Application of Novel Renewable Resource Based Advanced Composite Materials in Transportation Infrastructure in Delaware

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Richard P. Wool
Shantaram S. Morye

Department of Chemical Engineering and
Center for Composite Materials
University of Delaware

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DELAWARE CENTER FOR TRANSPORTATION

University of Delaware
355 DuPont Hall
Newark, Delaware 19716
(302) 831-1446
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RICHARD P. WOOL
SHANTARAM S. MORYE

Department of Chemical Engineering and
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University of Delaware
Newark, Delaware 19716

DELAWARE TRANSPORTATION INSTITUTE
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Newark, Delaware 19716

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*Delaware Transportation Institute*  
*University of Delaware*  
*Newark, DE 19716*  
*(302) 831-1446*
APPLICATION OF NOVEL RENEWABLE RESOURCE BASED ADVANCED COMPOSITE MATERIALS IN TRANSPORTATION INFRASTRUCTURE IN DELAWARE

DELAWARE TRANSPORTATION INSTITUTE

Shantaram S. Morye and Richard P. Wool
Center for Composite Materials and Department of Chemical Engineering
University of Delaware
Newark Delaware 19716

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Introduction

Polymer matrix composites are becoming increasingly important in transportation infrastructure applications. In this area the payoff from the replacement of more traditional materials like metals and wood by composites is expected to be the highest. This is due to the excellent mechanical properties, light-weight, long useful lives (due to their high corrosion resistance), dimensional stability and low assembly costs of composites. These advantages have been realized with the development of high strength fibers, matrix materials, interface treatments, manufacturing methods and design. A particularly important advantage of composites in infrastructure applications is their good corrosion resistance which prolongs their service life thereby reducing maintenance costs and traffic disruption during maintenance work.

Traditionally, polymer composites use a petroleum based matrix resin such as epoxy, vinyl ester and polyester and synthetic fibers such as glass, carbon and aramide increasing their cost. These resins are also non-biodegradable and depend upon the fast depleting petroleum reserves. In the Affordable Composites from Renewable Resources (ACRES) program, headed by Dr. Richard P. Wool, at the University of Delaware, soybean oil, a natural product, has been made amenable to polymerization using a broad range of chemical routes.

Soybean oil is a naturally occurring triglyceride. Tryglycerides are composed of three fatty acids connected by glycerol through ester linkages. The fatty acids in soy oil have 0 to 3 double bonds. These double bonds are, however, not suitable for polymerization. The soy oil can be epoxidized and the double bonds converted into epoxy functionality. In the ACRES program, the epoxidized soy oil has been converted into a range of materials including plastics, rubbers, foams and matrix resins for composite materials by using different chemical routes. Several patent disclosures have been filed on these novel materials. Of the several chemical routes investigated by the ACRES group, at least ten have yielded materials that can be successfully used as matrix materials for polymer composites. These resins have been combined with synthetic fibers like glass and natural fibers like hemp and flax to make composites. These composites offer a number of advantages as discussed below:

The properties of composites made using ACRES resins have been found to be equivalent to those of the synthetic resin based composites with similar reinforcement. Further development and commercialization of the ACRES resins will serve two important purposes: firstly, being based on soybean oil, it will help the agricultural community through the use of a crop that is produced on a large scale in the USA and secondly, help reduce the depletion of petroleum feedstock.

Because of the very low cost of the soy oil from which the resins are derived, projections for the ACRES resins suggest a price of half that of comparable vinyl ester resins. In large infrastructural projects this will represent a significant cost saving which comes without any sacrifice in properties and performance.
The replacement of traditional materials like metals and wood in infrastructural applications like bridges, pavements and highways with composites is expected to improve the service life of these constructions due to the high corrosion resistance of composites. The ACRES composites offer all the advantages of petroleum based composites at a low cost.

The following applications in the transportation infrastructure field have been identified for the ACRES composites:

- Lighting structures
- Communication towers
- Bearing pads
- Stay-in-place forms
- Box beams
- Temporary signage

The issues that are important in this application development exercise are selection of materials, composites manufacture, measurement of physical and mechanical properties and comparisons with traditional materials. These issues are discussed below in the sections on Experimental Work and Results and Discussion.

Experimental Work

The soy-based resins can be combined with natural and synthetic fibers to make composites. An important feature of the research is the study of hybrid composites wherein two different types of fiber are combined in the same composite. The properties and cost of the composites then depend upon the ratio of the two types of fiber and this offers another way for property-cost optimization.

Composites were manufactured using glass fibers in different constructions and flax fibers. Different ratios of glass fibers: flax fibers were also investigated to study the influence of fiber composition on mechanical properties of the composites. Composites were manufactured from plane woven glass fibers Knytex A260 from Owens Corning and Hybon HTX woven glass fibers from PPG Industries. The flax fibers were Durafiber Grad 2 from Cargill. These fibers were combined with glass fibers to make hybrid composites and study their properties. Composites were manufactured under optimized conditions using the Seemann Composites Resin Infusion Molding Process (SCRIMP) and Resin Transfer Molding (RTM) process. The work involved manufacture of the composites, curing and postcuring of the composite resin, machining of the composite panels into standard test specimens and mechanical property characterization. These properties were measured using ASTM standards.

In addition to the mechanical properties of the composites, their glass transition temperature and water absorption properties are also important and these were measured using Rheometrics Dynamic Mechanical Analyzer RSAII (DMA) and water immersion tests.
Results and Discussion

Mechanical Properties

The mechanical properties of ACRES composite are shown in Table 1. The composite uses E-glass fibers QM6408 from PPG Industries and was manufactured using SCRIMP. The matrix for this composite is based on acylated epoxidized soyoil cross-linked with styrene using USP 245 initiator. Mechanical properties for selected metals are also given for comparison.

Table 1: Mechanical properties of ACRES composite and selected metals

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass fiber/Soy resin</td>
<td>1732.4</td>
<td>20.8</td>
<td>390.3</td>
<td>31.0</td>
<td>385.5</td>
</tr>
<tr>
<td>Iron*</td>
<td>7701.9</td>
<td>190.0</td>
<td>330.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Structural Steel*</td>
<td>7868.2</td>
<td>200.0</td>
<td>450.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Aluminum*</td>
<td>2770.5</td>
<td>71.0</td>
<td>250.0</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*from reference 1

The properties of ACRES composite compare well with those of composites based on woven glass fiber and polyester resins which have a tensile modulus typically 12 to 24 GPa and a tensile strength typically 200 to 350 MPa at a density of around 1500 to 1800 kg/m³ [2]. The properties of metals are, however, higher than those of the ACRES composites. It is important here to note that the densities of metals are higher than that of the composite. The specific properties of the different materials are therefore compared in Table 2.

Table 2: Comparison of specific properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Modulus (GPa/kg/m³)</th>
<th>Specific Strength (MPa/kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass fiber/Soy resin</td>
<td>0.012</td>
<td>0.225</td>
</tr>
<tr>
<td>Iron</td>
<td>0.025</td>
<td>0.043</td>
</tr>
<tr>
<td>Structural Steel</td>
<td>0.025</td>
<td>0.057</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.026</td>
<td>0.090</td>
</tr>
</tbody>
</table>

As can be seen, the specific modulus of the metals is higher than that of the ACRES composite (by a factor of about 2) while the specific strength of the ACRES composite is
about 4.5 times that of steel and about 2.5 times that of aluminum. This indicates that on an equivalent weight basis the ACRES composites are much stronger than both steel and aluminum. This factor combined with their low cost makes the ACRES composites ideal for transportation infrastructure applications where they can replace steel and aluminum without any compromise on performance.

The mechanical properties of glass fiber : flax fiber hybrid composites are shown in Table 3. These composites were manufactured using RTM. The resin is acrylated epoxidized soyoil cross-linked with styrene using a peroxide initiator and a cobalt activator. This resin composition can be cured at room temperature thereby reducing energy consumption in composite manufacture. The glass fiber : flax fiber ratio is based on 100% by weight of fibers. The architecture of the hybrid composites involves flax fibers sandwiched between two layers of woven E-glass fibres.

<table>
<thead>
<tr>
<th>Glass Fiber: Flax Fiber Ratio</th>
<th>Density (kg/m³)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 : 0</td>
<td>1598.6 ± 29.0</td>
<td>10.4 ± 0.5</td>
<td>260.5 ± 12.5</td>
<td>15.4 ± 0.3</td>
<td>257.3 ± 2.8</td>
</tr>
<tr>
<td>80 : 20</td>
<td>1242.6 ± 1.8</td>
<td>3.5 ± 0.1</td>
<td>123.3 ± 5.4</td>
<td>6.9 ± 0.2</td>
<td>130.3 ± 3.0</td>
</tr>
<tr>
<td>60 : 40</td>
<td>1202.2 ± 10.6</td>
<td>3.2 ± 0.1</td>
<td>109.1 ± 1.0</td>
<td>6.0 ± 0.2</td>
<td>115.3 ± 2.5</td>
</tr>
<tr>
<td>40 : 60</td>
<td>1170.7 ± 8.2</td>
<td>2.9 ± 0.2</td>
<td>82.6 ± 2.4</td>
<td>5.8 ± 0.5</td>
<td>68.0 ± 5.4</td>
</tr>
</tbody>
</table>

On introduction of flax fibers into glass fibers, giving hybrid composites, the mechanical properties decrease. This is due to the lower mechanical properties of flax fibers compared with those of glass fibers. It is worth considering two important points at this stage:

1) Flax fibers are lighter than glass fibers and therefore the density of the hybrid composites is lower than that of the 100 % glass fiber composite. Also, amongst the hybrid composites, the density decreases with increasing flax fiber content.

2) Flax fibers are cheaper than glass fibers and therefore hybridization of glass fibers with flax fibers will reduce the cost of the composites.

Because of the lighter weight and lower cost, the hybrid composites can offer similar strength and stiffness as that of the glass fiber composites at an equivalent weight.

A typical stress-strain curve for a glass fiber/flax fiber hybrid composite loaded in tension is shown in Figure 1. The curve is identical to that of any other composite based on synthetic fibers like aramid, carbon and high modulus polyethylene. This shows that the
deformation behavior of natural fiber composites is similar to that of the composites based on synthetic fibers and involves fiber and matrix deformation, fiber/matrix debonding and pullout, fiber failure and matrix cracking.

![Stress-strain curve](image)

**Figure 1: Tensile stress-strain curve for 40:60 glass fiber : flax fiber hybrid composite**

The flexural properties of the hybrid composites were determined according to ASTM D 790 using three point bend geometry. The distribution of stresses in this test is such that the fibers below the mid-plane of the specimen are loaded in tension while those above it are loaded in compression. The gradual change in the stresses also gives rise to shear. The failure mode thus depends upon the material properties and stress distribution. In all the composites tested, glass fibers in the top layer of the specimen were found to fail in compression. Compressive failure occurs by the formation of kink bands and buckling and is commonly observed in organic fibers like aramid, carbon and high modulus polyethylene. Even after compressive failure of glass fibers, the specimens retained their rigidity and can carry high loads as can be seen in Figure 2. The composites can therefore carry higher loads even after compressive failure of the glass fibers upon flexural bending. This observation is very important in applications involving flexural loading, e.g., stay-in-place forms.
Figure 2: Flexural stress-strain curve for 60:40 glass fiber : flax fiber hybrid composite

Thermal Properties

The glass transition temperature of the composites was measured using Rheometrics Dynamic Mechanical Analyzer RSA II. The composites were tested dry, after immersion in distilled water and calcium hydroxide at 80°C until saturation (which took 11 days) and after redrying. The properties are shown in Table 4.

Table 4: Effect of water immersion on glass transition temperature

<table>
<thead>
<tr>
<th>Weathering Conditions</th>
<th>Glass Transition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>76.4 ± 0.3</td>
</tr>
<tr>
<td>Saturated in distilled water at 80°C Redried</td>
<td>61.3 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>74.2 ± 0.1</td>
</tr>
<tr>
<td>Saturated in calcium hydroxide solution at 80°C Redried</td>
<td>61.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>73.9 ± 0.4</td>
</tr>
</tbody>
</table>

On immersion in distilled water and calcium hydroxide solution, the composites absorb water. This water acts as a plasticizer reducing the glass transition temperature of the composites. The effect is, however, only temporary as on redrying and loss of the absorbed water the glass transition temperature almost regains its original value. This is
an important aspect as the composites in transportation infrastructure applications are exposed to cyclic changes in weather: temperature and humidity.

**Water Absorption Properties**

The water gain of the composites was monitored by immersing them in distilled water at 80°C for hydrothermal ageing and in calcium hydroxide solution at 80°C for chemical ageing. Calcium hydroxide was selected because it is an important ingredient of concrete. Figure 3 shows a graph of weight gain by the composite against square root of time.

![Graph of weight gain by glass fiber/AESO composite in distilled water at 80°C](image)

**Figure 3: Weight gain by glass fiber/AESO composite in distilled water at 80°C**

The diffusion of water in the composite is Fickian and can be represented by the following equation:

\[
D = \pi \left( \frac{h}{4M_s} \right)^2 m^2
\]

where
\[ D \] = diffusion coefficient
\[ h \] = specimen thickness
\[ M_s \] = saturation moisture level
\[ m \] = slope of the initial straight line region of the graph
The results obtained from the water absorption experiments are shown in Table 5.

Table 5: Diffusion of water in ACRES composites

<table>
<thead>
<tr>
<th></th>
<th>Immersion in distilled water at 80°C</th>
<th>Immersion in calcium hydroxide solution at 80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Woven Fiber Composite</td>
<td>Unidirectional Fiber Composite</td>
</tr>
<tr>
<td>Diffusivity ($10^{-12}$ m$^2$/s)</td>
<td>2.43 ± 0.17</td>
<td>1.26 ± 0.06</td>
</tr>
<tr>
<td>Time Required for Saturation (Days)</td>
<td>11</td>
<td>22</td>
</tr>
<tr>
<td>Saturation Moisture Level (%)</td>
<td>1.53 ± 0.01</td>
<td>2.73 ± 0.01</td>
</tr>
</tbody>
</table>

The data suggest that there is no difference between the diffusion of water molecules in the composite when the composite is immersed in distilled water and when it is immersed in a solution of calcium hydroxide (which represents concrete environment). The saturation moisture level of the ACRES composites is also similar to that of composites based on traditional matrix materials like epoxy, vinyl ester and polyester. Data reported by different authors on composites utilizing these matrix materials suggest that the saturation moisture level typically ranges from 1 to 3 % [3-5]. Although the diffusion is Fickian, water absorption also takes place through the fiber/matrix interface regions and fiber ends. The unidirectional fiber composite which has less number of fiber ends therefore takes more time to reach saturation level of moisture.

Conclusions

The following conclusions can be drawn from this experimental study:

1) The soybean oil based resins developed in the ACRES program at the University of Delaware can be successfully combined with a range of fibers, both synthetic and natural and their combination to make hybrid composites.

2) The properties of the glass fiber based ACRES composites are equivalent to those of composites based on traditional petroleum based matrix materials.

3) The specific tensile strength of the ACRES composites is 2 to 5 times that of steel and aluminum.

4) The glass fiber/natural fiber hybrid composites manufactured in the ACRES program offer equivalent properties when their lower densities and lower cost are taken into account.
5) On flexural loading, the glass fibers in the composite fail by compression. The composites retain their rigidity and can carry significant loads even after compressive failure of the glass fibers.

6) The composites absorb water reducing their glass transition temperature which returns to its original value on drying.

7) The saturation moisture level of ACRES composites is similar to that of the composites based on traditional petroleum derived matrix materials.

8) The above properties come at a significant price advantage because of the low cost of the soybean oil on which the matrix materials are based. In addition to this, the development of ACRES resins and composites will help the agricultural community of Delaware and help reduce the depletion of petroleum reserves.

References


Delaware Center for Transportation
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