles. The appearance of the flash around the edges of the panel was a clear dark amber colored material, free of bubbles.

Round Panel 4

Panel 4 was to be a repeat of the process used on panel 3 but the matrix solution stopped flowing into the mold after about 5 minutes into the mold fill time. The matrix plumbing lines were disassembled, cleaned and put back into service though it was 120 minutes before the matrix solution started flowing out of the top matrix port. The quality of this panel was about the same as the average porosity of panel 1.

MECHANICAL PROPERTIES (ROUND PANELS)

Panel Selection

Round panels 1, 2 & 4 were selected for mechanical testing. Panel 3, which was the best of the four, was chosen to be retained for other uses since there was not enough AMB-21 remaining to fabricate additional round panels.

C-Scan of Round Panels

The four panels were sent to QMI in Costa Mesa,CA for the c-scan test to determine the extent of porosity. The results were found to be as expected from the visual evidence. Panel 3 was very good, followed by panel 2, 4 and 1 in declining order. The mechanical test coupons were laid out on the panels to take advantage of the best areas of each panel.

Mechanical Properties

The mechanical properties determined were tensile, compression and shear. The tensile and compression test included ultimate, modulus and Poisson ratio. The shear test only involved the ultimate strength. Fiber volume for each panel was also determined. The short beam test procedure was performed as per ASTM D 2344. The fiber volume test was determined using sulfuric acid/hydrogen peroxide method defined in ASTM D 3171. The tensile properties were determined by methods described in ASTM D 3039. Compression test was the IITRI test described in ASTM 3410.

Mechanical Test Data

Table 1 is a presentation of the average value of results obtained from testing the coupons extracted the round panels.

Property	No. of Coupons/Panel	Panel 1	Panel 2	Panel 4
Tensile Properties	3			
Ultimate Tensile (ksi)		73.7	92.1	80.8
Modulus (msi)		7.4	9.0	7.6
Poisson Ratio		0.326	0.248	0.136
Compression Properties	3			
Ultimate Compression (ksi)		50.7	66.9	36.2
Modulus (msi)		7.0	7.8	6.3
Poisson Ratio		0.086	0.065	0.135
Open-Hole Compression (ksi)		43.9	44.3	37.0
Shear Properties	12			
Short-Beam (psi)		6501.0	7179.0	5301.0
Fiber Volume (%)	4	56.6	55.5	41.1

Table 1, Average Mechanical Properties

RESULTS AN CONCLUSIONS

Processing AMB-21

The processing experiments involving the simulated RTM of AMB-21 indicated it that was possible to:

- make a solvent solution of the polyimide matrix,
- inject the matrix solution into a RTM mold and
- without removing the impregnated preform from the mold, evaporating the solvents
- while preform is still in the mold, remove the volatiles of imidization

The diaphragm mold took the research one step further by illustrating it was also possible to:

- consolidate the imidized preform in the RTM mold at 600^{O}F and 200 psi

As stated elsewhere, there was only enough AMB-21 polyimide available to fabricate four round panels. This shortage of material prevented the number of replications that would be required to be certain the fabrication process details are valid.

Mechanical Testing of AMB-21/Carbon Fiber Composite

The mechanical properties determined and reported in table 1 for panels 1 and 4 are definitely suspect because of the high level of porosity. However, the data for panel 2 is probably fairly representative of a composite fabricated with this carbon fiber, fiber architecture, fiber volume and matrix. As mentioned earlier, there was insufficient AMB-21 to mold and test sufficient number of additional panels necessary to draw any firm conclusions.

ACKNOWLEDGEMENTS

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