STRUCTURAL COMPOSITES VIA LAMINATED OBJECT MANUFACTURING (LOM)

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ABSTRACT

An innovative, rapid prototyping (RP) technology is being adapted for the automated manufacture of composite tools and molds. The technology is a direct extension of the Laminated Object Manufacturing (LOM) process. LOM is an established technique that is used to create solid prototypes by sequentially cutting and laminating layers of adhesive paper. With this process a full scale, geometrically complex prototype can be created directly from a CAD image in less than a day. This report provides a description of how LOM is being applied for the production of functional composite laminates, such as composite tools and molds. Several material systems have been examined, including monolithic ceramics (SiC), ceramic matrix composites (SiC/SiC), and polymer matrix composites (glass/epoxy). Realistic tools and molds are being created from these materials using the LOM process with little modification. However, post processing (ceramic densification, polymer post cure) is necessary to obtain articles with good mechanical properties. Technical solutions are being developed for maintaining geometrical accuracy during the post processing cycles. The mechanical properties and performance of the LOM-produced parts are reported herein. Overall, this technology holds great promise for lowering the cost of tooling due to the ability to create geometrically complex objects rapidly using a highly automated processing sequence.

I. INTRODUCTION

The rapid prototyping and manufacturing of monolithic ceramics, ceramic matrix composites, and polymer matrix composites is being studied by an industry/university collaborative team lead by

University of Dayton and Helisys, Inc. This technology, based on Laminated Object Manufacturing (LOM), will provide a capability for producing high performance, near-net-shape ceramic and polymer matrix composites (CMCs and PMCs, respectively). The technical objectives of the program are: 1) to produce CMC parts with structural integrity similar to CMC parts made by current techniques, 2) to develop a commercially viable machine capable of automated fabrication of these parts, and 3) to demonstrate the generic nature of the technology by making PMCs suitable for structural applications. In this report, a description will be given of the technical progress achieved to date.

II. EXPERIMENTAL DEVELOPMENT AND DISCUSSION

LOM Process

The standard LOM process is illustrated in **Figure 1**. In this study, a LOM 2030 machine in its current commercial configuration was used for all work. As described herein, certain modifications to the process were employed, such as manual feed of sheet preform materials. However, some composite parts were able to be fabricated with the normal, fully automatic process.

Production of Ceramic Articles

The rapid prototyping and manufacturing of monolithic and composite ceramics is being addressed by an industry/university collaborative team funded by the Defense Advanced Research Projects Agency and the Office of Naval Research. This technology, based on LOM, will provide a capability for producing high density, near-net-shape ceramic matrix composites. As a necessary first step in the overall program, the production of monolithic ceramic objects is being developed. To date, monolithic silicon carbide (SiC) and aluminum nitride (AlN) parts have been produced. Among several others, tooling for polymer composites is a promising application for these ceramic systems. The favorable thermal conductivity of AlN or SiC would provide a durable tool with the inherent heat transfer advantage that a metal tool has to offer, but with less thermal expansion, and at a lower cost.

Appropriate ceramic preforms were developed using a standard tape casting process. These "tapes" contain a ceramic powder at approximately 60 vol% and a polymeric binder system. Ceramic tapes were made with thicknesses of 150-175 μm and 300-325 μm, widths of 20 cm, and lengths of 1 m. A significant effort was required to obtain the proper binder formulation for effective tape lamination. Three ceramic systems have been investigated: a coarse, infiltratable SiC composition with average diameter of 30 μm; a bimodal SiC composition with coarse and fine (≅2 μm) particles; and a sinterable AlN composition with average particle size near 2 μm.

Ceramic tapes were laminated to form three dimensional objects using a LOM 2030 machine at the University of Dayton. The placement of tapes was performed manually because the tapes were not long enough to form continuous rolls nor strong enough to survive the feed mechanism. Otherwise, the building of ceramic parts was conducted with the same degree of automation as with paper parts.

"Green" is a term that refers to the state of a ceramic article prior to densification. Green objects tend to be fragile and are prone to damage. Most LOM-produced green objects are soft and easily deformed due to the flexibility of the ceramic tapes. Therefore, a partial binder burnout cycle was used to stiffen the parts in order to facilitate green state handling. This cycle involved careful heating of a part to slowly volatilize the plasticizer while leaving the polymer intact. Prior to densification, the polymer binder was removed with a higher temperature burnout cycle developed using thermogravimetric analysis data.

SiC parts were densified by two separate processes, either by using silicon infiltration or reaction bonding (reactive metal infiltration). These methods of densification result in net shape parts with little or no dimensional change. In the reaction bonding process, free silicon reacts with *in situ* carbon that has been formulated with the ceramic tape. This reaction ($Si^0 + C \dashrightarrow SiC$) happens immediately upon infiltration and increases the SiC content of the part without significant shrinkage. The sintering of AlN parts has not yet been addressed. However, sintering shrinkage and warpage are expected to be primary issues.

Examples of parts made on the LOM system are given in **Figure 2** and in previous reports [1, 2]. The flexural strength of the infiltrated and reaction bonded SiC parts is approximately 160 MPa at room temperature (4-point bend test). This value is expected to increase significantly with current research aimed at improving the lamination efficiency.

Helisys, the manufacturer of the LOM 2030, has developed several hardware and software changes for improved ceramic handling. These modifications will be implemented on an updated LOM machine that will be made commercially available. To facilitate more efficient laser cutting of refractive materials, a pulsed CO_2 laser with a 700 W peak power will be used. To prevent oxidation of carbides and nitrides during laser cutting, a blower that supplies a thin layer of inert gas over the cutting surface has been implemented. Since ceramic prepregs are costly, the material feed mechanism has been redesigned to minimize waste while providing full automation.

Ceramic Matrix Composites

Work is also progressing toward the ultimate goal of producing ceramic matrix composites with the LOM system. Al_2O_3 and SiC ceramic tapes containing SiC whiskers or SiC continuous fibers are being considered. The initial challenge here is tape casting. Incorporating reasonable percentages of fibers uniformly distributed in tapes presents obvious challenges. Novel approaches to this are being developed as well as alternate approaches.

One alternate, novel approach to the fabrication of SiC/SiC composites involves the layup of separate, alternating layers of monolithic ceramic tape and fiber/resin prepregs. This concept was tested by using the same SiC ceramic tapes used to make monolithic, reaction bonded SiC parts (see previous section). A separate fiber preform was developed by making prepregs of continuous SiC fibers (Nicalon^{TM}, Dow Corning) and a furfural thermosetting resin (Furcarb UP-440, QO Chemicals). The advantages of this technique are the relative ease of preparation of the preforms, avoidance of fiber abrasion from the ceramic particles, and potential for high fiber volume fraction in the final CMC. Furfural resin was chosen because it produces a high char yield when heated to high temperatures. Therefore, the furfural serves a dual role: as a binder during the part fabrication, and as a carbon source during the reaction bonding process.

Several nine-layer CMC plates were fabricated by sequentially laminating ceramic tapes and fiber preforms by hand pressing with a warm iron (80-100 °C) for 5 seconds per layer. A copper vapor laser, subsequently described, was used to cut the preforms immediately after the lamination step. The furfural resin adhered well to the ceramic tapes. Subsequent post curing of the resin, performed by placing the final CMC plate in a heated press (175 °C, 5 psi), produced robust "green" CMCs. Traditional binder burnout was carried out in an oven, followed by pyrolysis of the furfural. Finally, reaction bonding was performed by infiltration with silicon.

CMC squares made by this technique are pictured in **Figure 3**. The initial experiments involved the determination of appropriate carbon levels in the ceramic tape and total furfural level in the fiber prepreg. After several formulation iterations, the ability to produce flat, visually attractive CMC panels with no delaminations was achieved as illustrated in **Figure 3**. This accomplishment demonstrated the basic feasibility of this CMC fabrication approach. However, the mechanical properties of these panels were low (flexural strength = 50 MPa, 25 °C, 4-point bend) due to significant porosity. Future work will increase the integrity of LOM CMCs by all of the following strategies: 1) minimize porosity with the use of a more appropriate cure cycle for the furfural resin (in this study not enough time was allowed for debulking of water and solvents from the prepreg, which accounts for most the porosity observed in the samples), 2) incorporate a necessary fiber interface through fiber coatings, and 3) minimize fiber degradation with lower infiltration temperature and/or SiC fibers with lower free oxygen content (e.g. "high Nicalon" or "stoichiometric" silicon carbide).

A second challenge in LOM processing of advanced fiber prepregs is cutting the fibers. CO_2 lasers cannot cut continuous fibers effectively due to severe burn damage near the cut region. The laser cutting of fiber prepregs is being investigated with a 20W, pulsed copper vapor laser that delivers 2.7 mJ per pulse at a repetition rate of 8000 Hz. The laser can be focused to a spot size of around 80 μm and is quite effective in "cleanly" cutting SiC fibers, as illustrated in **Figure 4**. The cutting mechanism involves photoablative erosion rather than pyrolysis.

Production of Polymer Composites

The feasibility of adapting the LOM process for the rapid prototyping and fabrication of polymer composite parts has been demonstrated. It was found that arbitrary, complex shaped parts can be made from a range of composite prepregs with an ease and versatility similar to the original LOM paper material. However, due to the transient temperature and pressure application associated with the LOM process, a secondary, post processing step is required for final part consolidation and cure advancement. Without the post cure, the functionality of LOM composite parts is severely reduced and the parts are not suitable for the targeted tooling applications. Currently, technical solutions are being developed for maintaining geometrical accuracy during the post processing cycles.

The performance of two composite prepreg systems has been evaluated in the LOM process. Both are epoxy/glass fiber systems. The first material was specifically designed for the LOM process to duplicate the handling characteristics of paper; it required no modifications to the current LOM machine or build sequence. The prepreg was comprised of a non-woven glass fiber mat coated on the bottom side with a layer of highly B-staged epoxy resin. This prepreg was supplied on nine inch wide rolls. Because the prepreg was primarily designed to process as similar to the LOM paper as possible, the measured properties of composites made from this material were not good. Due to the one-sided distribution of highly B-staged resin, LOM processing resulted in a layered structure with alternating resin rich areas and layers of unimpregnated fibers (see **Figure 5**). Since the resin did not flow significantly during processing, consolidation was poor. Additionally, fully cured parts were dimensionally stable only at temperatures up to 110^0C, as indicated by laboratory mechanical analysis results in **Figure 6**, because the fully cured matrix resin had a particularly low glass transition temperature.

Despite these findings there have been several preliminary field reports noting the adequacy of this prepreg for producing prototype injection molds. For example, a user at one beta test site was able to inject a total of 40 shots using polypropylene, acetal, glass filled acetal, neoprene, and nylon. The prototype mold, however, had to be treated differently than traditional tool steel because of its lower thermal conductivity and use temperature. For example, the runner length had to be extended to prevent hot, molten plastic from contacting the mold prematurely. Additionally, a cycle time as long as 5 minutes was required due to long cooling times. In an attempt to increase the wear resistance and thermal transport of LOM molds, Helisys has developed a metal coating process involving hydroforming of thin copper sheets.

The second material system, a commercially available aerospace-grade prepreg, was much more promising for creating high performance, functional polymer composite parts using LOM. This prepreg consisted of unidirectional "E" glass fibers in an epoxy matrix and was supplied on twelve inch wide rolls. Some modifications to the LOM build sequence were required to process this type of material. Most notably, fully automated processing was not possible with the current LOM machine. The prepreg was a "high flow" system since the resin was minimally B-staged and evenly distributed through the prepreg thickness. Thus a release ply was required on top of the layup to prevent the prepreg from sticking to the heated roller during the lamination step. Immediately after lamination, the cycle was again interrupted to manually remove the release ply (the prepreg carrier film was used in this case). However, the improved performance of the material compensated for the additional processing steps. The reduced B-staging of the resin, compared to that of the first prepreg, resulted in a better bond between layers (see **Figure 7**) which minimized delamination. Fully cured parts exhibited a use temperature of up to 200 ^{0}C and mechanical properties comparable to more traditionally made epoxy/glass composites (see **Figure 6** and **Table 1**, respectively). However, this material system has not yet been tested in field applications such as injection molding and autoclave tooling.

The use of an aerospace-grade composite material in the LOM process combines the best aspects of traditional polymer composite fabrication and rapid prototyping. The enhanced mechanical properties associated with polymer composites are not sacrificed to achieve the complex, freeform shapes common to rapid prototyping. But in order to further develop this promising new fabrication method, additional improvements are needed in both the LOM process and prepreg formulation. These developments include methods for automating the layup procedure and fine-tuning the prepreg's degree of B-staging and fiber volume to facilitate processing without forfeiting material performance. Issues involving mechanical automation are being addressed currently by Helisys, Inc.

III. FUTURE COMPOSITE DEVELOPMENTS

The process development component of the program is focused on machine modifications. These include a flat tape feed mechanism, a rotating building stage for changing fiber orientation layer-by-layer, an in-situ curing/heat treating device, and a curved layer layup capability. The latter is a highly innovative, key concept for composite fabrication by the LOM process. In conventional composites, the laminate plies conform to the surface of a tool. To facilitate such lamination on the LOM, in place of the current planar layup geometry, a "curved surface" algorithm is being developed. This algorithm also will improve surface finish and allow the fiber reinforcement to remain continuous in the plane of curvature. The curved layer building concept is illustrated in **Figure 8**. Also under development are various processing methods for improving the ease of part removal from the crosshatched support material.

IV. REFERENCES

1. Klosterman, D.A., R.P.Chartoff, and S.S. Pak, "Affordable, Rapid Composite Tooling via Laminated Object Manufacturing," Proceedings of the 41st International SAMPE Symposium and Exhibition, Anaheim, CA, March 24-28, 1996, pp. 220-229.

2. Klosterman, D.A., R.P. Chartoff, N.R. Osborne, G. Graves, and A. Lightman, "Structural Ceramic Components via Laminated Object Manufacturing," Proceedings of the International Conference on Rapid Product Development, Messe Stuttgart, Germany, June 10-11, 1996, pp. 247-256.

V. ACKNOWLEDGMENTS

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VI. ILLUSTRATIONS

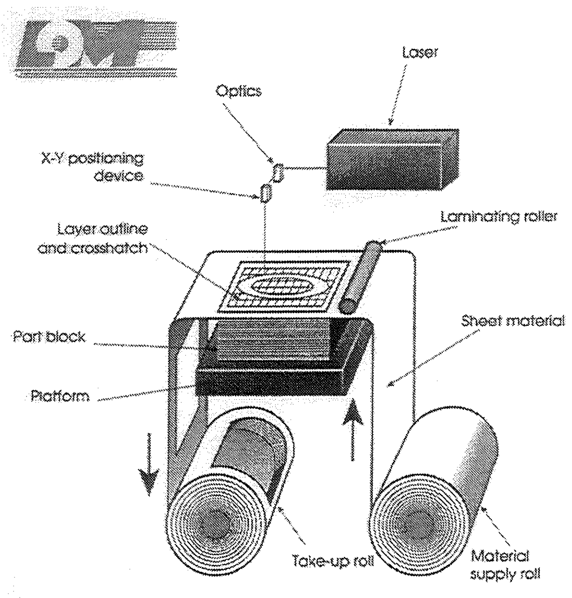

Figure 1 : Schematic of the LOM process for making paper prototypes.

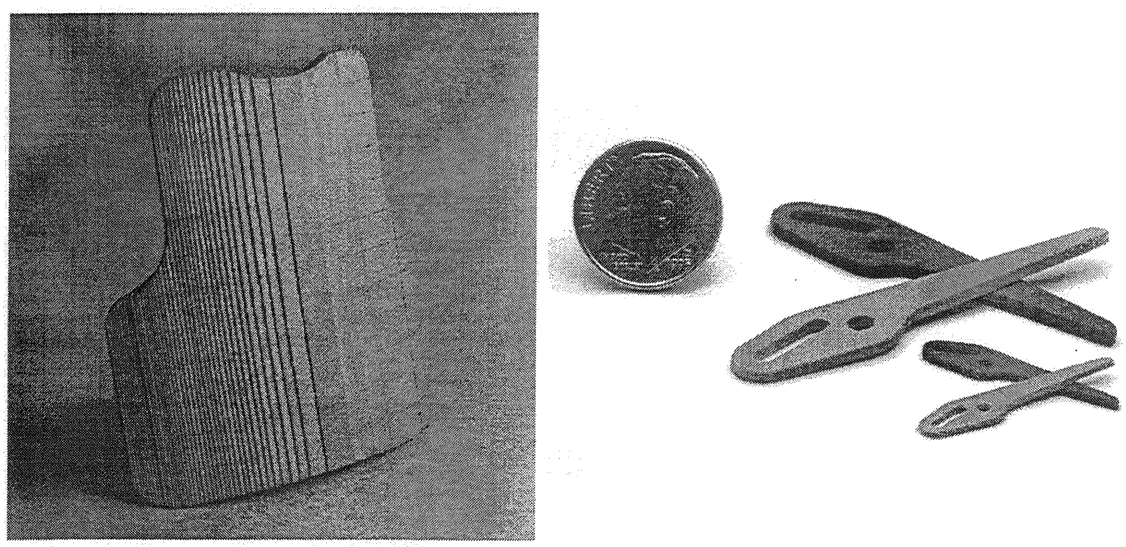

Figure 2 : (left) SiC, miniaturized body armor (7.5 cm x 7 cm x 1.6 cm) and (right) AlN and SiC laparoscopic cutters made with LOM.

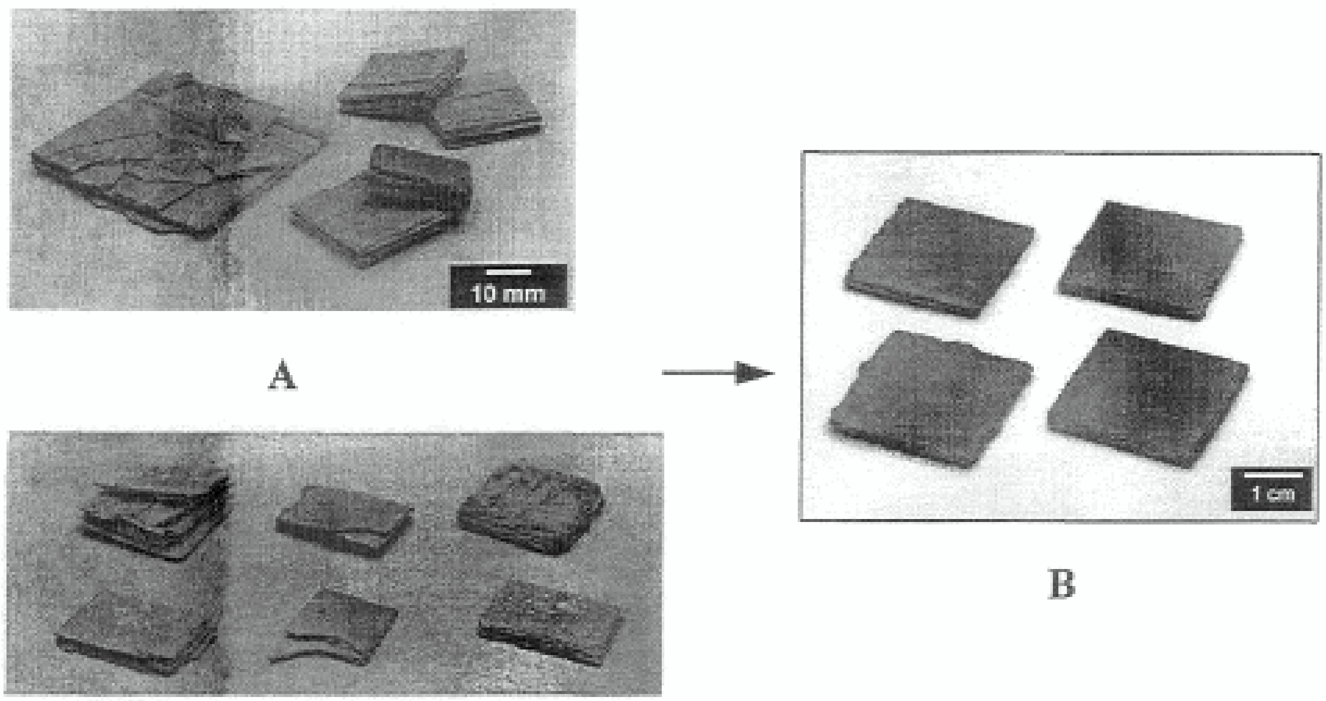

Figure 3 : CMC development has evolved from a) initial formulation screening for both ceramic tape and fiber prepreg, to b) the ability to form flat CMC plates without delamination. All samples were densified through the reaction bonding process.

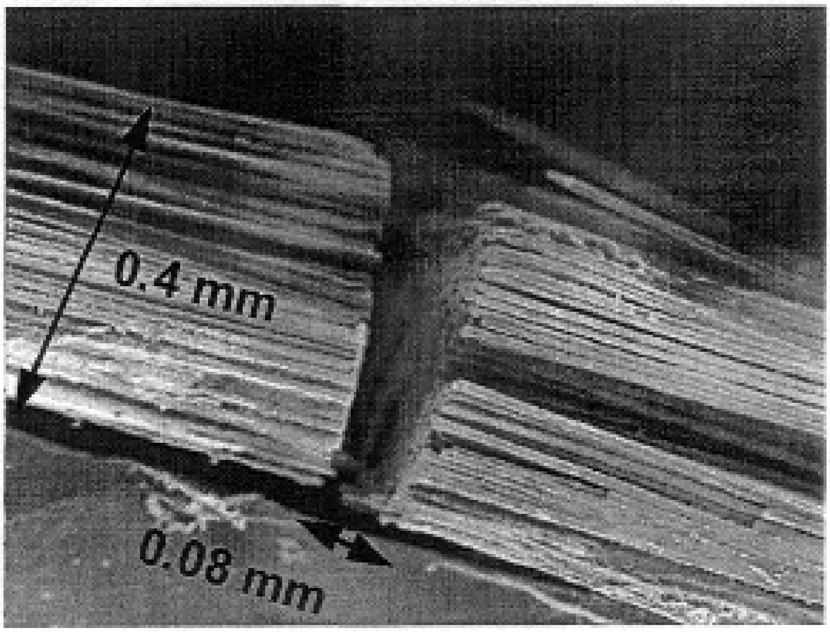

Figure 4 : Thick, SiC fiber prepreg cut with a copper vapor laser operating at 8000 pulses/sec and 2.7 mJ per pulse. Such high quality fiber cutting will be required to enable the LOM of polymer and ceramic matrix composites.

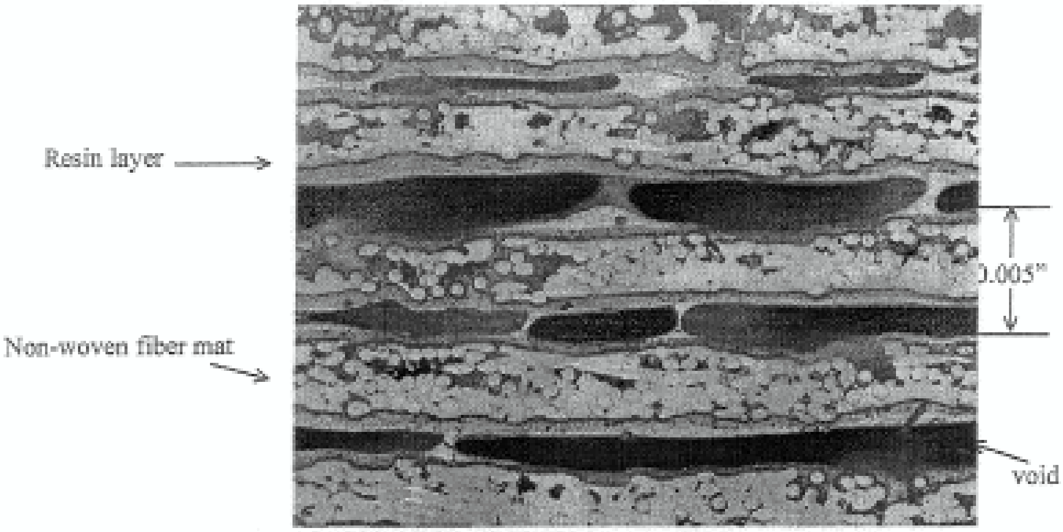

Figure 5 : Photomicrograph of a composite panel made with the LOM-designed prepreg. Note the resin's inability to penetrate into the fiber mat and the large scale voids entrapped in the resin rich layers.

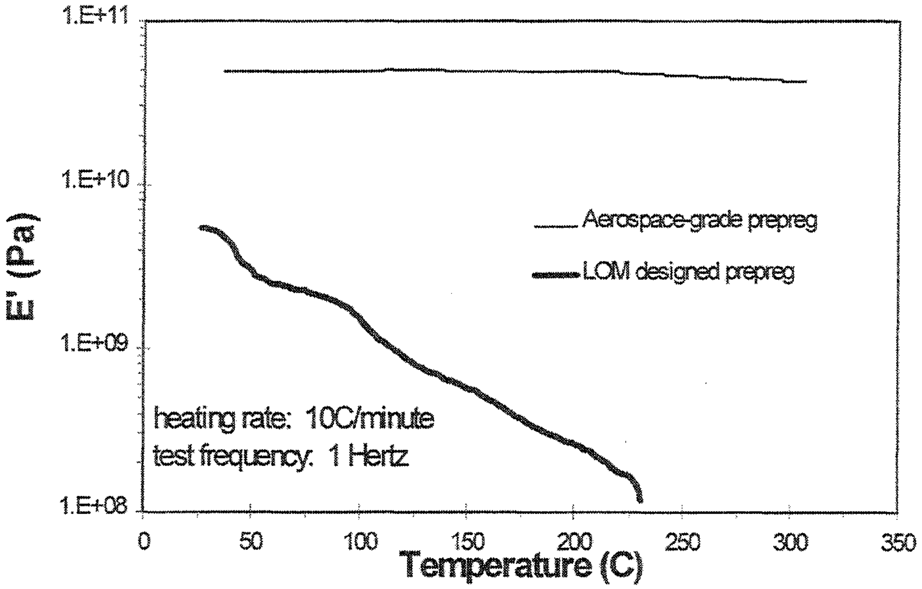

Figure 6 : Dynamic Mechanical Analysis, three point bend test method, of post cured LOM composites indicating useable temperatures for both materials.

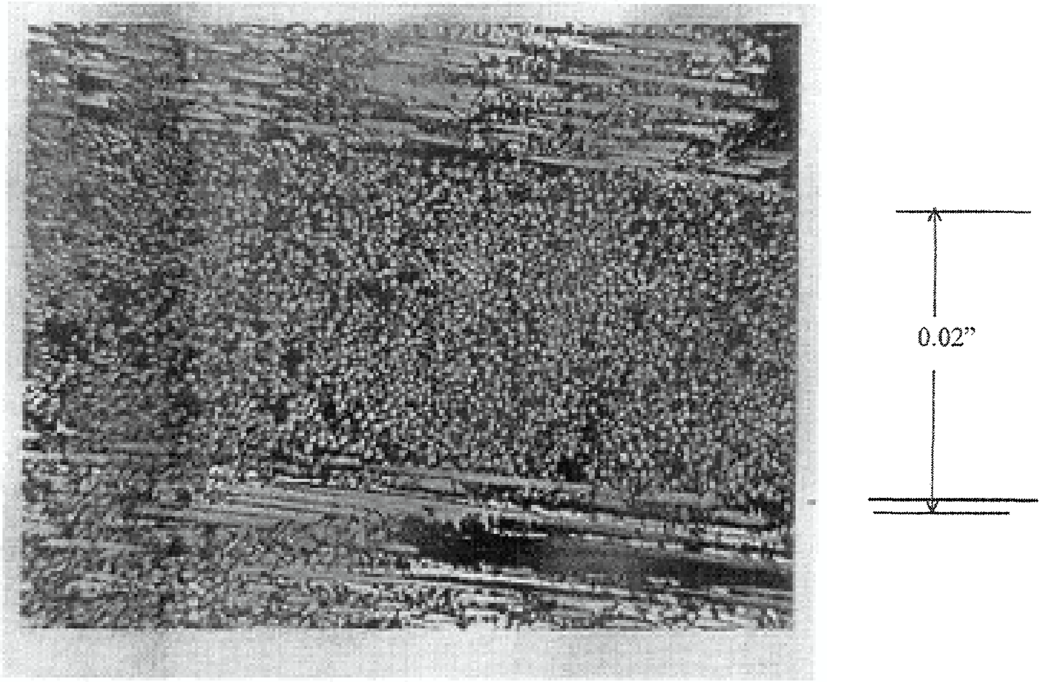

Figure 7 : Photomicrograph of a cross section of a LOM processed, aerospace-grade composite part. Shown in the field of view are four layers: 90°/0°/0°/90° (from top to bottom).

Table 1: Room Temperature Mechanical Properties of LOM Processed and Post Cured Aerospace-grade Composites

Test Method	LOM Processed Ultimate Strength (MPa)	Supplier Data Ultimate Strength (MPa)
Tension (0° orientation) ASTM-D-3039	712.9 ± 37.2	1000
Compression (0° orientation) ASTM-D-695	895.6 ± 57.9 357.1 ± 80.0 (no post cure)	792
Flexure (0° orientation) ASTM-D-790	1189.3 ± 51.0	1310
Interlaminar Shear (0°/90° orientation) ASTM D-2344	42.6 ± 3.9	55

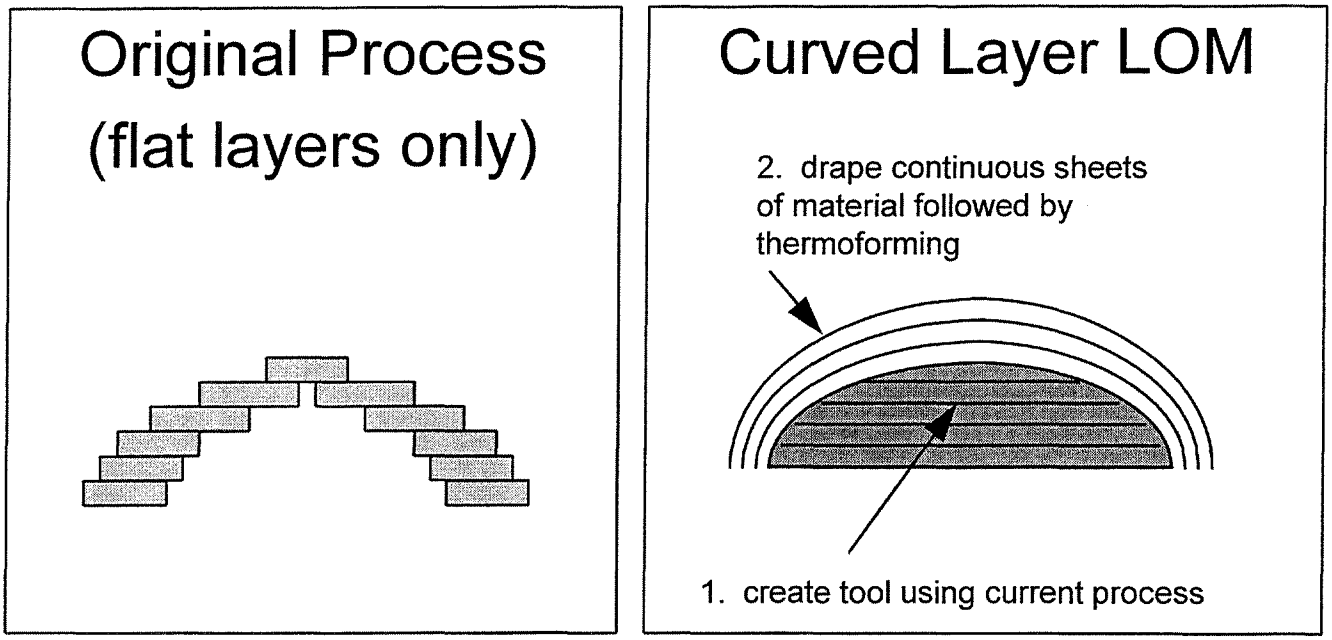

Figure 8 : Curved Layer LOM concept. Curved layer parts will be built by draping the composite preforms over a tool that has been custom prefabricated with the existing flat layer process. The draped sheets will be rolled or thermoformed into place.