A Bright Future for Light-Cured Composite Materials

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ABSTRACT

Although light-cured composite materials have been around for decades, their general use has been limited. Recent advancements in light-curing technology, such as the development of new photoinitiators, new monomers and oligomers, and new light sources, provide opportunities to expand the application space of light-cured composite materials.

In this talk, I will provide a basic overview of composite materials and highlight some of the unique benefits light-cured composites can enable for various applications, ranging from low-cost prototyping to high-rate production of lightweight composite parts. In addition, I will describe a specific example where light-cured composite materials are enabling a new, innovative approach for manufacturing custom footwear products.

1. OVERVIEW OF COMPOSITE MATERIALS

1.1 Example Applications

A composite is a multiphase material that is generally designed and manufactured to obtain improved material properties based on the principle of combined action. The majority of traditional composite materials on the market today are designed for improved mechanical performance over conventional engineering materials. However, composite materials can also provide additional benefits, such as corrosion resistance and improved vibration damping. FIG. 1 includes some example market categories and applications where composite materials are utilized.

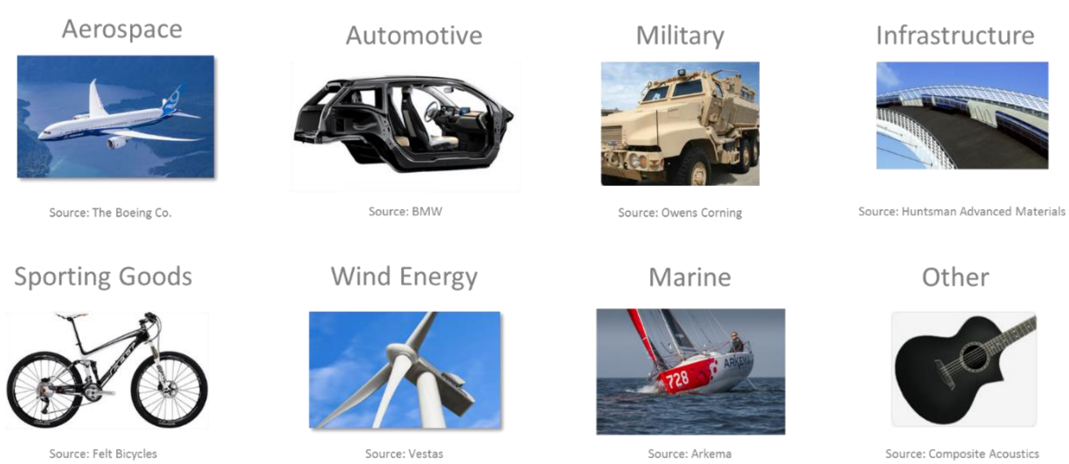

FIG. 1. Example applications and markets that utilize traditional composite materials.

1.2 Terminology

Composite materials are comprised of two primary phases: a reinforcement phase and a matrix phase (see FIG. 2). The reinforcement phase is discontinuous and held together by the continuous matrix phase. As categorized in FIG. 3, composite reinforcements can be particles or fibers of different shapes, sizes and aspect ratios.

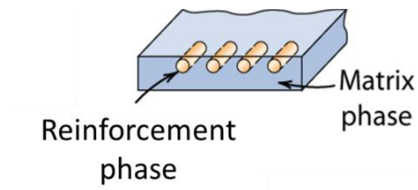

FIG. 2. A schematic representation of the two primary phases of a composite material. The discontinuous reinforcement phase is held together by the continuous matrix phase [1].

The mechanical properties of a composite material are highly dependent on a variety of parameters, including:

- Mechanical properties of the reinforcement phase
- Mechanical properties of the matrix phase
- Aspect ratio and orientation of the reinforcement phase
- Volume percent of the relative phases
- Interfacial properties between reinforcement and matrix phase

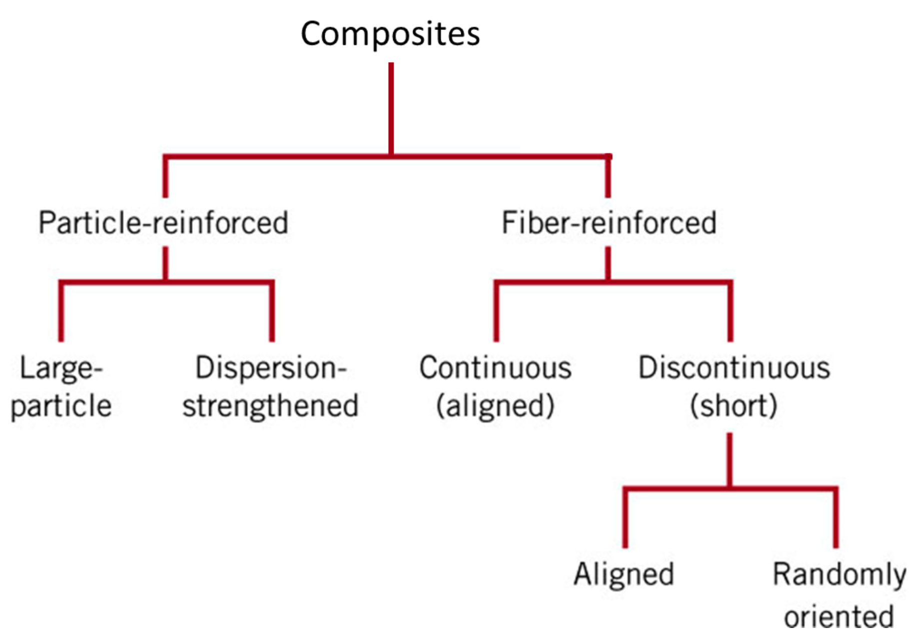

FIG. 3. An overview diagram of the different categories or classifications of composite materials [1].

1.3 Continuous Fiber-Reinforced Composite Materials

As shown in FIG. 3, there are a variety of reinforcement types. Continuous fiber-reinforced composite materials provide the greatest enhancement to mechanical properties, and thus will be the focus of this presentation.

The type of fibers and matrix used to make a composite material depends on the application. The most common fibers used for structural composites include glass fibers and carbon fibers held together with a polymer matrix; however, as shown in FIG. 4(a), traditional composites extend well beyond these materials.

Continuous fibers within a composite can be stacked unidirectional layers, where the fibers in each layer are oriented in a specific direction. Continuous fibers can also be woven in a variety of patterns, such as plain weaves, satin weaves, or twill weaves. FIG. 4(b) shows the top view and side view of multiple stacked layers of a plain weave woven fabric.

(a)

Matrix type	Fiber	Matrix
Polymer	E-glass	Epoxy
	S-glass	Polyimide
	Carbon (graphite)	Polyester
	Aramid (Kevlar)	Thermoplastics
	Boron	(PEEK, polysulfone, etc.)
Metal	Boron	Aluminum
	Borsic	Magnesium
	Carbon (graphite)	Titanium
	Silicon carbide	Copper
	Alumina	
Ceramic	Silicon carbide	Silicon carbide
	Alumina	Alumina
	Silicon nitride	Glass–ceramic
		Silicon nitride
Carbon	Carbon	Carbon

(b)

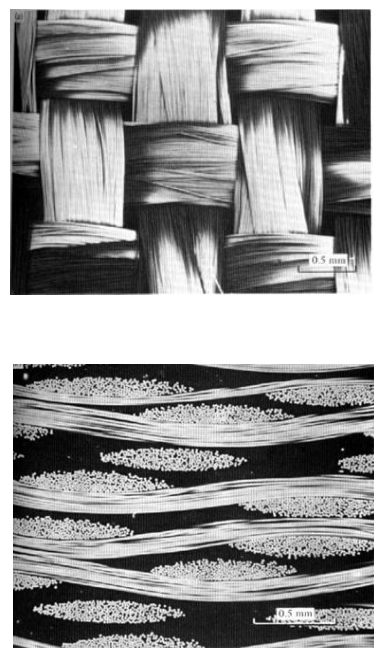

FIG. 4. (a) The different types of matrix and fibers materials commonly used to construct composite materials [2]. (b) a top and side-view cross-section of a woven fiber layer [3].

1.4 Mechanical Properties

The reinforcement phase can provide significant enhancement to the mechanical properties of a composite material, compared to the properties of the matrix material alone. However, continuous fibers provide added strength and stiffness in one direction. Therefore, aligning fibers in one direction within a matrix material, as in a unidirectional composite layer shown in FIG. 5, will result in a very anisotropic material, where the properties in one direction are very different than the properties in the orthogonal direction. In some cases, the mechanical properties, such the elastic modulus, can be over 20X in the longitudinal fiber direction, as opposed to the transverse direction.

Due to the anisotropy as a result of directional fiber reinforcement within a composite material, the material properties of a specific combination of fibers and matrix material are commonly defined by upper and lower bounds. The upper bound represents an isostrain condition for the fibers and matrix, whereas the lower bound represents an isostress condition.

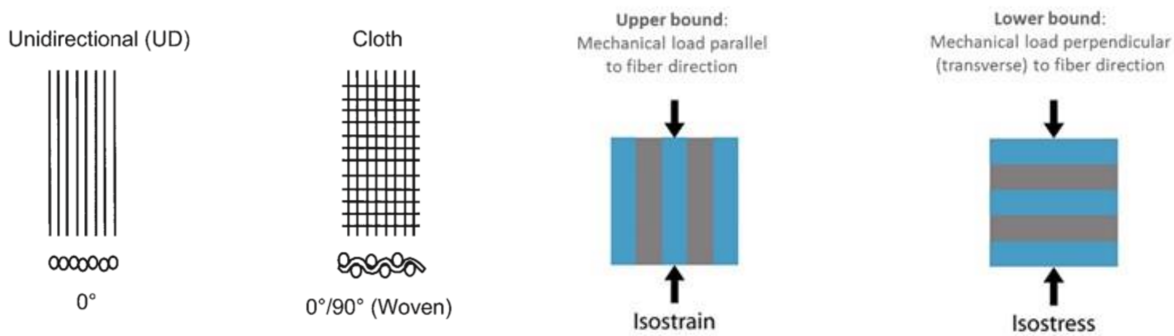

FIG. 5. Unidirectional composite materials are anisotropic, and are therefore generally utilized in laminates with fibers oriented in different directions [4]. The properties along the fiber direction represent the upper bound for mechanical properties, whereas the direction perpendicular to the fibers represents the lower bound.

Because of these anisotropic properties, designing a composite material for a specific application requires selecting both the fibers and matrix material, as well as designing the angle and orientation of the different fiber layers within the composite.

Although the specific details related to the design of composite materials is outside the scope of this paper, theses design parameters provide ample opportunity to design the optimum composite material for a specific application. However, the benefits of improved mechanical performance and material design capabilities generally come at a cost. That is, controlling these parameters adds complexity to the manufacturing of composite materials.

2. MANUFACTURING PROCESSES FOR FIBER-REINFORCED COMPOSITE MATERIALS

Over the last few decades, the manufacturing processes for continuous fiber-reinforced composite materials have expanded significantly and these new methods and techniques have improved quality and cost. For an extensive overview of the different types of manufacturing methods available for composite materials, see: http://composites.owenscorning.com/processes/processes.aspx.

Manufacturing methods used to make continuous fiber-reinforced composite materials include: Autoclave processing, resin transfer molding, resin infusion techniques, and wet lay-up. The relative resulting composite quality and cost between these methods is highlighted below in FIG. 6. Of the four processes discussed here, resin infusion and wet lay-up are the most amenable to manufacturing UV-cured composite materials.

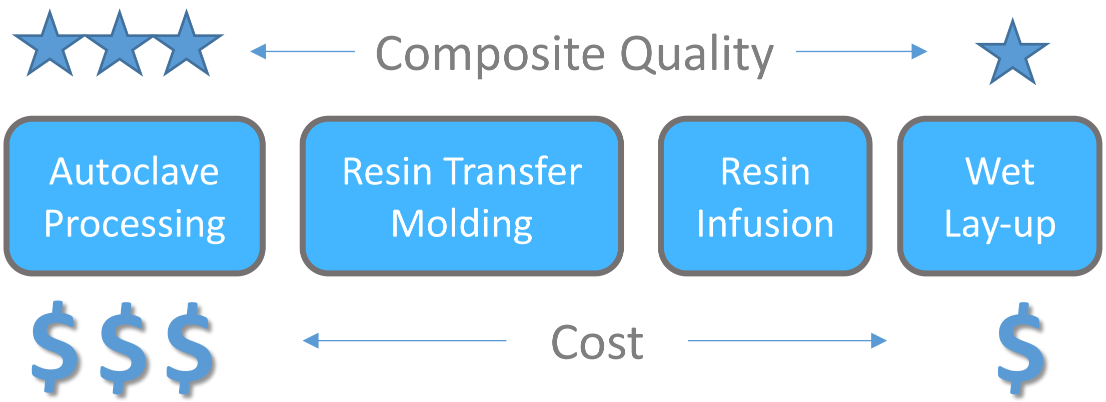

FIG. 6. Four major composite manufacturing processes for continuous fiber-reinforced composites include autoclave processing, resin transfer molding (RTM), resin infusion, and wet lay-up. Generally, the processes that result in the highest quality composite material are the most expensive.

2.1 Autoclave Processing

Autoclave processing is the most advanced form of processing for a composite material, and generally the most expensive. Autoclave processing commonly utilizes unidirectional prepreg layers (unidirectional fibers "pre-impregnated" with resin) to create a pre-cured laminate (see FIG. 7). The pre-cured laminate is cured in an autoclave on a hard tool. The autoclave provides uniform pressure and temperature over the curing cycle, and the vacuum bag helps draw off volatiles during the curing of the matrix polymer.

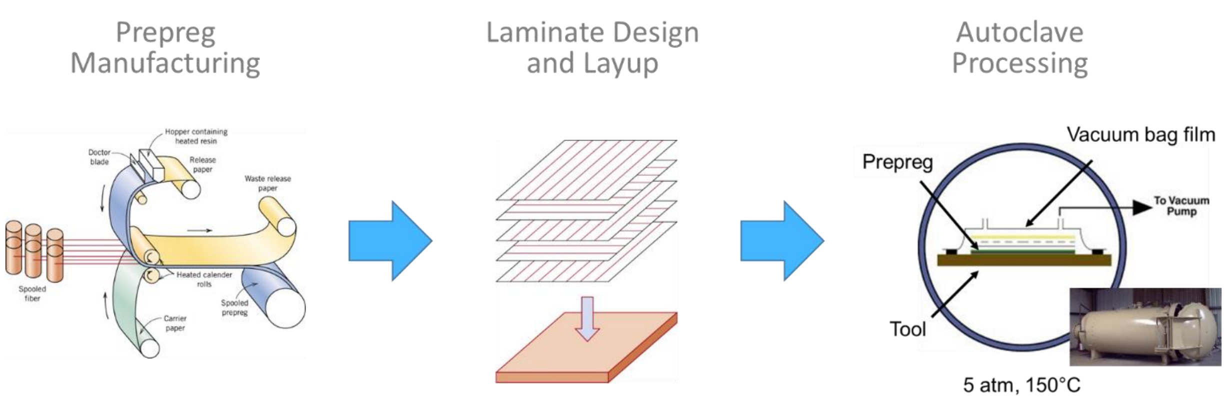

FIG. 7. A schematic overview of the autoclave process for composite materials.

2.1.1 Key advantages to autoclave processing [5]

- Resin/fiber content accurately set. High fiber contents can be achieved.
- Excellent health and safety characteristics, clean to work with.
- Fiber cost minimized in unidirectional tapes - no secondary process to weave into fabric prior to use.

- Resins can be optimized for mechanical & thermal performance, high viscosity resins possible.
- Extended working times (up to several months at RT) - structurally optimized, complex lay-ups readily achieved.
- Potential for automation, labor saving.

2.1.2 Key disadvantage to autoclave processing [5]

- Materials cost is higher for preimpregnated (prepreg) fabrics.
- Autoclaves required to cure. These are expensive, slow and size-limited.
- Tooling must withstand the process temperatures involved
- Core materials must withstand the process temperatures and pressures.

2.2 Resin Transfer Molding

Resin transfer molding, or RTM, utilizes a closed, hard tool to manufacture composite materials with a smooth side on both surfaces (see FIG. 8). RTM involves injecting a liquid, thermosetting resin into dry fibers that have been secured inside the closed mold. Once the fibers are wet-out with the resin, the resin is cured (most commonly with an elevated temperature cycle).

Vacuum assisted resin transfer molding, or VARTM, is an extension of the RTM process, where vacuum is applied to the closed mold to help draw the resin through the fibers. VARTM generally yields better properties than RTM alone, because the vacuum assist can help eliminate air pockets and voids within the matrix.

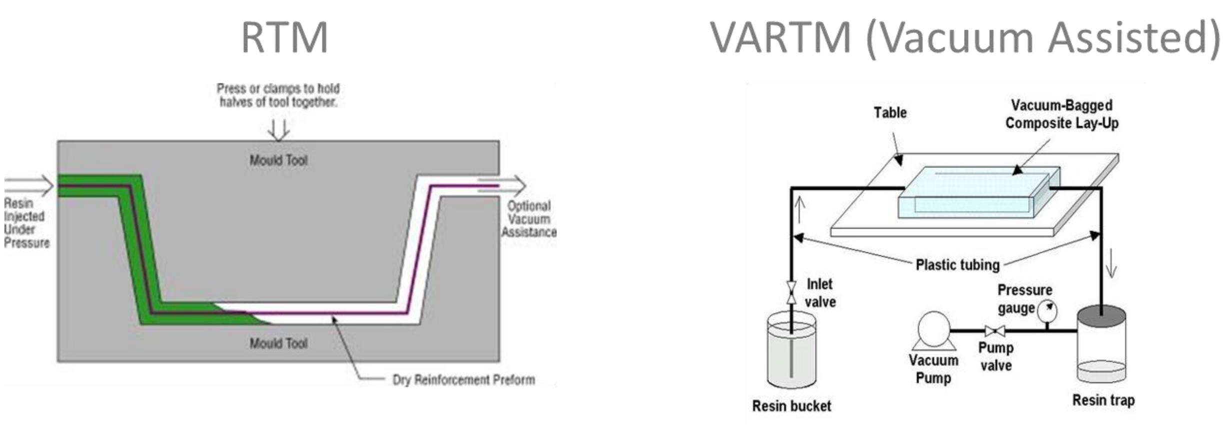

FIG. 8. A schematic overview of the resin transfer molding (RTM) process for composite materials.

2.2.1 Key advantages to RTM and VARTM processing [5]

- High fiber loading, low void content.
- Closed mold - Good health and safety, environmental control.
- Possible labor reductions.

- Both sides of component have a molded surface.

2.2.2 Key disadvantages to RTM and VARTM processing [5]

- Matched tooling is expensive, heavy (to withstand pressures).
- Generally limited to smaller components.
- Unimpregnated areas can occur resulting in costly scrap.

2.3 Resin Infusion

Resin infusion molding is similar to RTM, but instead utilizes an open mold rather than a closed mold (see FIG. 9). A vacuum bag is used on the opposite side of the hard tool used to define the composite shape. Applying vacuum with the vacuum bag draws resin through the fibers and applies compaction pressure during the curing processes. Because the vacuum bag can be transparent to UV light, resin infusion techniques are the most amenable to creating a high-quality composite part using a UV-cured polymer matrix.

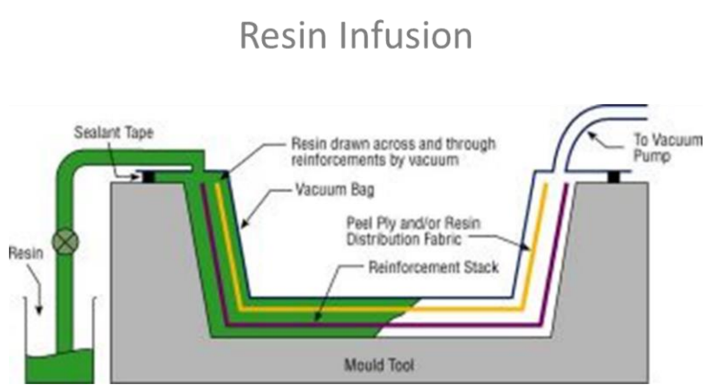

FIG. 9. A schematic overview of the resin infusion process for composite materials.

2.3.1 Key advantages to resin infusion processing [5]

- Similar to RTM, except only one side of the component has a molded finish.
- Much lower tooling cost (half of the tool is a vacuum bag), and lower strength requirement for hard tool.
- Large components can be fabricated.
- Standard wet lay-up tools may be able to be modified for this process.
- Cored structures can be produced in one operation.

2.3.2 Key disadvantages to resin infusion processing [5]

- Relatively complex process to perform well.
- Resins must be low in viscosity, comprising mechanical properties.

- Unimpregnated areas can occur resulting in expensive scrap.
- Some elements of the process are covered by patents (SCRIMP).

2.4 Wet Lay-up

Wet lay-up is the simplest, and generally the lowest cost process to create a composite part. As the name denotes, wet lay-up involves simply spreading wet (liquid) resin over fibers on a hard tooling surface (see FIG. 10). Most commonly the resin is applied by hand. Resin used can be room-temperature cured, thermally cured, or UV-cured.

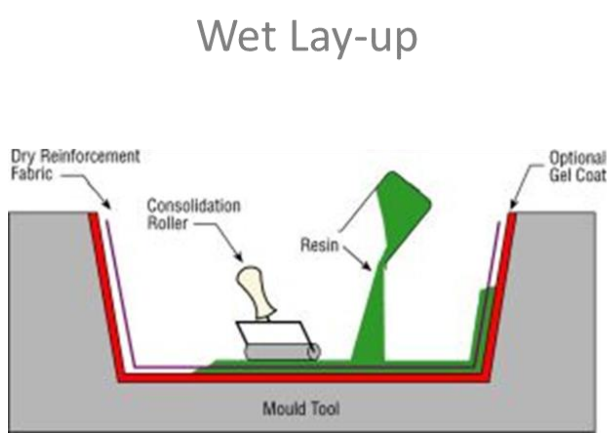

FIG. 10. A schematic overview of the wet lay-up process for composite materials.

2.4.1 Key advantages to wet lay-up processing [5]

- Widely used.
- Simple principles.
- Low cost tooling, if RT cure resins used.
- Wide choice of suppliers and material types.
- Higher fiber contents, and longer fibers than with spray lay-up.

2.4.2 Key disadvantages to wet lay-up processing [5]

- Laminate quality skill-dependent.
- Health and safety considerations of resins.
- Limiting airborne styrene concentrations to legislated levels from polyesters and vinyl esters requires expensive extraction systems.
- Resins must be low viscosity to be workable by hand, compromising mechanical/thermal properties.

3. MATERIALS AND MANUFACTURING PROCESSES FOR LIGHT-CURED COMPOSITES

Light-cured composite materials require one distinct difference from traditional, thermally cured composite material: the liquid resin that will become the polymer matrix of the composite requires exposure to light. This very simple, yet distinct difference generally eliminates autoclave processing and RTM / VARTM as viable manufacturing options for light-cured composites. As mentioned above, resin infusion and wet lay-up are the most amenable manufacturing processes for light-cured composites.

3.1 Fibers

As shown in FIG. 4, there are a variety of types of continuous-fibers that can be used to manufacture traditional composite materials; however, only glass fibers are sufficiently transparent to light and thus amenable for light-cured composites. Although, light-cured composites are generally limited to utilizing only one type of fiber, glass fibers are the most widely used fiber type and are produced in large volumes and are available at relatively low-cost (as compared to other fiber types). For example, glass fibers can cost 10X less than carbon fibers.

The established use of glass fibers within the composites industry has resulted in a large supply base offering variety of different fiber and fabric patterns, as shown in FIG. 11. The different available types of woven, stitched, or knitted glass fabrics still enables opportunity to design the light-cured composite material for a specific application.

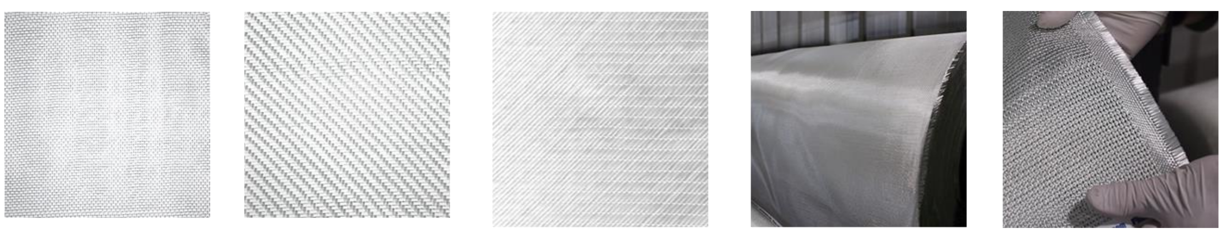

FIG 11. Images of different types of commercially available glass fiber reinforcement layers for composites, including woven, unidirectional stitched, and knitted (Source: Fiber Glast Development Corporation).

3.2 Polymer Matrix

The availability of different types of light-curable monomers and oligomers that could be used as the matrix material of a composite is quite extensive. Cationic or free-radical cured materials are both possible for light-cured composites, thus enabling a wide-range of epoxy-based, acrylate-based, or hybrid resins formulations with properties tuned for a particular application. As with all light-cured applications, the photoinitiator(s) would be selected based on the emission spectra of the light source and the formulation chemistry. Typically, with light-cured composites, the optimum wavelength range would be at or near the border of the UV-Visible spectrum because light penetration through the thickness of the composite is a primary requirement.

Also, unlike formulations for coatings and inks, light-cured composite formulations would be tailored for wetting and adhesion to glass fibers, as well as the strength, modulus, and fracture toughness of the polymer, which would dictate load transfer between the glass reinforcement fibers.

3.4 Advantages and Disadvantages of Light-Cured Composites

- Relatively low-cost materials (compared to range of traditional composites)
- Materials design flexibility (resin formulation, laminate design, etc.)
- Simple processing techniques
- Room temperature processing enables low cost tooling and co-cure options
- Rapid cure times

3.4 Disadvantages of Light-Cured Composites

- Glass fibers will limit mechanical performance (e.g. compared to carbon fibers)
- Requires line-of-sight exposure, prohibiting very complex shapes

4. HOW CAN UV-CURED COMPOSITES BENEFIT YOUR COMPANY?

As discussed in Section 1.1, traditional composite materials have made significant in-roads into different applications; however, these applications are not necessarily the applications that offer the greatest potential for light-cured composite materials. Light-cured composites have unique advantages over traditional composites, and therefore, applications that can benefit from light-cured composites should be identified based on these unique advantages – not simply a replacement option for traditional composites.

Light-cured composites cannot compete with traditional carbon fiber composite materials, when based solely on mechanical performance. However, when cost is a consideration, light-cured composites can provide a better material option than common plastics and metals, while remaining cost competitive. In some cases, light-cured composites can provide a true cost advantage over other material options, particularly where tooling costs are high.

5. EXAMPLE APPLICATION: CUSTOM ORTHOTICS

Light-cured composite materials offer benefits to manufacturing footwear products, such as custom orthotics. For conventional custom orthotics, a patient's foot shape is typically captured using a plaster cast or a foam impression, which is then used to create a positive mold of the patient's foot. The custom support plate for the orthotic is generally thermoformed on the positive mold of the patient's foot (at an elevated temperature and pressure).

Given that light-cured composite materials can be cured at room temperature and without substantial external pressure, light-curing can be used to form a lightweight composite support plate for a custom orthotic where the "mold" used to generate the shape of the orthotic is the person's foot [6].

The precursor materials used to make the custom orthotic, termed "Prethotic", includes a flat, size-specific top foam material packaged together with a pre-preg light-curable composite support plate. The pre-preg support plate includes two, multiaxial E-glass fiber layers impregnated with an acrylate-based resin.

A light box, as depicted in FIG. 12, includes UV LEDs designed to cure the light-curable resin inside the Prethotic. A thin, stretch film is drawn over an opening on top of the light box and the Prethotic is placed on the film. A medical practitioner then positions the patient's foot on the Prethotic and presses the patient's foot down into the light box. The film stretches and conforms the Prethotic to the plantar (bottom) surface of the patient's foot. After the Prethotic is shaped to the patient's foot, the light is turned on, which simultaneously cures the custom-shaped composite support plate and bonds the composite plate to the top foam material. The complete curing process takes 2 minutes per foot, and the patient is able to immediately wear the custom orthotics in their shoes [7].

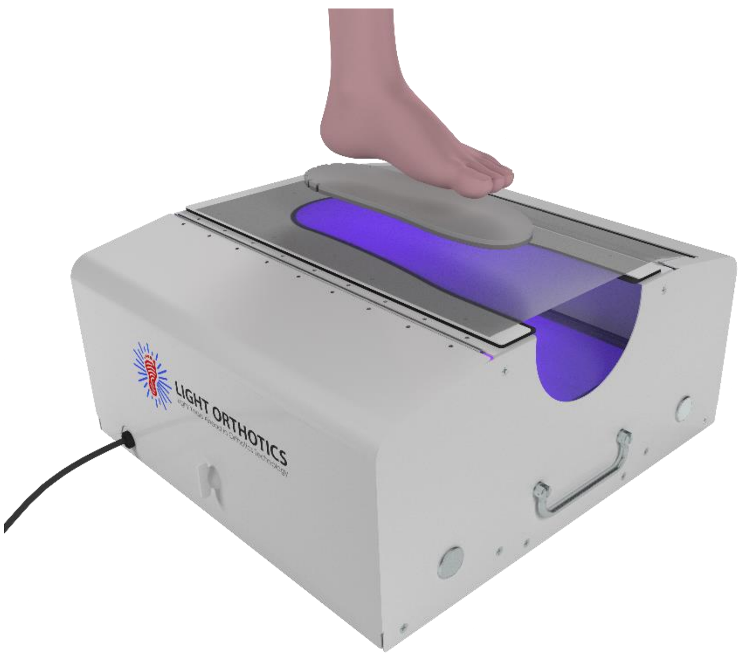

FIG. 14. UV-LED light box used for making custom orthotics.

6. CONCLUSIONS

Light-cured composites offer unique opportunities for new application space. Because light-cured composites generally require the use of low-cost glass fibers and are most amenable to the lower-cost composite manufacturing processes, such as resin infusion and wet lay-up, this materials technology can enable a lower cost solution and better material options for many applications while still maintaining the design flexibility of traditional composite materials. The custom orthotics example described in this paper is just one of many applications where UV-cured composite materials could be utilized.

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[7] See https://www.powersteps.com/lightorthotics and US Patent Application US20180014607 A1.