NOVEL COST CONTROLLED MATERIALS AND PROCESSING FOR PRIMARY STRUCTURES

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SUMMARY

Textile laminates, developed a number of years ago, have recently been shown to be applicable to primary aircraft structures for both small and large components. Such structures have the potential to reduce acquisition costs but require advanced automated processing to keep costs controlled while verifying product reliability and assuring structural integrity, durability and affordable life-cycle costs. Recently, resin systems and graphite-reinforced woven shapes have been developed that have the potential for improved RTM processes for aircraft structures. Ciba-Geigy, Brochier Division has registered an RTM prepreg reinforcement called “Injectex” that has shown effectivity for aircraft components. Other novel approaches discussed are thermotropic resins producing components by injection molding and ceramic polymers for long-duration hot structures. The potential of such materials and processing will be reviewed along with initial information/data available to date.

INTRODUCTION

The Advanced Composite Technology (ACT) program has shown that textile laminates and enhanced processing such as automated fiber placement can significantly reduce the acquisition cost of advanced composite primary aircraft structures. To satisfy such development and reduce the development time for production implementation, further advancements in materials and processing are needed. Among the industry available developments in the resin transfer molding process is a registered technique called Injectex (R) by Ciba-Geigy. Ciba has also developed a lower than usual density epoxy matrix which can provide intrinsic weight savings without loss of structural integrity.

Several other industry developments that can possibly address the goals of the ACT program are the injection molding of self-reinforcing thermotropic resins and rapid thermal processing of ceramic polymer prepregs for high-temperature structures.

This paper presents the early developments of such technology and is given to review the technical base available and stimulate ideas/improvements to speed successful development of the ACT program.
TEXTILE LAMINATES

Five years ago, the BROCHIER division of Ciba-Geigy in France studied and developed the application of the liquid resin injection process for reducing the acquisition cost of secondary aircraft structures and named the reinforcement for the Resin Transfer Molding (RTM) process INJECTEX. The process, using high-performance graphite fibers at high volume content (i.e., 60 \%\text{\text{\text{o}}}) and epoxy resins certifiable to aircraft specifications can be suitable for reduced-cost primary structural components.

The technical difficulties of liquid resin RTM manufacturing of structural components for aeronautical applications are:
- Providing void free high fiber volume laminates
- Complete and rapid injection of resin
- Control of fiber orientation and elimination of fiber wrinkling and/or fiber fracture
- High quality, especially for large components.

To address such concerns, Ciba has developed a formable textile reinforcement weave including lightweight tow encasement fibers (servings) to increase resin permeability along the major axis of the woven cloth, a patented reactive chemical binder (epoxy compatible) to hold weave orientations, and the development of low viscosity epoxy resins (<100 cps) to permit complete infiltration at low resin pump pressures to assure minimum fiber disarray. The service temperature of the developed resin systems are 250°F and 350°F.

Laminates manufactured using these materials have been produced within one hour and found to be satisfactory, as determined by NDT, for aeronautical applications. Typical room temperature mechanical properties for a balanced carbon fiber weave and the 250°F resin system are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Injectex Laminate* Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TENSILE</strong></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
</tr>
<tr>
<td>• MODULUS, Msi</td>
</tr>
<tr>
<td><strong>FLEXURE</strong></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
</tr>
<tr>
<td>• MODULUS, Msi</td>
</tr>
<tr>
<td>INTERLAMINAR SHEAR STRENGTH, ksi</td>
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</tbody>
</table>

* 57 VOLUME PERCENT FIBER; <1 VOLUME PERCENT VOIDS

Studies have shown that, utilizing vacuum degassed low-viscosity epoxy resins and enhanced permeability woven graphite reinforcements, the liquid injection method of the RTM process can be effective even for large aircraft components. Figure 1 shows the enhancement possible to reduce resin injection time between a standard plain weave 3-ply aramid fabric, 2-ply standard fabric with center ply Injectex, and 3-ply Injectex. As noted in the figure, the all-Injectex fabric wets-out twice as fast as the hybrid fabric which, in turn, is more than twice as fast as the standard fabric.
Figure 1. Wet-out factors for resin injection of the RTM process.
Such materials have already been utilized in the Aerospace industry. Typical components using graphite 2-D weaves and epoxy matrices molded by liquid injection RTM include access doors for civil aircraft (Figure 2) and fuselage stiffened panels as shown in Figure 3.

Matrix Enhancement

Some three years ago, Ciba-Geigy developed an improved 250°F hot-wet service temperature epoxy resin suitable for Aerospace applications. Among the attractive features of this resin, designated Vicotex M18, is a 3.7% lower laminate density due to a lower resin specific gravity. This represents an automatic weight savings compared with the currently used graphite laminates, without any known reduction in required structural integrity or durability. Further, resin cost is similar to other multi-func-
tional epoxies and does not contain any OSHA restricted components. Typical laminate properties for a unidirectional 197 g/m² prepreg at room temperature using 12K-HTA graphite fiber are given in Table 2.

The resin system was evaluated on intermediate modulus graphite fiber and demonstrated satisfactory properties, including damage tolerance testing, as shown in Table 3.

Currently, to take advantage of the lower resin density, Ciba-Geigy is evaluating this type of formulation with reduced viscosity to allow for resin infiltration RTM for ACT components needed for Grumman structures.
Table 2. M18 Resin Laminate Typical Properties

<table>
<thead>
<tr>
<th></th>
<th>AS CURED</th>
<th>AFTER 1000 HR AT 160°F/95% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TENSILE 0°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
<td>309</td>
<td>314</td>
</tr>
<tr>
<td>• MODULUS, Msi</td>
<td>21</td>
<td>–</td>
</tr>
<tr>
<td>TENSILE 90°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
<td>8.8</td>
<td>8.4</td>
</tr>
<tr>
<td>• MODULUS, Msi</td>
<td>1.8</td>
<td>–</td>
</tr>
<tr>
<td>COMPRESSION 0°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
<td>185</td>
<td>189</td>
</tr>
<tr>
<td>FLEXURE 0°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
<td>246</td>
<td>–</td>
</tr>
<tr>
<td>• MODULUS, Msi</td>
<td>16</td>
<td>–</td>
</tr>
<tr>
<td>INTERLAMINAR SHEAR 0°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• STRENGTH, ksi</td>
<td>14.0</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Table 3. Vicotex M-18/ Celion G40-600 (60 V/o) Laminate Mechanical Properties (at Room Temp) for Unidirectional Laminates

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0° TENSILE STRENGTH</td>
<td>398 ksi</td>
<td></td>
</tr>
<tr>
<td>0° TENSILE MODULUS</td>
<td>25.3 msi</td>
<td></td>
</tr>
<tr>
<td>90° TENSILE STRENGTH</td>
<td>11.1 ksi</td>
<td></td>
</tr>
<tr>
<td>90° TENSILE MODULUS</td>
<td>1.9 msi</td>
<td></td>
</tr>
<tr>
<td>0° COMPRESSION STRENGTH</td>
<td>180 ksi</td>
<td></td>
</tr>
<tr>
<td>90° COMPRESSION STRENGTH</td>
<td>32.6 ksi</td>
<td></td>
</tr>
<tr>
<td>ILSS</td>
<td>14.1 ksi</td>
<td></td>
</tr>
<tr>
<td>OPEN-HOLE-TENSION (QUASI-ISOTROPIC)</td>
<td>137 ksi</td>
<td>13.3 ksi</td>
</tr>
<tr>
<td>±45° TENSION</td>
<td>6.6 in.-lb/in.²</td>
<td></td>
</tr>
<tr>
<td>GIIIC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FILLED-HOLE-COMPRESSION (QUASI-ISOTROPIC)</td>
<td>DRY</td>
<td>75.7 ksi</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WET (95% RH)</td>
</tr>
</tbody>
</table>

THERMOTROPIC RESINS

Liquid Crystal Polymers (LCP) form ordered systems, either in solution or in the melt forming matrices, that are anisotropic in the heating or cooling direction and are known as thermotropic materials.

The most popular LCP, a copolyamide in fiber form, is Dupont’s Kevlar. The currently studied LCPs are aromatic copolyesters and several are currently commercial realities. The LCP ordered structure provides exceptional mechanical, chemical, and thermal stability properties. Most currently available LCPs are semi-crystalline rigid rod chains, although Dupont has recently introduced an amorphous resin designated HX-2000.
The major semi-crystalline materials are available from Amoco, under the tradename of Xydar, and Hoechst Celanese, under the brand name of Vectra. These resins are solvent-resistant, show very low moisture absorption, and display low coefficients of thermal expansion. Properties in the melt direction are significant, including high matrix modulus and reasonable elongation. The material is effective in long-term stability at 400°F and inherently self-extinguishing.

LCP resins process readily compared to other high-temperature-resistant resins and easily fill molds during injection molding or pultrusions. Currently, these resins are particulate filled to reduce material cost, currently at $10/lb for volume quantities of material. Some studies are being undertaken for continuous-reinforced LCP suitable for structural components, but the major resin outlets are for electronics, automotive, and microwave cookware. Table 4 shows typical injection-molded properties of the neat resin tested in the melt flow direction.

<table>
<thead>
<tr>
<th>Property</th>
<th>Xydar G540 at Room Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, ksi</td>
<td>21.2</td>
</tr>
<tr>
<td>Tensile Elongation, %</td>
<td>1.5</td>
</tr>
<tr>
<td>Flexural Modulus, Msi</td>
<td>2.3</td>
</tr>
<tr>
<td>264 psi Heat Distortion Temp, °F</td>
<td>465</td>
</tr>
</tbody>
</table>

LCPs are currently of high interest, since forecast of high volumes are expected within the next few years which is expected to reduce current costs. Several Japanese resin suppliers such as Sumitomo, Sekisui, and Nippon Petrochemical, as well as Rhone-Poulenc, Bayer, and BASF of Europe, produce LCP resins. As supply increases along with development of continuous reinforced prepregs, an improved material system will be available for structural components. It is expected that early aircraft parts will be processed by thermoforming as well as injection molding and pultrusion, and utilized for aircraft interiors and secondary structures operating at elevated temperatures. It is forecasted that with increased development the LCP laminates will be utilized for primary aerospace structures across a broad service temperature range. Table 5 provides trade literature data for three specific neat resins from longitudinal test bars prepared to net dimensions by injection molding.

<table>
<thead>
<tr>
<th>Property</th>
<th>Material Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cc</td>
<td>VECTRA A130   Xydar RC210   HX-2000</td>
</tr>
<tr>
<td>Tensile Properties</td>
<td></td>
</tr>
<tr>
<td>Strength, ksi</td>
<td>20</td>
</tr>
<tr>
<td>Modulus, Msi</td>
<td>2.2</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>2.3</td>
</tr>
<tr>
<td>Notched Izod Impact, ft-lb/in.</td>
<td>2.0</td>
</tr>
<tr>
<td>Heat Deflection at 264 psi, °F</td>
<td>446</td>
</tr>
</tbody>
</table>

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CERAMIC POLYMERS

Currently, Government and Industry development personnel have renewed interest in long-duration hot structures for high-speed commercial aircraft and extremely hot structures for short duration in highly oxidizing environments for hypersonic vehicles. As is known, structural materials that perform under such conditions must be of minimum weight to allow for reasonable payloads. Several ongoing developments in this regard are based on both reinforcing fibers and matrices made from polymer precursors. Hercules and Hexcel, among the current suppliers of polymer prepregs for aerospace structures, are developing ceramic prepregs that hold high promise for high-strength, high-modulus composites suitable for future aircraft structures.

Several U.S. universities are developing specialty materials that could result in affordable structural materials in the ceramic matrix composite category. The University of New Mexico has developed boron nitride fibers from polymer precursors that show microstructure similar to currently used carbon fibers. The fibers are produced by the commercial process of die extrusion fiber spinning. Other non-oxide fibers are under study such as silicon carbide, aluminum nitride, and silicon nitride. Consistent mechanical properties are current limitations, but with continued study it is expected that such problems will be overcome. At the University of Michigan, an economical silicate process is being developed to obtain a low-cost range of polymers and glasses suitable for high-temperature composites. Applications currently of interest are 800°F stable polymers, conductive polymers, and a wide variety of silicon compounds. At the University of Illinois, micro-controlled blended extremely fine powder ceramics have resulted in high mechanical strength. With optimized reinforcements that can resist high temperature and high pressure, hot pressed weight effective aerospace structures will be possible.

In 1990, Rhone-Poulenc of France introduced a carbonitride ceramic fiber with oxidative stability to 2550°F with the trade name Fiberamic. The developed fiber is a continuous textile yarn of 250 to 500 filaments obtained via pyrolysis of polysilazane, as shown in Figure 4. Although the fiber was at the pilot plant scale, production commitment has not yet been announced and is herein noted because the future will surely contain such textiles so that output of the ACT program can be utilized in the current studies for HSCT. Molding developments currently under study for ceramic structural components include high solids injection molding, tough nonporous green preforms, and crack-free fired parts with silicon nitride matrices. Other structural fabrication techniques demonstrated are lamination, corrugation, winding, and thermoforming.

CONCLUSIONS

A number of studies and developing thrusts to enhance and/or enable attainment of low-cost, reliable primary structures for the Aerospace industry are appearing and hold high promise for application to future high-speed commercial aircraft.

The ongoing research is a necessary key ingredient to the industry’s technological readiness to reduce implementation time and assure continuing developments. The developments have been focused to
the needs of the end-user and, with their willingness to accept some risk, a significant advancement in our airframe industry will shortly become a reality.