SOC1-97/1

EB CURING OF VARTM FABRICATED MARITIME COMPOSITE STRUCTURES

Contract USZA22-97-P-0013
CDRL A002

Prepared for

USSOCOM
7701 Tampa Point Blvd.
MacDill AFB, FL 33621-5419

September 19, 1997

by

DAMILIC Corporation
14670 Southlawn Lane
Rockville, MD 2085

CONTENTS

Acknowledgment

The authors are grateful for the support provided by Irradiation Industries, Inc. of Gaithersburg, Maryland.

SECTION I

INTRODUCTION

Electron beam (EB) curing can be used to manufacture composite material components at higher speeds and with greater production flexibility than conventional techniques. Because curing is not initiated until irradiation, timing restrictions associated with lay up and resin infusion can be relaxed, leading to reduced scrap and rework. Furthermore EB curing systems are generally "solventless", with fewer VOCs, and therefore more environmentally friendly. This report describes a Phase I SBIR project with the objective of demonstrating the feasibility of the practical application of this technology in the boat building industry.

SUMMARY

With the intent of demonstrating that EB curing can become a practical process for the manufacture of SOCOM marine vehicles, a representative section of a boat hull was produced. The section selected for demonstration included a geometry more complex than any other reported to be cured with EB irradiation. The section included the hull bottom and side, spray strake, and longitudinal support layed-up and cured as one component in a single step. The section incorporated materials typically used in current boat construction: fiberglass chopped mat, Kevlar fabric, plastic foam core, vinylester resin, and a commercially available white gel coat. A photograph of this component is shown in Figure 1.

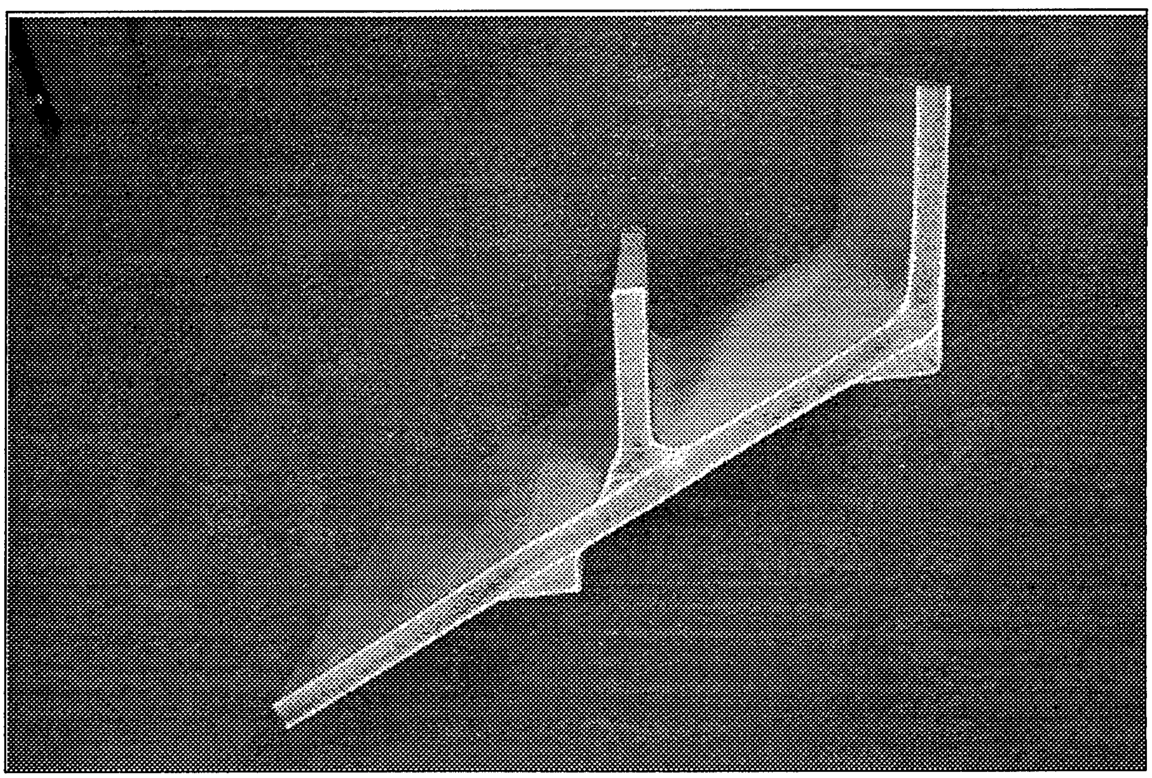

Figure 1: Demonstration section of boat hull cured with EB radiation.

The part was layed up on inexpensive wood/formica tooling. A vacuum assisted resin transfer molding technique was used for resin infusion. Immediately after resin infusion, the part was irradiated as required to achieve satisfactory cure. Although the cure was sufficient throughout the part, delamination was observed in several regions of the part. The delamination zones appear to be "resin starved", implying that the delaminations resulted from the resin infusion process, not the EB curing step.

CONCLUSIONS

The project successfully demonstrated that electron beams can successfully penetrate complex boat structures and satisfactorily cure off the shelf resins.

The practical use of low cost tooling with EB curing systems was reinforced.

Although the specific cause(s) of observed delamination are not known, they result from inadequate process control during lay up/resin infusion. It is also possible that EB processing's ability to instantly initiate cure immediately following resin infusion results in a requirement for an additional process quality check prior to irradiation.

SECTION II
PROJECT DETAILS, DATA

DEMONSTRATION PART GEOMETRY

The part selected for manufacture in this Phase 1 program is a sub-section of a typical small marine craft (see Figure 2). The specific hull sub-section (see magnified section of full boat cross-section in Figure 3) consisted of a short lower hull section (including bottom and side elements), a spray strake, and a longitudinal support. The completed structure was approximately three feet long and two feet wide with the vertical structures standing approximately 8 inches above the hull section.

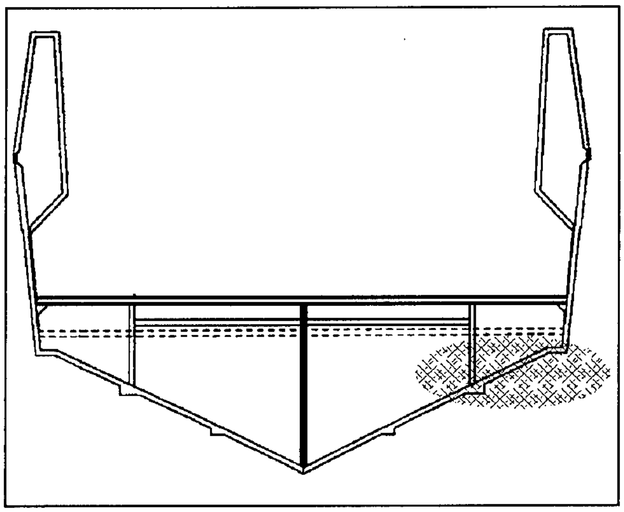

Figure 2: Full boat cross section. Section fabricated for demonstration is marked with cross hatch pattern.

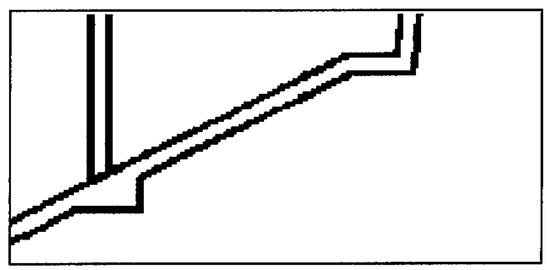

Figure 3: Magnified section of boat hull section selected for fabrication.

MATERIALS AND RELATED CHEMISTRY

The materials used to construct the demonstration part were selected because of their common use in the composite boat building industry and were used without modification. They include; CoRezyn white gel coat (Interplastics Corporation), Divinycell H grade plastic foam core (DIAB Group), Advantex glass fiber M723 chopped strand mat (Owens Corning), Kevlar fabric, and Derakane 8084 vinyl ester resin (Dow Chemical Company).

In this work, the role of the radiation is to produce alkyl free radicals throughout the resin, creating the same initiating species that traditional chemical initiators might produce. Once these free radicals are created, the vinyl monomers in the resin add to the free radical, propagating the free radical, and curing the resin. In fact, after the free radicals have been produced, the cure proceeds via conventional kinetics.

Unlike conventional curing, however, the radiation process can insert the initiating free radicals in a fraction of a second. Although desirable from a process perspective, the resulting exotherm could destroy the part. The very high initiation rate (dose-rate) would also enhance radical-radical reactions (that would cause premature termination of the propagating chain) with a concomitant reduction in the average chain length. For these reasons, the resin was cured with a series of low-dose irradiations.

Effect of Radiation on Chemistry, Materials

This feasibility demonstration follows previous laboratory work in radiation processing and, therefore, focused on a practical application of industrial e-beam curing for the production of a boat hull section. Consequently, the effect of dose, dose-rate, temperature, and additives were not evaluated. These factors can produce profound effects in the cure kinetics and the properties of the final polymer. However, prior work by DAMILIC Corporation[1] has shown that a well controlled radiation curing process can yield mechanical strength properties similar to those of conventionally cured processes with dimensional improvements (flatness, void reductions) resulting from lower thermal impact. Similarly, prior work by others, as described in the following paragraphs, has shown that radiation damage of the selected materials is very unlikely.

Glass Fibers

Glass is one of the most radiation resistant materials known. Inorganic glass is currently under investigation by the Department of Energy as an encapsulation medium for radioactive waste and has demonstrated its resistance to radiation levels many orders of magnitude greater than the cure doses experienced during the EB curing of a composite marine structure. In the vitrification process, radioactive materials are incorporated into the glass matrix. As the radioactive materials decay, they irradiate the glass to total accumulated doses of 1 to 100,000 kGy (the composite cure dose in this demonstration was 200 kGy). Early published references to the radiation resistance of silicate glasses include the book Radiation Damage in Solids[2]. Since that time there have been hundreds of publications, many coming from DOE support work (mostly funded by the DOE office of Environmental Management).

Closer to composite marine craft, many researchers have studied radiation effects on polymer and glass-fiber/composites used in fusion magnets. These studies have examined several types of glass-epoxy and glass-polyimide composites systems[3]. These systems are so robust, that the lowest dose evaluated was 20,000 kGy, approximately 100 times greater than the cure dose for this demonstration..

---

[1] U.S. Army Contract DDAEO7-94-C-RO43, "Radiation Cured Composites, SBIR - Phase II

[2] D.S. Billington and J.H. Crawford, Princeton University Press, 1961

[3] S. Egusa, T. Seguchi, M. Hagiwara, H. Nakajima, S. Shimamoto, M.A. Kirk, and R.C. Birtcher, "Radiation-Degradation Studies of the Mechanical Properties of Polymer Matrix Composites Used in Fusion Magnets", published in Radiation Effects in Polymers, edited by R. Clough and S. Shalaby, American Chemical Society Series 475, page 591, 1991

There is no basis to suspect that the radiation doses used to cure the composite boat hull section degraded the glass fiber in any way.

Kevlar Fibers

There is less known about the effect of radiation on KEVLAR (compared to glass). However, there is already a host of publications on the performance of KEVLAR composite structures. Notable is the work published by NASA[4,5] . In this work, KEVLAR is identified as a "preferred "material for space applications (the highest rating they gave any material). Although the work does not give a specific dose at which the material is appreciably altered, the cut-off threshold (as identified in the report for space applications) for "preferred materials" is greater than 10,000 kGy. This is not unexpected, since organic materials with ring structures (such as polystyrene) are the most radiation resistant polymers[6, 7].

Also, some have reported the successful use of KEVLAR in radiation cured composites[8] . In these works, there is no evidence that the radiation curing process damages the KEVLAR fiber. Like the glass fiber, there is no basis to suspect that the radiation doses used to cure the composite hull section degraded the KEVLAR fiber in any way.

Polyesters (Vinyl-ester Polymers)

Polyesters are a common industrial polymer that are used in a range of commercial applications. They are well known as radiation resistant polymers that can withstand doses far in excess of the cure doses used in this program[9]. Also, several have already published on the radiation curing of vinyl ester resins. The results confirm our results, showing that vinyl resins can fully cure when exposed to ionizing radiation, producing a polymer with properties that match the

---

[4] Contract No. NAS 7-100, C.J. Morrissey, "Degradation of Dielectrics in Space", 1985

[5] JPL Invention Report NPO-16003/5915, 1985

[6] W.E. Skeins & J.L. Williams, "Ionizing Radiation's Effects on Selected Biomedical Polymers", Corporate Report available from Radiation Sterilizers, Incorporated

[7] *Radiation Effects on Organic Materials*, edited by R.O. Bolt and J.G. Carroll, Academic Press, New York, 1963

[8] C.B. Saunders, A. Singh, V.J. Lapata, S. Seier, G.D. Boyer, W. Kremers, and V.A. Mason, "Electron curing of Aramid-Fiber Reinforced Composites, Radiation Effects on Polymers, edited by R. Clough and S. Shalaby, ACS Symposium Series 475, 251, 1991

[9] *Radiation Effects on Organic Materials*, edited by R.O. Bolt and J.G. Carroll, Academic Press, New York, 1963

properties of conventionally cured vinyl esters.[10, 11] The second study, further demonstrated that the use of low-temperature EB curing reduced the amount of volatiles released during the cure cycle. These publications strongly suggest that vinyl esters should radiation cure, and if cured, should survive doses far in excess of the cure doses used in this demonstrtion.

Foamed PVC

Although there is little published on foamed PVC, the effect of radiation of the bulk form of this material is well understood and published. The irradiation of PVC can cause the release of small amounts of HCl followed by the crosslinking and/or scission of the polymer chain. The scission reaction is minimized when the irradiation is performed in vacuum. Hard, high-strength resins show only small losses in tensile strength at 1,000 kGy and impact strength is even more radiation resistant.[12]

PVC is also a biomedical material common in the production of medical devices and, as a result has been extensively studied. These studies show that PVC will discolor darkly when irradiated to sterilization doses, 10-30 kGy.[13] Although important for medical applications (and equally un-important for the SOCOM application), the color change in irradiated PVC can be corrected by additives and/or additional processing steps.

Although PVC would be expected to discolor upon exposure to ionizing radiation, the color change is a result of the creations of harmless color centers in the polymer matrix, not the effect of deleterious change in the mechanical properties of the PVC. As a result, we fully expect the foam to survive the doses used in this work. However, of the materials used to construct the hull structure, the PVC is the most radiation sensitive.

LAY-UP

The materials were laid-up on a laminated wood tool (described in the next section), according to the following schedule:

---

[10] D. Beziers and J.P.Denost, "Composite Curing: A New Process", American Institute of Aeronautics and Astronautics, 1989

[11] S.L. Iverson, C.B. Saunders, T.E. McDougall, W. Kremers, V.J. Lopata, A. Singh, and D. Kerluke, "Radiation-Curable Composites: Environmental Advantages", presented at the International Symposium on Applications of Isotopes and Radiation in Conservation of the Environment, IAEA-SM-325/141, 1992

[12] *Radiation Effects on Organic Materials,* edited by R.O. Bolt and J.G. Carroll, Academic Press, New York, 1963

[13] J. Stubstad, "Aging Studies of Radiation Sterilized IV Sets", Proceedings of the Medical Design & Manufacturing Conference, 108-9, 1997

Hull bottom
Gel coat
1 ply 1 oz. mat
4 plies 0-90 biaxial Kevlar
1 inch thick polymer foam core
1 ply 1 oz. mat
4 plies 0-90 biaxial Kevlar

Spray strake
Gel coat
1 ply 1 oz. mat
4 plies 0-90 biaxial Kevlar
1 inch thick polymer foam core

Longitudinal
4 plies 0-90 biaxial Kevlar
1 inch thick polymer foam core

TOOLING

The tool was constructed from ¾ inch plywood then covered with a Formica laminate (see Figure 4). Tool contours were modified using epoxy fillets or plastic molding. The completed tool was vacuum tested after construction.

The tool cost approximately $200 to construct and weighs 45 pounds.

Because EB cures can be achieved at room temperature, no special consideration for high temperature operation was included in the tool design and construction. Unfortunately, the elevated temperature (ref. Figure 7), resulting from exothermic reaction during cure, exceeded the rated operating temperature of the epoxy fillet. This resulted in loss of vacuum during the EB cure, exacerbating the part's delaminations, and some local contamination of the hull outer surface with epoxy. This particular tool will require some minor rework for additional use. However, the use of a more appropriate epoxy would render this tool reusable for many production runs.

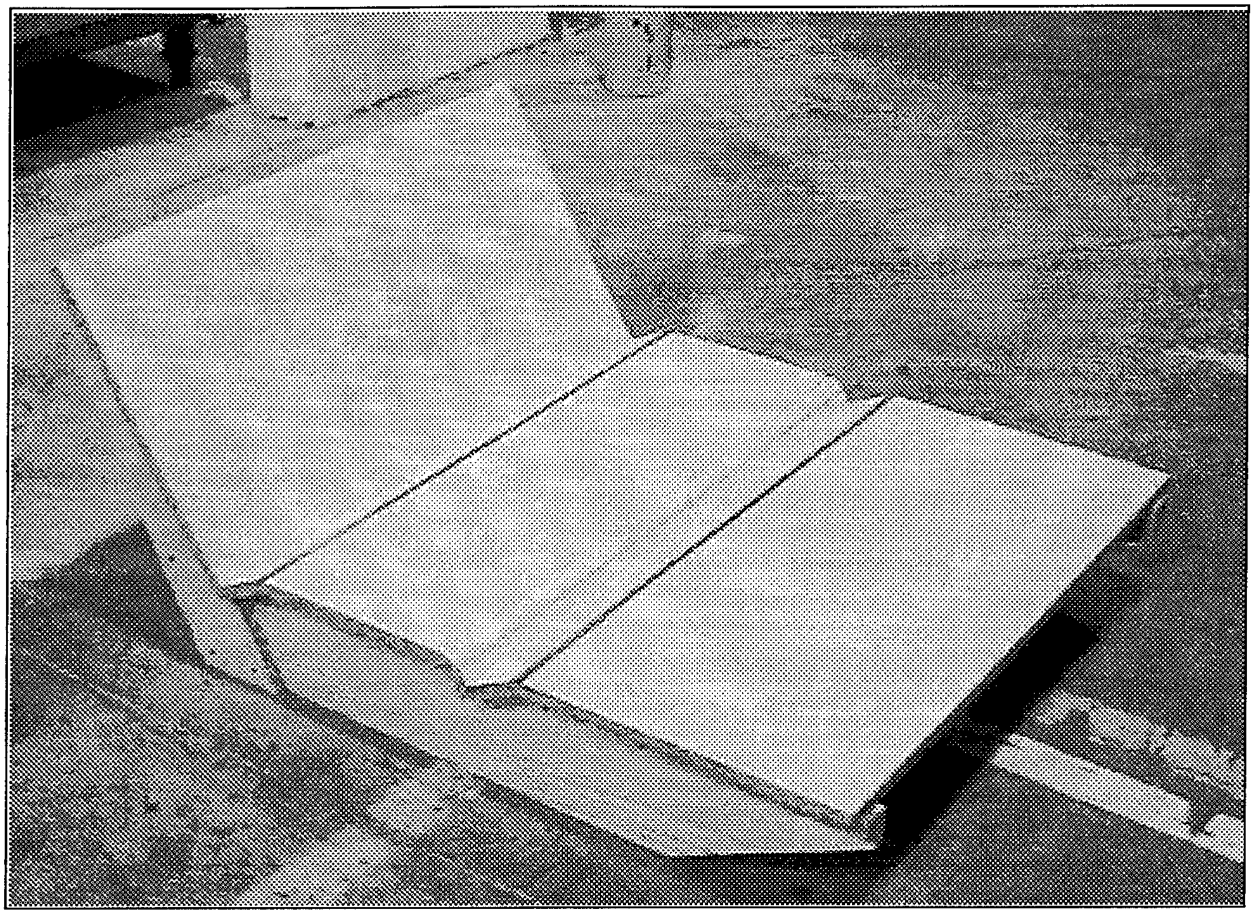

Figure 4: Tool was constructed of wood and Formica.

PROCESS DEVELOPMENT

Because the specific materials and geometry had not previously been incorporated into an EB cure process, several issues had to be resolved prior to actually producing the part:

1) dose required to fully cure resin

2) ability to include the longitudinal support in a single lay up

3) irradiation facility requirements

4) effect of radiation on gel coat.

Required Dose

To confirm that EB irradiation would achieve the expected cure, several neat samples of the Derakane 8084 resin were irradiated to various levels of dose. The resin was considered fully cured when color and tackiness disappeared, and the material's hardness exceeded 30 Barcol. This task confirmed that the resin required no additives or chemical modification to achieve cure with a reasonable dose. This task also demonstrated a sensitivity to dose rate. Resin samples receiving a high radiation dose in a single pass exhibited non-uniform cure and evidence of "foaming". Following the initial work with neat resins, coupons incorporating both the glass and Kevlar fibers were produced to confirm adequate cure was achieved with the combination of fiber and resin.

Lay-up Incorporating Longitudinal Support

Sample lay-ups incorporating fiber, foam core, and resin were produced and irradiated to further confirm cure dose and material compatibility. One of these lay-ups included two sections of foam core forming a 'T' with an outer sandwich of glass and Kevlar fiber. This activity confirmed that the longitudinal support could be incorporated into the proposed structure in a single lay-up and resin infusion operation.

Gel Coat Irradiation

To establish the impact of EB irradiation on the selected gel coat, samples with varying amounts of catalyst (ranging from none to the manufacturer's recommendation) were produced and irradiated to various levels of dose. This step confirmed that irradiation does increase the gel coat cure (becomes harder), but does not show any apparent damage when irradiated to the levels of interest. Furthermore, there was no apparent change in color of the gel coat finish.

Radiation Dosimetry

The cure of the resin is initiated by the radiation absorbed as the part passes though the radiation vault. Thus, the energy absorbed per gram (or dose) must be understood and subsequently controlled to ensure uniform cure though the thickness of the part. Computer simulations accomplish this task.

In this work, the Integrated Tiger Series (ITS) was used to model the hull section and to determine the dose profile across the part when exposed to 9.5 MeV electrons. The program permits the exact modeling of the individual layers of materials (including such elements as bagging materials) and, through the use of Monte Carlo calculations, the dose deposited across each material can be determined. In order to ensure that 9.5 MeV electrons will successfully penetrate even the thickest hull cross-section, it was assumed that the electrons would enter the part at a 45° angle then traverse the part, passing through the longitudinal support, the hull, and the strake. Figure 5 demonstrates the very good uniformity of dose deposited in the part as a function of the electron's range as it traverses the part.

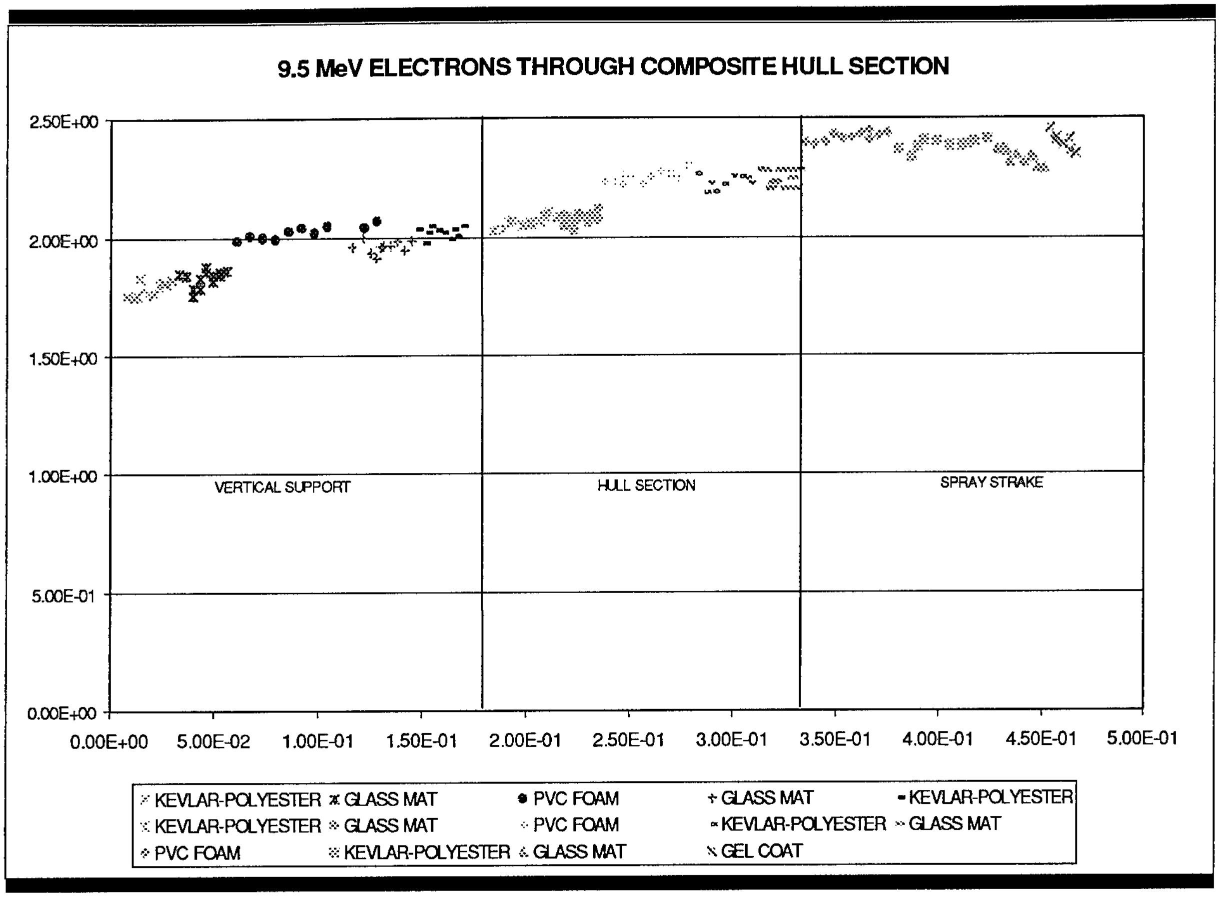

Figure 5: Dose absorption as predicted by computer model.

IRRADIATION

The irradiations were performed at EBeam Services, Inc. (Cranbury, NJ) using a 9.5 MeV electron accelerator. The tight electron beam (approximately 1 cm diameter) is scanned uniformly over individual carts as they pass through the shielded vault.

The part (while under static vacuum bagging on the tool), was placed on an aluminum cart, and automatically taken though the maze into to irradiation chamber (Figure 6). As the part moved under the electron beam it received a dose of 20 kGy. Upon exiting the shielded area, the part was examined, the temperature at various locations was measured, and it was sent back into the vault for additional cure. This process was repeated 9 times until the part received a total absorbed dose of 180 kGy.

Although the temperature of the part is expected to rise slightly from the direct effect of the irradiation, a more significant, and important, temperature rise is expected from the exotherm generated during the polymerization of the resin. For this reason, five thermocouples were embedded into the resin-fabric regions of the part and monitored after each pass through the radiation vault.

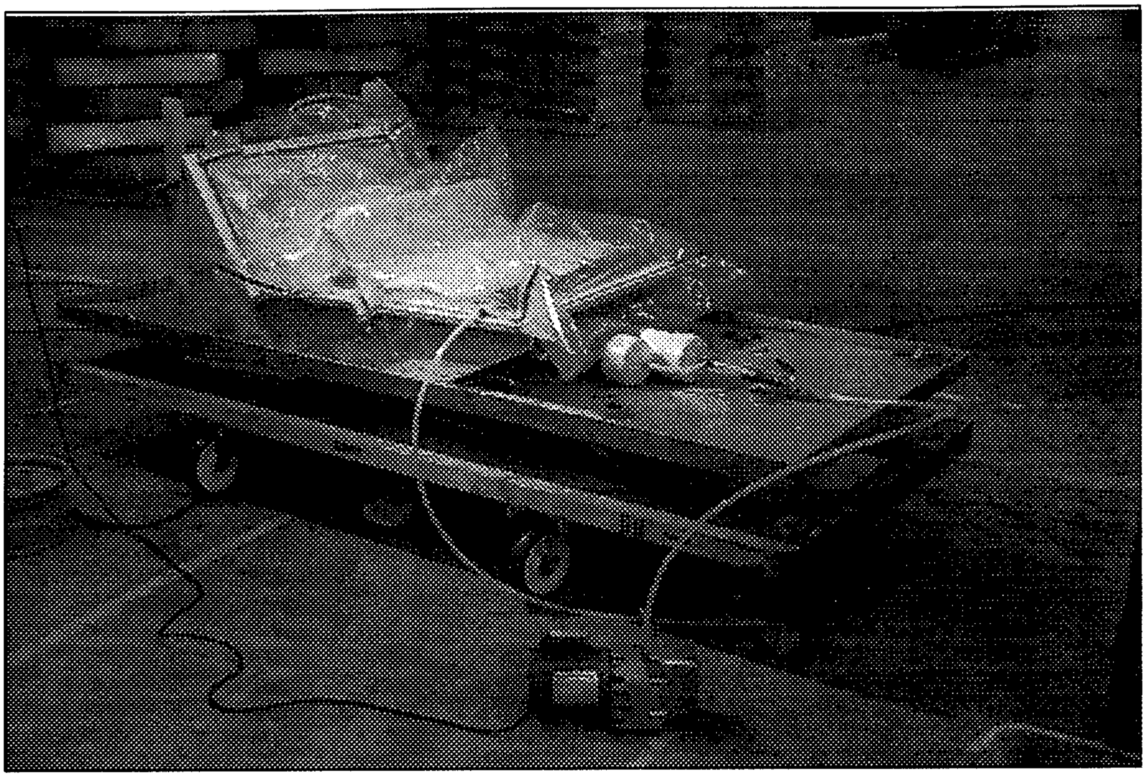

Figure 6: Vacuum bagged part on cart ready for irradiation.

The results are shown in Figure 7. The relative thermocouple placement locations are shown in Figure 8:

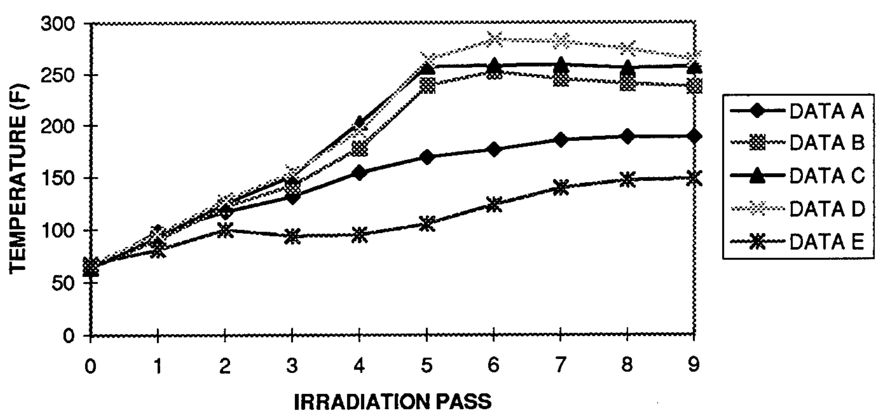

Figure 7: Temperature of thermocouples imbedded in part following each irradiation pass.

'A' is between the two outermost Kevlar fiber plies.

'B' and 'C' are between the outer chopped glass mat and Kevlar plies

'D' is between the hull foam core and Kevlar .

'E' is between the hull Kevlar plies and the longitudinal overplies.

PART EVALUATION

Following irradiation, the part was immediately separated from the tool and its edges cleanly removed. The part appeared to be fully cured through its thickness.

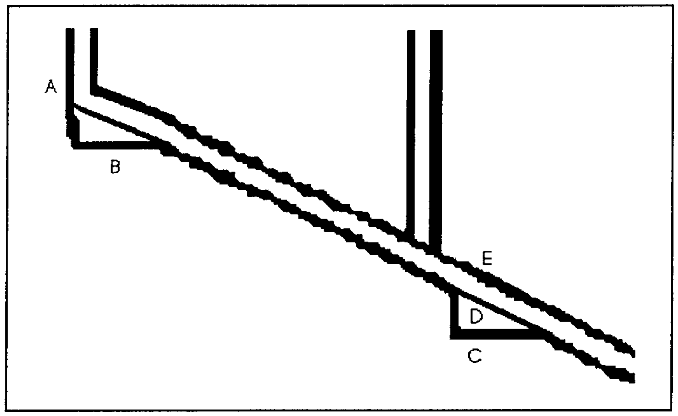

Figure 8: Thermocouple Locations

Delamination

Four regions of delamination were observed:

1) An elliptical area approximately 5" x 10" between the individual Kevlar fabric layers on the inside surface of the hull (i.e. the side with the longitudinal support structure) was observed immediately after removing the part from the tool. This is the upper delamination shown in Figure 9.

2) A 5" x 18" area roughly rectangular in shape between the hull plies and the strake over-plies (between spray strake and boat side). This is the lower delamination shown in Figure 9.

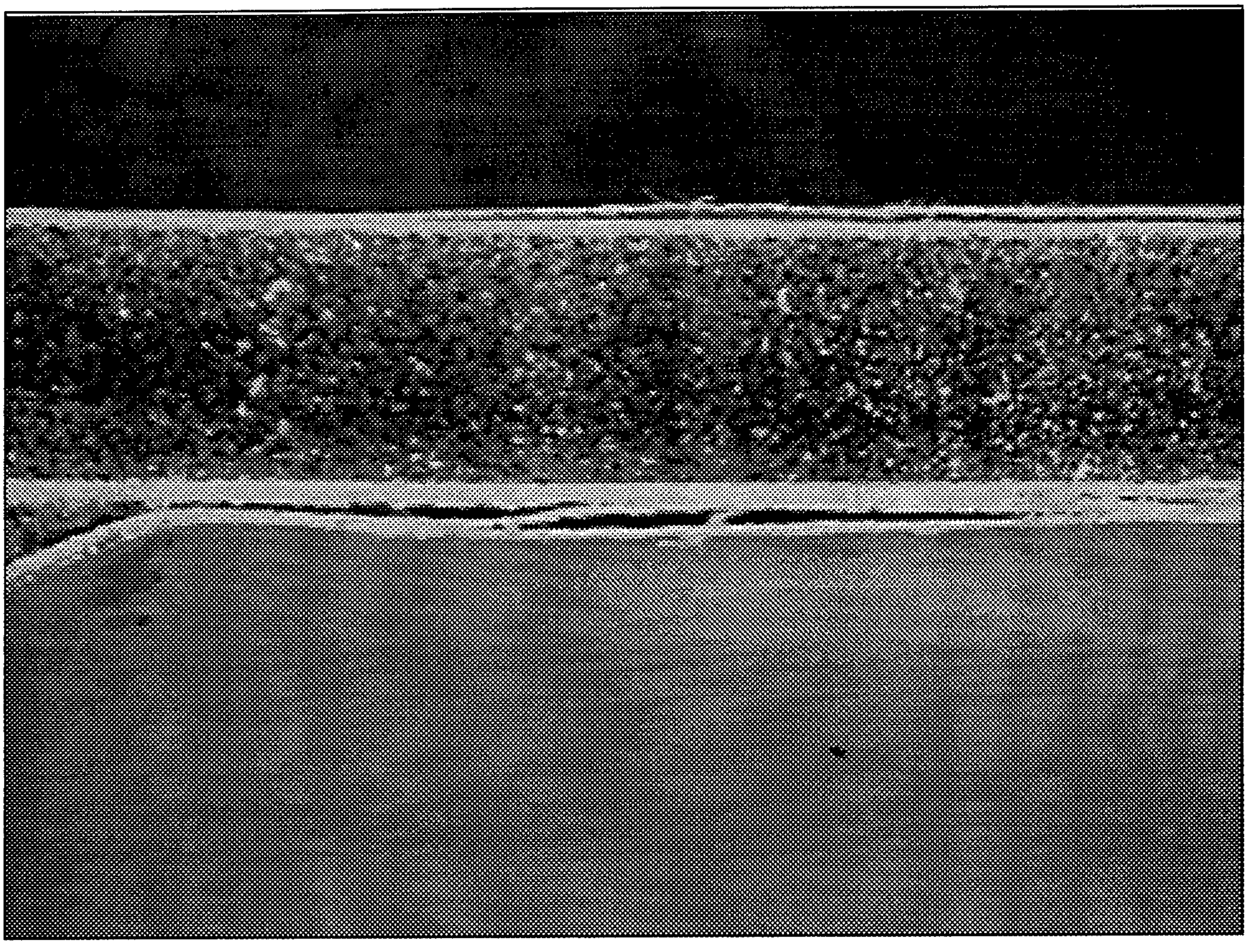

Figure 9: Both delamination and stains from the tooling were observed.

3) A region approximately 4" x 12", below the spray strake. This region, also in the outside layers, does not run to the machined edge, but is similar in characteristic to, and believed to be, delamination the hull plies and the strake overplies.

4) A region approximately 2" x 18" within the outside layers on the upper hull side (this delamination did not extend to machined edge of the part).

The cause of the delamination appeared to be a lack of proper wetting. Samples of fiber were removed for microscopic evaluation. Optical inspection was not more conclusive, so further magnification to 2000 X using a scanning electron microscope confirmed insufficient wetting in the region of delamination (Figure 10), while the sample from a region having no delamination exhibited complete coverage of the fibers with resin (Figure 11).

Other Observations

In addition to the regions of delamination, there are voids between the foam core and adjacent plies at the strake (see example in Figure 12) and longitudinal support. All regions with voids and delamination appear to be resin starved.

Minor flaws considered to be essentially cosmetic in nature were also observed:

1) Thin gel coat gave the appearance of several scratches.

2) A variety of discolorations that are typical of EB curing were also observed, particularly in the foam core. However, there is no apparent change in color for the cosmetically important gel coat finish.

3) Regions of radius formed by the tooling have epoxy on the gel coat surface as described on page 7 (see Figure 9).

Other minor flaws can be observed, such as thin gel coat, and a variety of discolorations.

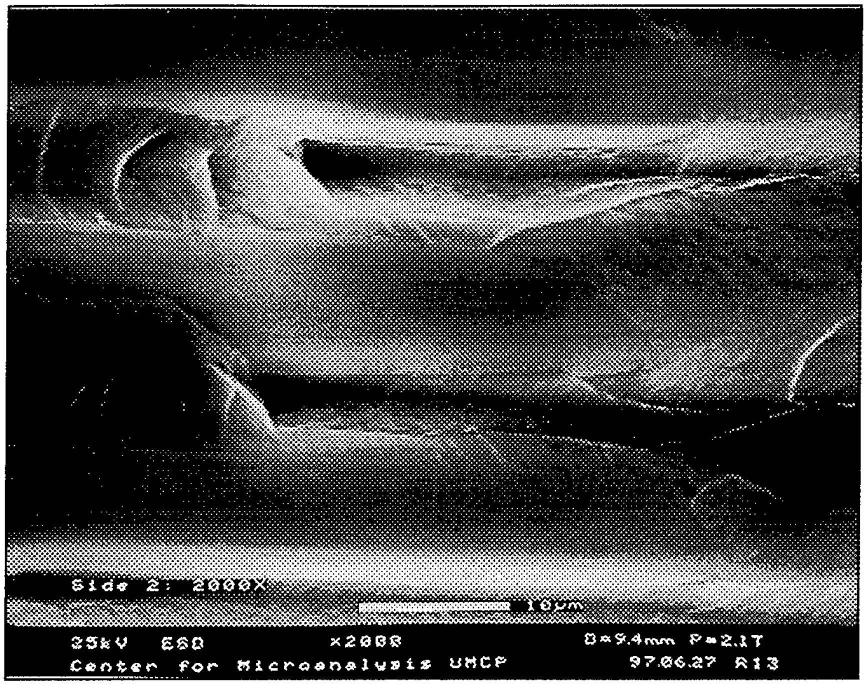

Figure 10: Fibers in region of delamination show lack of resin coverage.

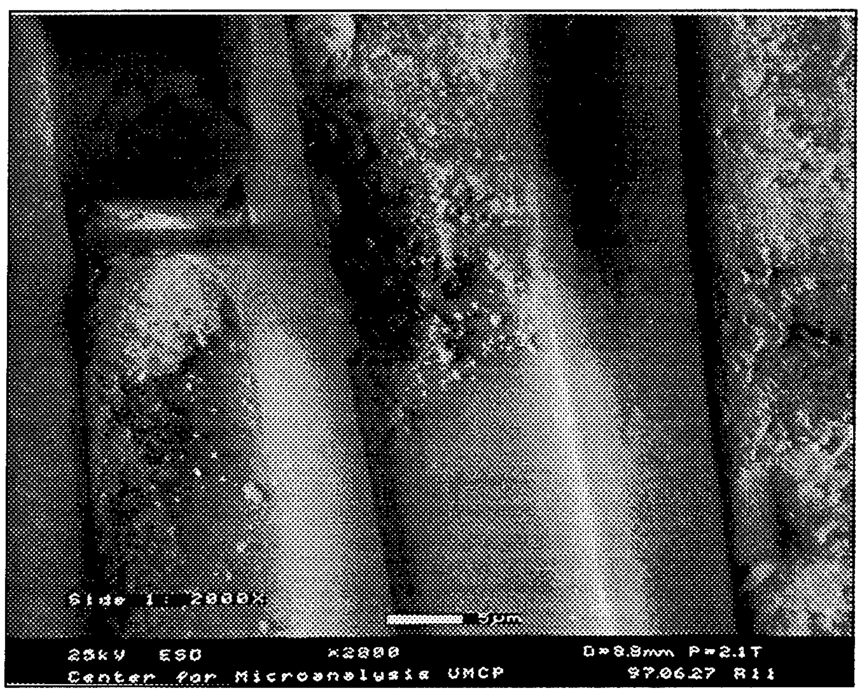

Figure 11: Fibers in region with no delamination have complete resin coverage.

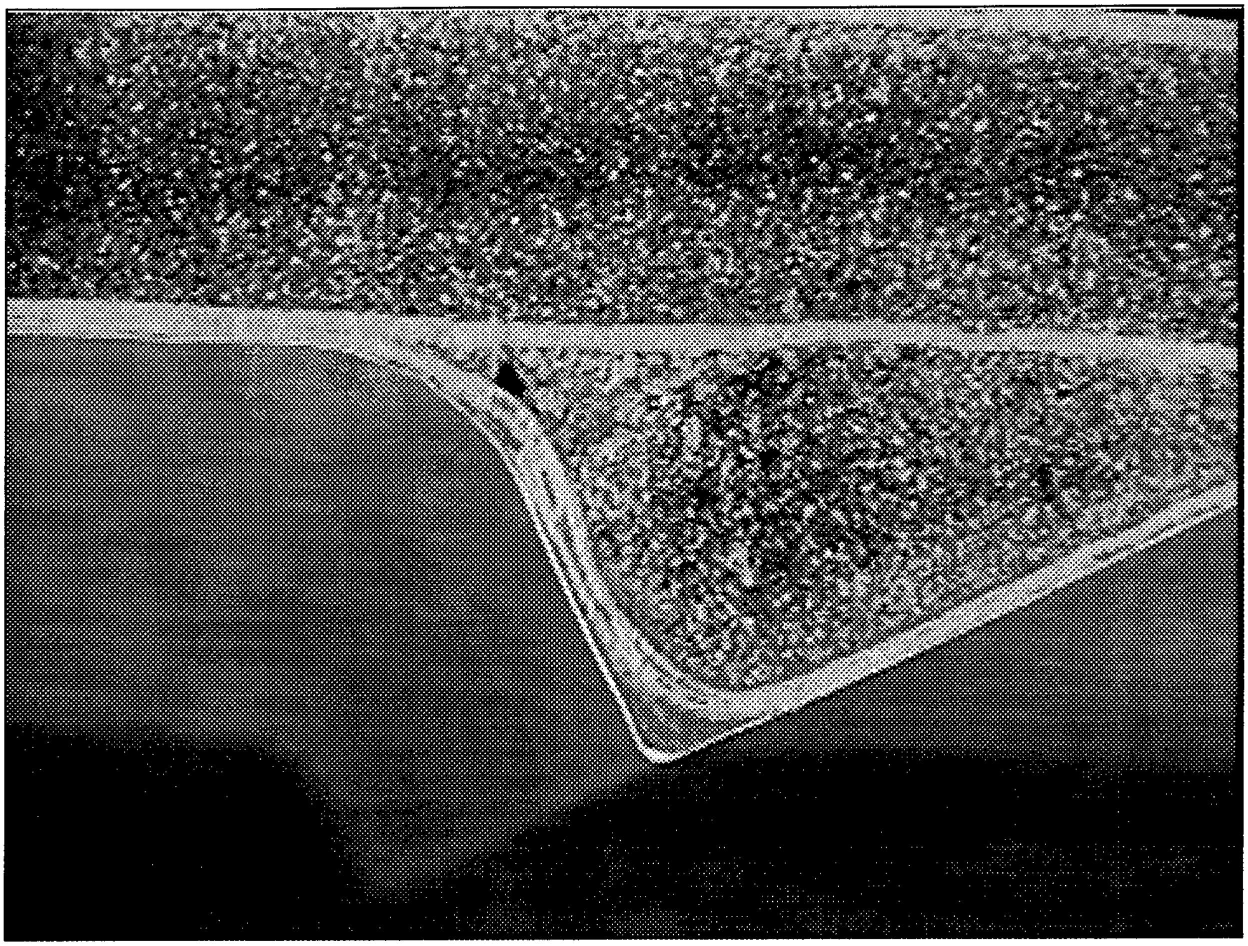

Figure 12: Void in the spray strake

TECHNICAL SUMMARY

The program successfully demonstrated that off-the-shelf vinyl esters resins commonly used in the production of SOCOM marine craft can be successfully cured with EB radiation. In addition, traditional part forming and resin infusion processes can be used to create complex marine structures on inexpensive tooling, and that standard industrial EB equipment can cure these complex structures.

Although the final EB cured part did exhibit several flaws, they appear to be unrelated to the EB process. In fact, our evaluation of the delaminations and the general imperfections strongly indicate that minor refinement of the resin lay-up and infusion process would remove all of the observed problems. Further, it is believed that simple modification of the resin formulation could result in a reduction of dose, a reduction of the styrene content, and an improvement in the performance properties of the matrix.

In conclusion, the most important elements of the original program plan were accomplished. Based on this preliminary work, there is strong technical basis for the successful development of an inexpensive vinyl ester resin and a commercially viable process for the construction of single piece marine structures

FUTURE WORK

This Phase I program demonstrated EB curing's capacity to quickly cure thick section, multi-element composite strictures. The program also identified a number of technical questions that need to be addressed before the practical application of this technology can be applied to the construction of SOCOM marine vehicles. Some of these issues include:

1. Resin optimization for EB curing.
    - Development of low-dose curable resins
    - Exotherm reduction and/or control
    - Evaluation of dose-rate effect
    - Evaluation of dose fractionation effect
    - Effect of multi-functional monomers
    - Replacement of styrene with environmentally friendly monomer

2. Fiber/fabric optimization for EB curing
    - Evaluation of sizing on radiation chemistry
    - Evaluation of spray-tack on radiation chemistry
    - Evaluation of post-infusion delays on cure

3. Lay-up and resin infusion development
    - Evaluation of effect of tool on final product

4. Development of improved dose v. cure profiles
    - Mechanical testing of resin (DMA, static tensile, etc.)
    - Thermal Testing of resin (TMA, DSC, etc.)
    - Mechanical testing of composite (DMA, static tensile, etc.)
    - Thermal Testing of composite (TMA, DSC, etc.)

5. Development of improved cure v. depths profiles
    - Radiation transport code modeling
    - Radiation dosimetry profiling

6. Failure Mode Effects Analyses
    - Cause of delaminations
    - Cause of discoloration

7. Engineering Evaluations
    - Production costs
    - Facility designs