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INTERFACE MODIFIED GLASS FIBER/THERMOPLASTIC MATRIX COMPOSITES

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This Phase I SBIR program is applying a proprietary interface-modification process to improve the interaction between glass fibers and thermoplastic resin composite matrices. In our accomplishments thus far, we have selected PEEK as the thermoplastic matrix resin and chosen three candidate interface-modifier resins. Fiber wetting experiments will determine which of these candidates is best suited for use on the program. A glass fiber tow spreader that effectively separates the tow into a narrow ribbon of fibers was constructed. Extraction experiments have demonstrated that the oil-based, PEEK compatible sizing can be effectively removed from glass fibers without damage by extraction with an appropriate solvent. Equipment was constructed for winding separated glass tow onto a large diameter drum, then processing the separated tow to remove the present sizing and coat with interface-modifier resin solution while the fibers remain in place upon the drum. Coated fibers will also be staged-dried and heat-treated in place, forming interface-modified glass fibers that have been protected from abrasive damage during the entire interface-modification process. A mold that is equipped with rapid cooling for preparing glass fiber/PEEK composite panels has been fabricated. (JJS)

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INTERFACE MODIFIED GLASS FIBER/THERMOPLASTIC COMPOSITE

Statement of the Problem

The overall objective of this project is to develop the technology for improved glass fiber reinforced/high performance thermoplastic composites. Compared to carbon fiber reinforced composites, which are electrically conductive, glass fiber composites would be expected to be useful in electrical applications and in environments where galvanic corrosion might occur. Other desirable properties would include high mechanical strength, stiffness, light weight, toughness, solvent and chemical resistance, low-flammability and low-smoke generation. Advanced glass fiber composites with this combination of features should be useful in low detectability structures for naval vessels such as pressure hulls for submarines. Composite structures based on PEEK and S-2 glass would seem to be ideal candidate materials to provide the balance of properties listed above.

The glass fiber/high performance thermoplastic composites prepared to date display unacceptably low mechanical properties that are far below theoretical predictions and that are especially susceptible to moisture degradation. This deficiency can probably be attributed to inadequate adhesion in the glass/polymer interphase region, which is related to the lack of an appropriate coupling agent. In general, coupling agents have two primary functions: (a) to strongly bind the fibers to the matrix material, thereby allowing for optimal transfer of the applied load to the reinforcing fibers and (b) to form a hermetic seal at the fiber/matrix interphase to prevent the ingress of corrosive reagents such as water and air, that would otherwise degrade the performance of the composite. In the case of glass, a third function is (c) to protect the fibers. That is, glass fibers are extremely damage and abrasion sensitive and must be protected during all phases of composite processing. In practice, this protection is provided by over-coating the fibers with either starch or silicone oil sizing, which must be removed just prior to the application of a coupling agent, or by originally over-coating the fibers with a durable coupling agent. The latter approach has obvious advantages over the former. An often overlooked additional requirement of a coupling agent is that its thermal and environmental resistance be at least as good as those of the matrix and reinforcement materials.

Traditional coupling agents, such as amino silanes used in epoxy/glass composites, for example, have not worked well with advanced thermoplastics. This failure can be attributed to (a) a lack of reactivity or poor affinity of the available coupling agents for the polymers and (b) inadequate thermal stability. Thus, a novel, broadly applicable approach to solving the glass fiber/polymer bonding problem is required to obtain a truly advanced glass fiber reinforced thermoplastic composite.

Foster-Miller's Approach to Interface Modification

Although it is generally known that the adhesion of polyimides (PI) to glass is inherently poor, a technique has been devised to utilize polyimides as coupling agents which does not rely on the inherent affinity of the coupling agent/resin to the glass. This novel approach utilizes the application of a dilute solution of the PI, polyamic acid (PAA) precursor to the glass fiber, followed by removal of the solvent and then imidization. PAAs have been shown to have a high affinity for glass surfaces; and, in particular, it has been demonstrated that PAA solutions will wet out clean glass fibers. Thus, a PAA-solvent film deposited onto clean glass fibers should shrink during solvent removal and imidization, thereby mechanically locking a PI film around the individual fibers via a "shrink-fit" mechanism. The ideal PI for this task should be (a) tough enough to protect the glass fibers during processing, (b) highly impervious to moisture and other undesirable reagents and (c) sufficiently compatible with the matrix resin to ensure adequate reinforcement bonding. The target during Phase I of this program is to demonstrate that this approach will lead to a 40 percent improvement in shear and compressive strengths as well as a marked reduction in the effects of hot/wet conditions on these properties.

Summary of Significant Results to Date

The candidate combination of materials selected for evaluation during Phase I is (a) Owens-Corning's S-Glass (OC-933AA) treated by O-C with a proprietary PEEK compatible sizing agent, (b) NASA's LARC CPI as the interfacial modifier and (c) ICI's PEEK as the matrix resin. The major ingredient in the Owens-Corning S-2 glass sizing was found by Foster-Miller to be an ordinary silicone oil, which could be completely removed by THF extraction. PEEK was chosen as the matrix material because it is readily available and because of its outstanding combination of properties, which include high mechanical strength, stiffness, light weight, toughness, solvent and chemical resistance, low-flammability and low-smoke generation. LARC CPI is a new semi-crystalline, thermoplastic PI, also with an outstanding balance of properties, including toughness and water and solvent resistance. Since its structure resembles that of PEEK, it was thought that the two resins might be sufficiently compatible for LARC CPI to serve as a coupling agent for this system; the limits of this compatibility are being established by DSC analysis. The affinity of the LARC CPI PAA for the de-sized, S-2 glass fibers has been demonstrated; the fully imidized material formed the expected protective fiber overcoat. The drum-shaped glass tow separator, previously described, has been constructed and its ability to separate the individual strands and for a wide ribbon ready for sizing has been demonstrated. PEEK composites based on the as-supplied S-2 glass have been fabricated to serve as controls for this study; their evaluation is in progress.

As previously outlined, our approach during Phase I involves six tasks. Their status is as follows:

- Selection of composite components: accomplished; no further action anticipated.
- Glass fiber tow spreading: apparatus constructed and method developed. Effective tow-spreading demonstrated.
- Sizing removal: Methodology developed; drum trials in progress. Sizing removal from OC-933AA glass fibers demonstrated to be effective using the solvent.
- Application of LARC CPI to de-sized glass fibers: wet-out and coating demonstrated; drum trials in progress. Optimum concentration of interface-modifier determined by fiber wet-out studies.
- Glass fiber/PEEK composite fabrication: control composite fabricated using OC-933AA PEEK-compatible glass fibers supplied by Owens-Corning.
- Composite testing: control composite testing in progress. Compression test specimens cut from control composite.

Details concerning work accomplished during this report period and work in progress is described below.

Glass Fiber Tow Spreading

Figure 1 illustrates the apparatus that has been constructed at Foster-Miller and evaluated. As shown, this device utilizes a series of steel rollers with converging gap widths. The ability of the device to spread and separate the 1/16 in. diam OC-933AA, S-2 fiber tow into a 1/2 in. wide ribbon, as well as to wind this ribbon onto the drum and align successive passes of the ribbon so as to form a continuous and uniform, wide tape, also illustrated in Figure 1, has been demonstrated. Actually, it was found during early experiments that passing the glass fiber tow around one set of steel rollers in an S-shaped fashion and under constant light tension was sufficient to separate the 1/8 in. wide tow into a 1/2 in. wide ribbon, containing flattened bundles

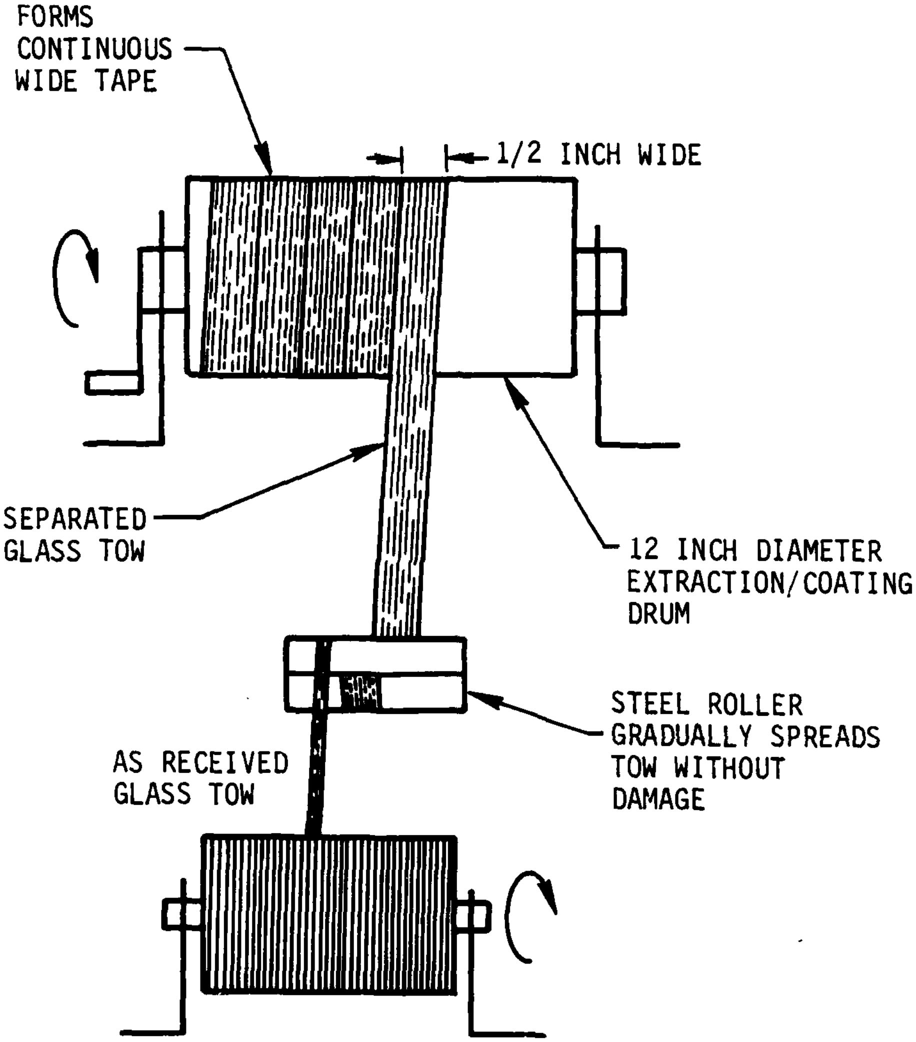

Figure 1. Glass Fiber Tow is Separated Prior to Winding upon the Drum

of individual glass fibers. Only one set of rollers was therefore used to separate the glass fiber tow prior to winding upon the drum. The sizing will be removed from the glass fibers by THF solvent extraction, the CPI PAA will be applied, the solvent will be removed and the PAA imidized while the fibers are wound and aligned on the drum as illustrated.

Sizing Removal

It has been shown that two THF extractions will remove virtually all the 0.2 wt.-percent loading of sizing reported by Owens-Corning. The nature of this proprietary, allegedly PEEK-compatible sizing material, was analyzed by thin layer chromatography and infrared special analysis. Its composition was found to resemble a mixture of silicone oil and minor amounts of a vegetable oil-like substance.

The next step is to accomplish this extraction and dry the fibers, preparatory to PAA impregnation, while they are wound on the drum as illustrated in Figure 2. As previously indicated, uncoated fiber is especially vulnerable to damage. Thus, it is imperative that all of these steps be accomplished without disturbing the fibers while they are wound on the drum.

In practice, the best way to accomplish all of this would be to coat the fibers with the PAA solution, dry them and carry out the imidization in series as the fibers are formed in the fiber making operation. Unfortunately, Owens-Corning would not permit this approach to be taken at this time. Also, because of its lack of damage tolerance, Owens-Corning could not supply un-sized S-2 glass. Suffice it to say, that if the use of PAA/PI coupling agents for glass proves to be successful, it will not be necessary to follow the complicated procedure outlined here to enable full-scale production utilizing this technology.

Interface Modifier Coating/Imidization

Bundles of de-sized OC-933AA fibers were hand-dipped into DMAc solutions containing 1, 2, 3, 4, and 5 percent LARC CPI PAA. The solutions rapidly wicked into the fiber bundles as they were dipped into the solutions, clearly indicating a high degree of fiber wet-out. Most of the solvent was removed from these coated fiber bundles by drying in a forced draft oven for 60 min at 100°C for 15 min at each temperature. Figure 3 shows optical micrographs of coated imidized fibers prepared from a 1 percent DMAc solution; the fibers appear to be well separated and fully coated with a uniformly thick layer of the LARC CPI resin.

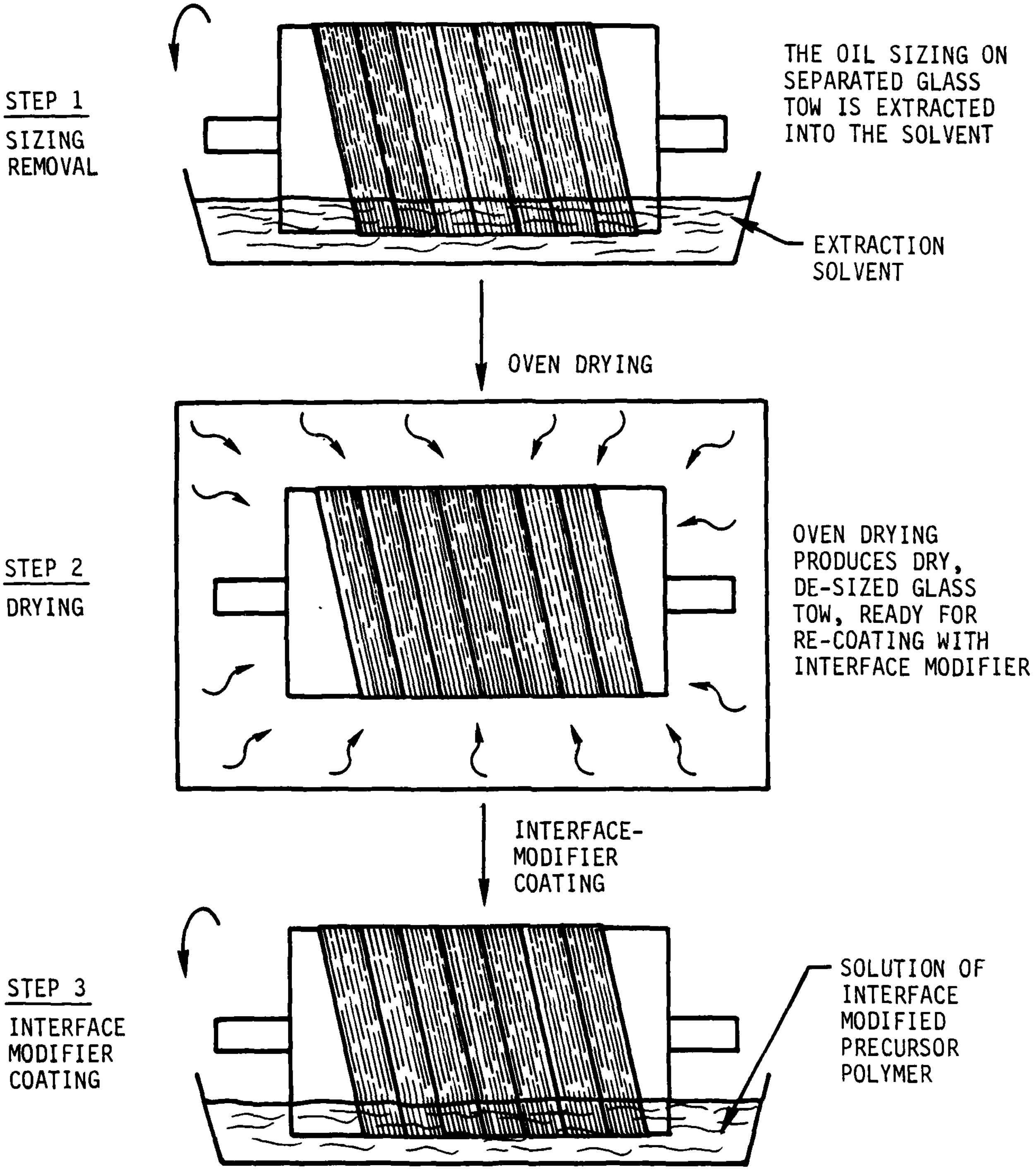

Figure 2. Separated Glass Tow is Extracted of Sizing and Coated with Interface Modifier While Wound Upon the Drum

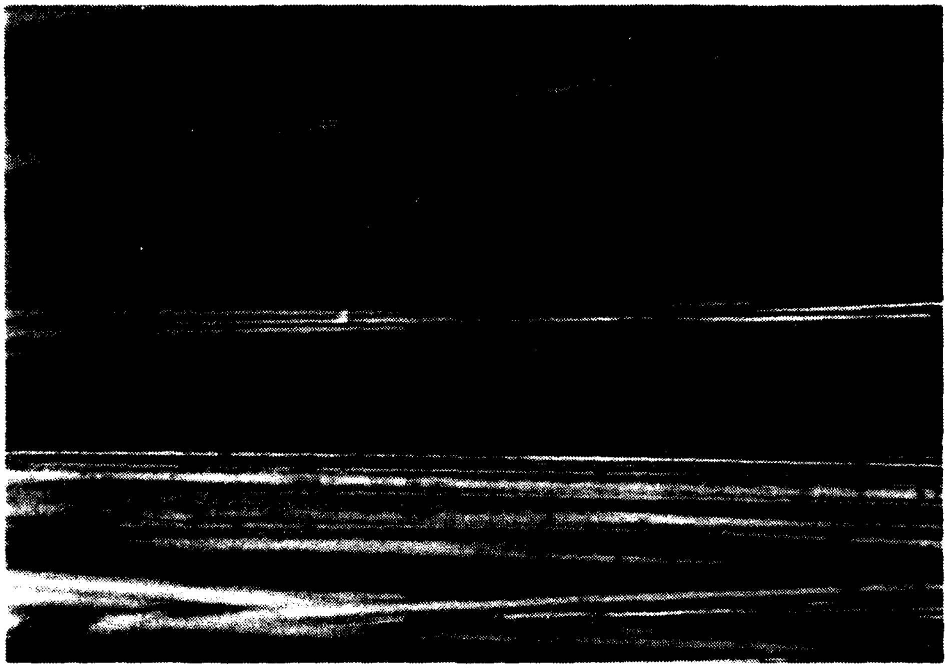

Figure 3. Optical Photomicrograph Showing LARC CPI Overcoating De-Sized S-2 Glass Fibers

The next step is to coat the de-sized drum wound fiber ribbon, wound and de-sized as described above.

DSC analysis will be performed to establish the temperature and composition limits of PEEK/LARC CPI miscibility. Intimate physical mixtures of fine powders of the two polymers with various compositions will be placed in a sample pan and scanned to show that the transitions of the parent polymers can be clearly resolved. The mixtures will be annealed at 400°C for several minutes, quenched and then re-scanned. The appearance of single transition peaks, between those of the parent polymers, will be indicative of blend miscibility. A series of such experiments should establish the miscibility limits of this polymer pair. This information will be important in establishing the degree of interaction between interface modifier coating and PEEK thermoplastic matrix.

Composite Fabrication

Uniaxial composite test plaques, containing 60 volume-percent glass fiber and measuring 3 in. x 5 in. x 0.125 in. will be fabricated using the procedures described below. In commercial practices, it should be possible to apply the PI interfacial modification technology using established pultrusion equipment to form a conventional pre-preg tape. It is also expected that such tapes will be suitable for processing in conventional thermoplastic composite forming equipment.

The following procedure was used to form pre-cursor structures suitable for fabrication of control composite plaques. The controls were fabricated using as-supplied, Owens-Corning O-C933AA S-2 glass fibers, still containing the sizing applied by the manufacturer. A single layer of a 1 mil thick PEEK film was first wound onto the two spreader drum, illustrated in Figure 1. The OC-933AA S-2 glass was spread and wound over this film as described in Section 1. This bi-layered PEEK/glass ribbon structure was stabilized by the application of several strips of adhesive tape. The structure was removed by slitting it with a utility knife along the drum axis direction and then peeling it away from the drum. This bi-layered structure was flattened with manual pressure and die cut into 3 in. x 5 in. pieces. These pieces were placed into the composite fabrication press, illustrated in Figure 4. An extra PEEK film was inserted so that both faces of the composite were faced with a PEEK rich phase. Control composite plaques were consolidated at 200 psi and 400°C for 15 min. with a thickness of 0.125 in. and a nominal glass composition of 60 volume-percent. The plaques were cooled in the mold to room temperature by air cooling within about 5 min. The plaques seemed to able well consolidated and the fibers appeared to be uniformly spaced, in close parallel alignment. Property evaluation is underway.

The interfacially modified composites will be prepared using the following procedure. The as-supplied, OC-933AA glass fibers will be spread and wound on the drum as illustrated in Figure 1. The following steps will be accomplished as described in detail in Sections 2 and 3 and as illustrated in Figure 2. The sizing will be removed with two THF extractions; the fibers will be dried; the LARC CPI PAA DMAc solution will be applied; the DMAc will be removed by drying and the PAA coating will be imidized. This LARC CPI interface modified S-2 glass fiber ribbon should be sufficiently stable so that it can be removed from the drum as described above, but adhesive tape can be applied if that is required to stabilize the fiber winding. Composite test plaques will be fabricated using the same consolidation conditions as outlined above for the control plaques.

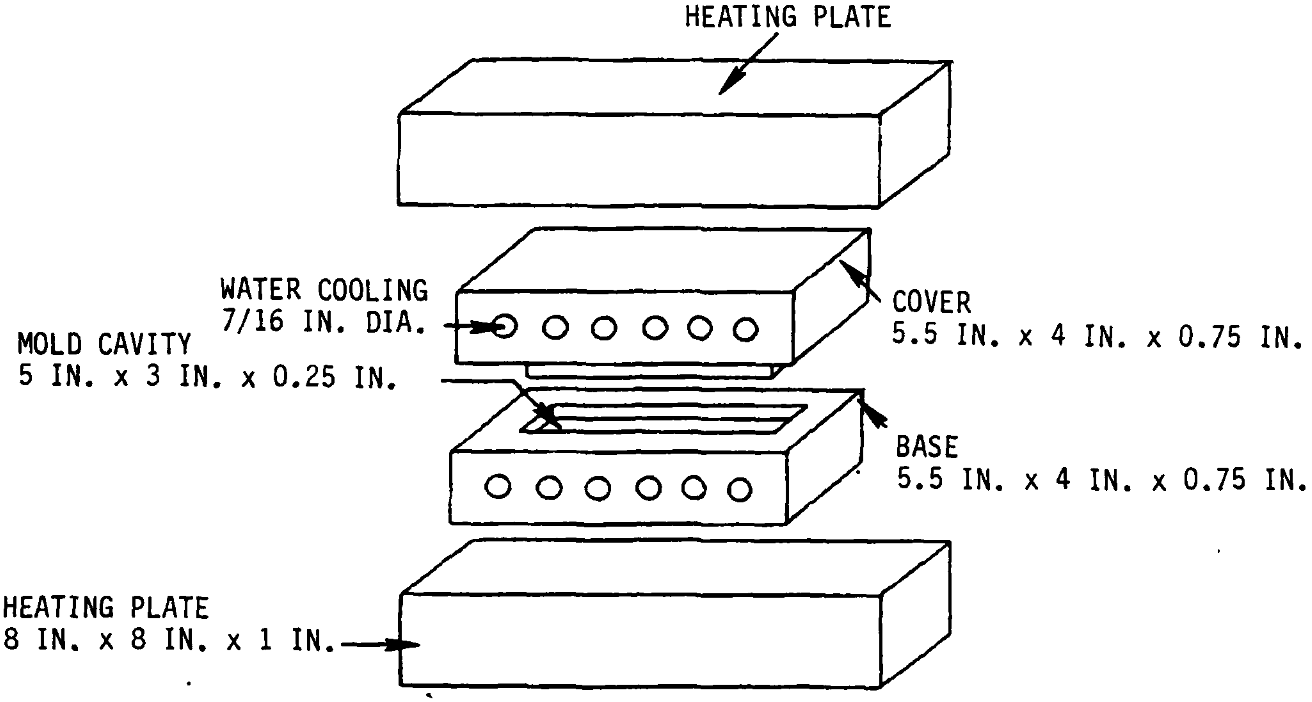

Figure 4. Mold Used for Preparing Composite Test Plaques

Composite Testing

The composite plaques, fabricated as outlined in Section 4, will be evaluated using (a) density to measure void content, (b) resin pyrolysis to measure fiber content, (c) DSC to measure the crystallinity of the PEEK phase, (d) optical microscopy to measure the LARC CPI interfacial coating thickness, (e) short beam shear strength to measure interfacial adhesion and (f) axial compression to measure interfacial adhesion.

The samples will also be evaluated for interfacial adhesion under how-wet conditions, as per (e) and (f). Failed compression test plaques, from both wet and dry experiments, will be examined by optical and scanning electron microscopy to elucidate the mechanism of failure.