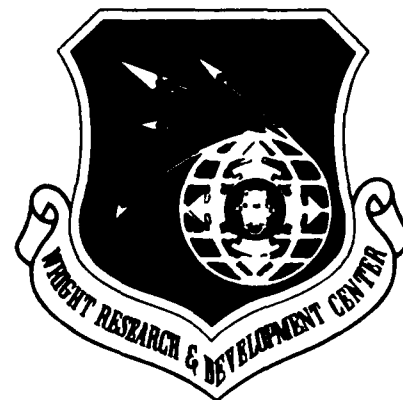


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EMERGING RESIN CHARACTERIZATION



Northrop Corporation
Aircraft Division
Hawthorne, California 90250-3277

30 April 1989

Interim Report for Period July 1987 - July 1988

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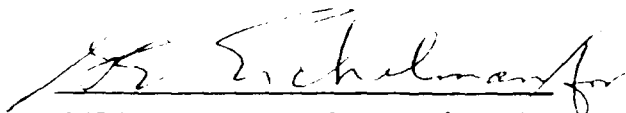


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The synthesis of a bisbenzocyclobutene (BCB)-terminated aromatic imide oligomer has been completed. This BCB oligomer resin was prepared from the condensation reaction of two moles of 2,2-bis (4-phthalic anhydrido)-hexafluoropropane, one mole of m-phenylenediamine and two moles of 4-aminobenzocyclobutene. The 4-aminobenzocyclobutene was prepared from the nitration and subsequent hydrogen reduction of benzocyclobutene obtained from Dow Chemical. Approximately 1,200 grams of the BCB oligomer resin have been prepared. Preliminary high performance liquid chromatography (HPLC) and differential scanning calorimetry (DSC) analyses indicated this material to be equivalent to BCB oligomer resin previously synthesized by the Materials Laboratory.											
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FOREWORD

This report covers work performed under Contract No. F33615-87-C-5223 during the period from 29 July 1987 to 29 July 1988. The contract entitled "Emerging Resin Characterization" was initiated and administered under the direction of the Materials Laboratory, Wright Research Development Center, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Ms. L. R. Denny as the Project Engineer.

The work described in this report was conducted jointly at Northrop Corporation and the University of Dayton Research Institute (UDRI) with Mr. P. J. Dynes directing all activities at Northrop Corporation and Dr. R. P. Chartoff directing all activities at UDRI.

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SECTION 1

INTRODUCTION AND APPROACH

Advanced composites are rapidly emerging as a primary material for use in near-term and next-generation aircraft because they provide greater structural efficiency at lower weight than equivalent metallic components. Composite materials are significantly impacting the design and manufacture of high performance fighter aircraft. Present composite technology has advanced to the point where all recent and emerging production military aircraft (F-14, F-15, F-16, F/A-18, AV-8B, and C-17) contain progressively increasing numbers of composite components.

The next generation of tactical aircraft will impose stringent demands on composite materials in terms of service temperature capability, durability, and damage tolerance. Currently available composite materials satisfy those demands only marginally. Epoxy-based composites are brittle and have a maximum service temperature of 220°F to 250°F in a moisture-saturated condition. Although the more advanced bismaleimide (BMI) composites have higher service temperature capabilities (approximately 400°F), they are brittle and subject to impact damage. Polyimide (PI) resins are capable of even higher temperatures (500°F to 600°F), but are also brittle and are much more difficult to process than epoxies or bismaleimides. Thermoplastic composite materials are being developed, but the higher temperature thermoplastics for 350°F to 400°F service that are currently available are difficult to process and manufacture. Composite matrix resins for propulsion systems, with 700°F service capability, are at an early state of development.

Research is currently ongoing at the Air Force to develop matrix resin systems that will satisfy composite performance requirements of future aircraft. Synthesis of these advanced resins is typically limited to small samples (50 to 100 grams) because of cost considerations. These advanced materials are evaluated as neat resins for thermal properties, processing characteristics, and neat resin mechanical properties. Although useful for preliminary evaluation and screening purposes, neat resin data are insufficient to predict composite properties or manufacturing viability.

The objective of the current program is to provide synthesis scale-up, extensive neat resin evaluation and composite characterization of new high performance thermosetting and thermoplastic resins. New polymer resins that have been identified in Air Force or other research programs will be synthesized in this program in approximately 1,000-gram quantities and characterized by chemical, rheological and thermal testing. Neat resin and composite test specimens will be fabricated and tested to determine physical and mechanical properties. The test data will be analyzed to assess the potential of these resins for meeting Air Force requirements.

The program objectives will be accomplished through performance of a 36-month effort consisting of six tasks. In Task 1, up to five thermosetting and/or thermoplastic resins will be submitted and synthesized using procedures provided by the Air Force Project Engineer. The polymer samples will be prepared at minimum cost, and the purity of all samples will be verified and documented to exceed 99 percent. Submittal of 50 grams of resin to the Air Force will be made from an initial synthesis test run using the Air Force procedure. If the material satisfies Air Force validation testing, a scaled-up 500- to 1,000-gram batch will be prepared. A 50-gram samples of this material, with

purity documentation, will be submitted to the Air Force for evaluation.

In Task 2, the polymer samples synthesized in Task 1 will be further analyzed to verify that their chemical, thermal, rheological and mechanical properties are equivalent to the smaller samples (50 grams) previously characterized by the Air Force. Polymer systems that satisfy validation testing will be selected for further evaluation upon authorization by the Air Force Project Engineer.

In Task 3, neat resin processing cycles will be developed for the validated resins. Processing cycles will be optimized with respect to full development of neat resin mechanical properties, cure cycle feasibility and adaptability for subsequent composite processing. These objectives will be accomplished through dynamic and isothermal rheometry, thermal analysis, tensile testing and microstructural analysis of failed tensile test specimens.

In Task 4, neat resin microtensile specimens will be fabricated, and a data base of tensile strength, modulus and strain-to-failure will be established over a range of temperatures and moisture conditions. Fracture behavior will be characterized with scanning electron microscope examination of tensile failure surfaces.

In Task 5, the methodology to fabricate high quality laminates will be established. The resins will be prepregged on AS-4 or equivalent graphite fiber using either a hot-melt or solvent prepregging technique. Composite fabrication procedures will be developed to produce high quality, void-free laminates with press and/or autoclave processing.

In Task 6, sufficient unidirectional and angle ply laminates will be fabricated to characterize the behavior of each resin as a composite matrix material. The mechanical testing will include 0-degree four-point shear, 0-degree four-point flexure, 90-degree four-point flexure, edge delamination and double cantilever beam Mode I toughness testing. The four-point shear and flexure tests will be conducted in both dry and moisture-saturated conditions.

The mechanical tests will be augmented by moisture uptake analysis of the test specimens to determine equilibrium moisture content. Scanning electron microscopy will be used to characterize the fracture behavior of the failed specimens.

SECTION 2

TECHNICAL DISCUSSION

TASK 1 - MATERIAL SYNTHESIS AND SCALE-UP

The Air Force selected the first two resins to be evaluated in the program. Both of these resins are based on bisbenzocyclobutene-terminated thermoset resin chemistry developed by the Materials Laboratory.

The first resin to be studied will be the bisbenzocyclobutene (BCB) oligomer based on the reaction of two moles of 2,2-bis(4-phthalic anhydrido)-hexafluoropropane, one mole of m-phenylenediamine and two moles of 4-aminobenzocyclobutene.

The second system to be evaluated will be an equimolar blend of the BCB oligomer with 4-4'bismaleimidodiphenylmethane, a bismaleimide (BMI) resin. The chemical structures of the first two resin systems are shown in Figures 1 and 2, respectively.

The starting materials used for the synthesis of the BCB oligomer resin were 2,2-bis(4-phthalic anhydrido)-hexafluoropropane from American Hoechst, Somerville, New Jersey, m-phenylenediamine from Aldrich Chemical Company, Milwaukee, Wisconsin and benzocyclobutene from Dow Chemical Company, Midland, Michigan. A 200-gram sample of benzocyclobutene was also obtained from the Materials Laboratory which was synthesized by Fluorochem Inc., Azusa, California.

The first step in the synthesis of the BCB oligomer resin is the conversion of benzocyclobutene to 4-nitrobenzocyclobutene. The 4-nitrobenzocyclobutene is then reduced to 4-aminobenzocyclobutene in a second step. The step-by-step procedures for synthesis of these two intermediate materials, as well as the

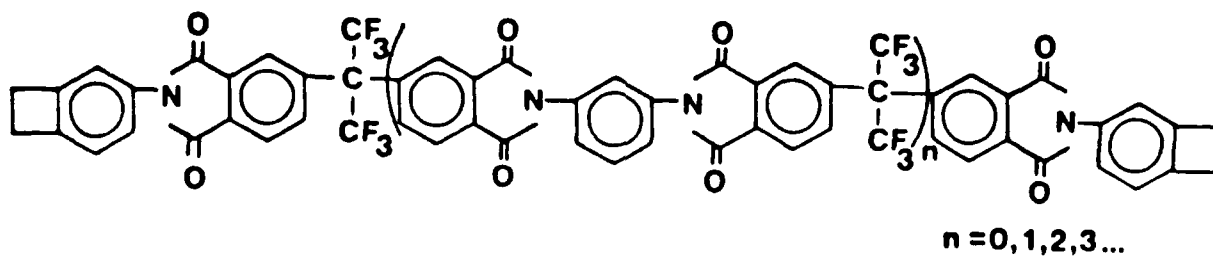
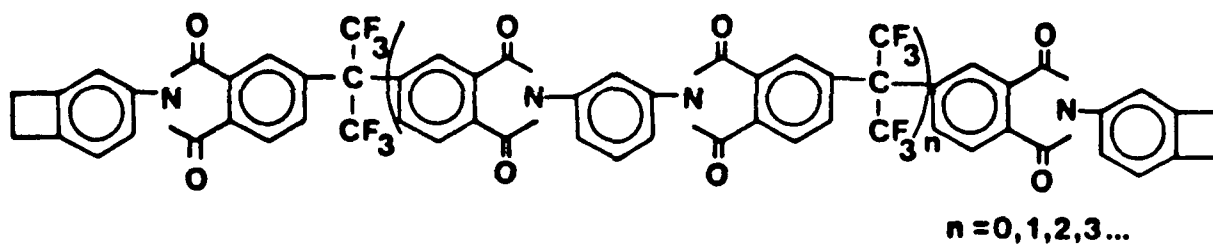


Figure 1. Chemical Structure of BCB Oligomer Resin



BCB oligomer

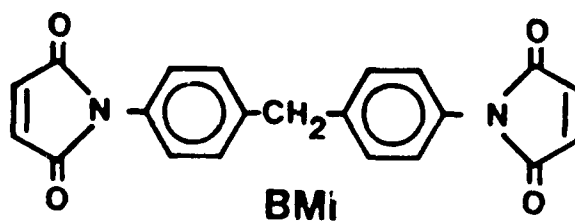


Figure 2. Chemical Structures of BCB Oligomer/BMI Blend

final BCB oligomer resin product, are described in Procedures I through III in the Appendix. A discussion of the BCB oligomer synthesis is given below.

Synthesis of 4-Nitrobenzocyclobutene

The initial synthesis of the BCB oligomer resin was conducted using a 200-gram sample of benzocyclobutene prepared by Fluorochem Inc. and obtained from the Materials Laboratory. The synthesis scheme for conversion of the benzocyclobutene to 4-nitrobenzocyclobutene is shown in Figure 3. The first nitration reaction to convert benzocyclobutene to 4-nitrobenzocyclobutene was found after clean-up to produce only 36 percent of the theoretical yield. It was suspected that the low yield might be due to impurities present in the benzocyclobutene starting material. Evidence of an impurity in the benzocyclobutene was found using reverse-phase high performance liquid chromatography (HPLC). The chromatogram of the BCB starting material is shown in Figure 4A. Two distinct peaks are resolved, indicating the presence of at least two components in the benzocyclobutene. One of the two peaks must be due to an impurity, since benzocyclobutene can exist in only one isomeric form. The ratio of the areas for the two peaks in the chromatogram is 1.14 to 1.00, in the order of their elution.

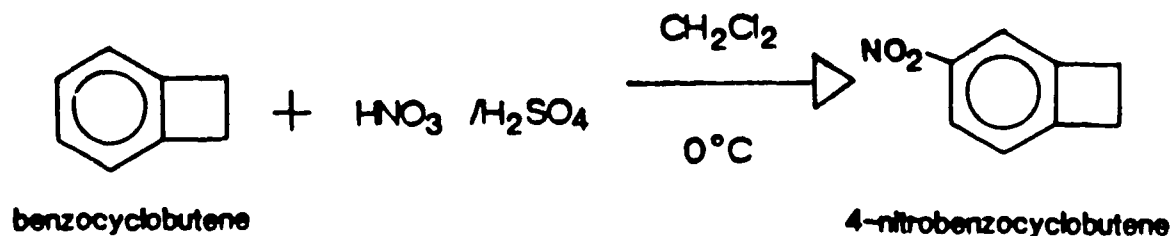


Figure 3. Synthesis of 4-Nitrobenzocyclobutene from Benzocyclobutene

The chromatogram for the final product of the nitration step is shown in Figure 4B. Three major peaks are indicated, having peak area ratios of 1.0 to 2.5 to 1.3, in the order of their elution. Like benzocyclobutene, 4-nitrobenzocyclobutene exists in only one isomeric form; thus, impurities must also be present in this product.

Synthesis of 4-Aminobenzocyclobutene

The next step in the synthesis of the BCB oligomer is conversion of the 4-nitrobenzocyclobutene to 4-aminobenzocyclobutene. The synthesis scheme is shown in Figure 5. A 10-gram sample of the 4-nitrobenzocyclobutene product was hydrogen reduced, according to the procedure described in the Appendix (Procedure II), to give a 48 percent yield of product. The chromatogram of the 4-aminobenzocyclobutene product is shown in Figure 4C. The chromatogram shows two peaks, with the larger one accounting for 90 percent of the peak area, indicating that the product is relatively pure.

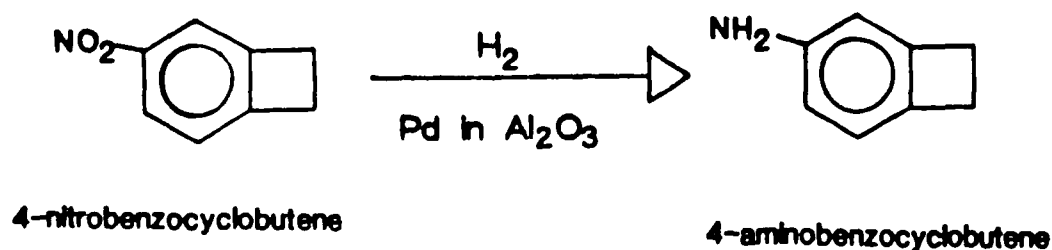


Figure 5. Synthesis of 4-Aminobenzocyclobutene from 4-Nitrobenzocyclobutene

A total of 175 grams from the 200 grams of benzocyclobutene prepared by Fluorochem Inc. was used to prepare 4-aminobenzocyclobutene. To improve on the yield and purity of the 4-aminobenzocyclobutene, a column chromatographic technique using silica

gel and methylene chloride as the solvent was developed for purifying the crude product obtained after the initial nitration step. The purified 4-nitrobenzocyclobutene was then hydrogen reduced to provide a 70 percent yield of 4-aminobenzocyclobutene.

Synthesis of BCB Oligomer Resin

Three syntheses of the BCB oligomer resin were performed with 15 grams of the 4-aminobenzocyclobutene, 50 grams of 2,2-bis(4-phthalic anhydrido)-hexafluoropropane and 6 grams of m-phenylenediamine. The chemical structure of these ingredients are shown in the synthesis scheme in Figure 6. The procedure provided called for extraction of the crude reaction product in methylene chloride. Extraction of the crude product yielded a small amount of methylene chloride soluble material (30 percent based on the weight of the crude). This material was subjected to column chromatography. The yield of the BCB oligomer resin was approximately 7 grams. The second and third synthetic preparations yielded similar results.

To obtain more product, all of the crude materials were soaked in a large excess (10 times the recommended amount) of methylene chloride for 2 weeks. Several additional grams of material were obtained after evaporation of the methylene chloride. The purity of the BCB oligomer obtained from this synthesis was poor as determined by HPLC analysis.

A 1-pound sample of benzocyclobutene from Dow Chemical was received. The material was water white in color. The HPLC analysis of this material showed one major peak with a shoulder. The benzocyclobutene previously received from Fluorochem was amber in color and showed two major peaks by HPLC, both in equal area.

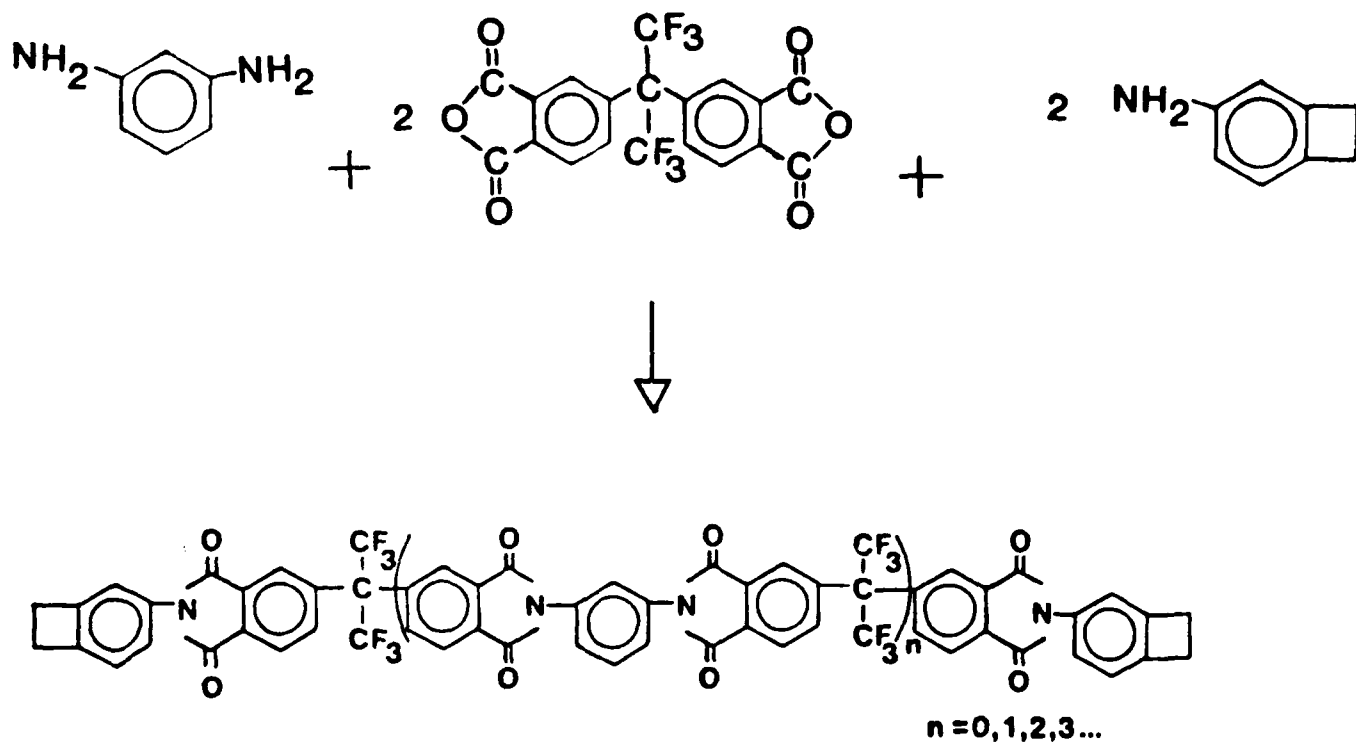


Figure 6. Synthesis of BCB Oligomer Resin

Two BCB oligomer syntheses were performed using the previously described procedures and utilizing the Dow Chemical benzocyclobutene material. A total of 82.1 grams of BCB oligomer was prepared. The preparation of the BCB oligomer was much easier using the benzocyclobutene supplied by Dow Chemical. Fifty grams of this material were delivered to the Materials Laboratory for evaluation.

The Materials Laboratory tested the 50-gram sample of BCB oligomer by HPLC. The material contained the correct distribution of BCB oligomers; however, an impurity peak was observed. Further studies by the Air Force identified this impurity as indole which can be formed in the synthesis of the 4-aminobenzocyclobutene intermediate used in the preparation of the BCB oligomer resin.

A meeting was held at the Materials Laboratory to decide if the indole impurity in the BCB oligomer resin could be removed by a hot water extraction. In addition to being present in the Oligomer resin as an undesirable impurity, the indole also affected the stoichiometry of the reaction. To compensate for the reduced amount of 4-aminobenzocyclobutene endcapping reagent caused by the indole, it was necessary to react the purified BCB oligomer with additional 4-aminobenzocyclobutene to complete endcapping of the BCB oligomers. A 43.7-gram sample of reworked BCB oligomer resin was resubmitted to the Materials Laboratory. The HPLC analysis of the reworked BCB oligomer resin by the Air Force showed no evidence of an indole impurity. This material is undergoing further chemical and mechanical evaluation by the Air Force.

The conversion of benzocyclobutene to 4-aminobenzocyclobutene was completed for the first pound of material received from Dow Chemical. The initial nitration step in the synthesis of 4-aminobenzocyclobutene was conducted at -10°C rather than at 0°C

as previously done. The change to -10°C was made based on conversations with L-Seng Tan of the Materials Laboratory and Norm Madison of Dow Chemical. The crude 4-nitrobenzocyclobutene product obtained was subjected to the hot water extraction step to remove any indole which might be present in the sample. The material was then purified by column chromatography. The HPLC analysis of this material indicated the presence of only one component. The reduction of the reaction temperature from 0°C to -10°C resulted in a marked increase in the yield of purified 4-nitrobenzocyclobutene. The reduction in reaction temperature also has provided a material easier to purify.

A second pound of benzocyclobutene was received from Dow Chemical and converted to 4-aminobenzocyclobutene. Three batches of approximately 400 grams of BCB oligomer resin were prepared with the benzocyclobutene obtained from Dow Chemical. A 50-gram sample from one batch and 5-gram samples from the other two batches of BCB oligomer resin have been submitted to the Air Force for evaluation. Synthesis of a fourth batch of 400 grams of BCB oligomer resin is in progress. The approximately 1,600 grams of BCB oligomer resin synthesized will be sufficient for evaluating the pure BCB oligomer and the BCB oligomer/BMI blend in Tasks 2 through 6.

SECTION 3

ENVIRONMENTAL IMPACT

The environmental consequences of the technology being developed in the project will be assessed at three stages: (1) during synthesis and characterization of the polymers, (2) during prepregging of the polymers with regard to any solvents used, and (3) during handling and processing of the prepreg into composites. Environmental problems which might occur in scaling up the technology in the current project will also be reported to the Air Force and suggestions will be made to make the technology environmentally acceptable. The economic impact these suggestions might cause will also be evaluated.

At both Northrop and UDRI, operational safety and handling of toxic materials are of vital interest. It is most important to have concerned, knowledgeable personnel and experienced, dedicated supervision. The project team for this program meets these needs. As more is learned about both the short- and long-range toxic effects of chemicals, more attention is being focused on these concerns in the laboratory.

To assess particular safety hazards for general chemical and physical agents, the "TLV's (Threshold Limit Values) of Workroom Environments" published by the American Conference of Industrial Hygienists will be used as a guideline. For less common materials, TOXLINE, a computerized data bank on toxicity of chemicals, will be searched. Materials that are suspected to be toxic by examination of their chemical structure, but for which no information on toxicity can be found, will be treated as if they are toxic. Information on the potential hazards of particular chemicals used in this program, or products resulting from it, will be reported to the Air Force.

Environmental problems are not expected for the scale at which the program will be operating. Synthesis in the current project is limited to the preparation of 500 to 1,000 grams of five polymers. Waste solvents and chemicals will be disposed of by an approved chemical disposal firm.

If particular hazards are perceived to exist, recommendations will be made to the Air Force concerning the large scale use of products from this program.

We suggest that final products which might be suspected carcinogens, based on their chemical structures, be screened by the Air Force by Ames bacterial mutagenicity tests. NASA/Langley has done this screening for a variety of aromatic amine high temperature polymer intermediates, and the Air Force has done the same for some of the compound types used for this program. These tests can be done on a purchase order basis, a nominal cost per compound, depending on the number of bacteria strains included.

SECTION 4

CONCLUSIONS

Two matrix resin candidates have been selected for evaluation in the program. The first is a bisbenzocyclobutene-terminated imide (BCB oligomer) and the second is a mixture of the BCB oligomer and 4,4'-bismaleimidodiphenyl-methane (BMI resin).

The scale-up synthesis of the BCB oligomer has been developed. The synthesis was conducted in three steps. In the first step, benzocyclobutene was converted to 4-nitrobenzocyclobutene. The 4-nitrobenzocyclobutene was then reduced to 4-aminobenzocyclobutene in the second step. The BCB oligomer resin was prepared in a third step by combining two moles of 2,2-bis(4-phthalic anhydrido)-hexafluoropropane, one mole of m-phenylenediamine and two moles of 4-aminobenzocyclobutene. Three batches of approximately 400 grams of BCB oligomer have been prepared. Synthesis of a fourth 400 grams of BCB oligomer resin is in progress. A 50-gram sample of one batch and 5-gram samples of the other two batches of BCB oligomer are being evaluated by the Air Force. If the purity of the four BCB oligomer resin batches is validated, the materials will be thoroughly blended together by ball milling. This material will then undergo further chemical, thermal rheological and mechanical validation tests in Task 2.

APPENDIX

PROCEDURE I. PREPARATION OF 4-NITROBENZOCYCLOBUTENE FROM BENZOCYCLOBUTENE (BCB) MONOMER

1. Place 117.7 grams (1.1282 moles) of benzocyclobutene monomer and 1130 ml of methylene chloride in a 2-liter, 3 necked, round-bottom flask equipped with a thermometer, an overhead stirrer, an addition funnel, and an ice/salt bath.
2. Cool the mixture to -10°C while stirring it.
3. Place a solution of nitric acid and sulfuric acid (120.5 grams of conc. HNO_3 and 230.5 grams of conc. H_2SO_4) in the addition funnel.
4. Slowly add the acid solution to the reaction mixture over a time period of 2.5 hours, while maintaining the temperature of the reaction mixture at -10°C .
5. Stir the reaction mixture for another hour after the completion of addition, keeping the mixture temperature at -10°C .
6. After an hour of stirring, remove the ice bath and allow the reaction mixture to warm up to room temperature.
7. Separate the organic layer from the reaction mixture and wash it with water (1X1000 ml).
8. Neutralize the organic layer with a saturated aqueous solution of Na_2CO_3 .

9. Wash the methylene chloride solution with water (3X1000 ml). It may be necessary to add NaCl to the water in order to achieve a better separation of the two layers.
10. Dry the methylene chloride layer with anhydrous magnesium sulfate, and remove the solvent using the roto evaporator. Save and weight the residue.
11. Neutralize the acid layer from the reaction mixture with an aqueous solution of NaOH and ice.
12. Upon neutralization, combine the aqueous phase with the aqueous washings from the treatment of the original methylene chloride layer.
13. Extract the entire solution twice with 1 liter of methylene chloride.
14. Wash the methylene chloride layers with water (2X500 ml). Then dry the layers with anhydrous MgSO_4 .
15. Remove the methylene chloride from the solution using roto evaporator and save the residue.
16. Combine and weigh the residues from steps 14 and 15.
17. Dissolve the combined residue in petroleum ether and pass the solution through a column filled with Woelm silica gel (approximately 400 ml silica gel-dry). The impurities will stay in the column.
18. Remove the petroleum ether from the solution by roto evaporation and weigh the residue.

19. Mix the residue with 160 grams of Woelm silica gel and place the mixture into a dry column packed with silica gel (570 grams).
20. Slowly drip the petroleum ether into the top of the column and collect 50 ml fractions.
21. Evaporate each fraction to dryness and weigh the residue.

This procedure should yield approximately 76 grams of nitrobenzocyclobutene.

PROCEDURE II. PREPARATION OF 4-AMINO BENZOCYCLOBUTENE FROM 4-NITRO BENZOCYCLOBUTENE

1. Place 55.5 grams 0.3721 moles of 4-nitrobenzocyclobutene and 4.5 grams of 5% Pd/Al₂O₃ in a hydrogenation bottle containing 180 ml of methanol.
2. Subject the resultant mixture to catalytic hydrogenation (about 60 psi H₂/room temperature) until no more uptake of H₂ is observed (should take about 6 to 8 hours).
3. Filter the mixture through a bed of Celite, that was previously washed with 100 ml of methanol, to remove the catalyst.
4. Subject the filtrate to roto evaporation with water bath temperature at 40 to 45°C.
5. Weigh the residue.

6. Dissolve the resultant viscous residue in 150 ml of methylene chloride. Dry the solution with MgSO_4 .
7. Remove the methylene chloride by roto evaporation with water bath temperature at approximately 45°C .
8. Weigh the residue.
9. Vacuum dry the final amber red viscous liquid at room temperature for two hours.
10. Weigh the residue.

This step should yield approximately 39.3 grams of the 4-amino derivative. This material should be stored at 0°C or lower and used as soon as possible for the next step.

PROCEDURE III. PREPARATION OF OLIGOMERIC BCB

1. Place 100 grams (0.225 mole) of the 6F-dianhydride and 400 ml of dimethyl acetamide into a 1-liter, 3-necked, round-bottomed flask equipped with an overhead stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube.
2. After complete dissolution of 6F-dianhydride, add 12.0 grams (0.111 mole) of m-phenylenediamine, that was previously washed with hexane/acetone and hexane, to the solution in small portions.
3. Immediately after adding the m-phenylenediamine, a dark amber solution will form. Stir the solution at room temperature for 72 hours under nitrogen.

4. Add 30.0 grams (0.252 mole) or freshly prepared 4-aminobenzocyclobutene to the reaction mixture, followed by 100 ml of dimethyl acetamide.
5. Stir the resultant reaction mixture at about 45°C under nitrogen for 24 hours.
6. After 24 hours, add a mixture of 88 ml (95.2 grams, 0.93 mole) of acetic anhydride and 70 ml (68.5 grams, 0.87 mole) of pyridene to the reaction mixture. Keep stirring for another 20 hours at 45°C under nitrogen.
7. After 20 hours, cool the reaction mixture to RT. Pour the mixture into a solution of 420 ml of concentrated hydrochloric acid and 5000 ml of water while stirring.
8. Stir the resultant mixture for another hour.
9. Collect the solid by suction filtration, and wash the collected solid on the filter with 4 liters of water.
10. Air dry the solid over night.
11. Extract the crude solid with 800 ml of methylene chloride. The residual water can be separated by a separatory funnel if needed.
12. Dry the organic solution over anhydrous magnesium sulfate.
13. Filter the dried solution through a filter system consisting of a layer of Celite, a layer of 100 grams of silica gel, and a layer of sand in a 600 ml coarse porosity filter funnel which was saturated with hexane.

14. Wash the filter system with methylene chloride until the filtrate is colorless.
15. Subject the filtrate to rotary evaporation to remove the solvent.
16. Dry the resultant yellow product in a vacuum oven at about 100 to 110°C for 24 hours.
17. Weigh the residue.

The yield should be approximately 120 grams.