

Featherweight Composites Manufactured by Selective Nanobridization with Potential Applications in the Automotive Industry

Carl Justin Kamp
Polymeric Composites Laboratory/MIT

James Seferis and Michael Arnold
Polymeric Composites Laboratory

Vasileios Drakonakis
University of Nevada at Reno

ABSTRACT

Nanobridization is a nano-inspired process by which scalable material structures can be designed and manufactured by combining the concept of 'Nano Free Volume' with specific material molecules defining a systemic density (nano-density). This approach explores nanotechnology from a porosity perspective rather than nanoparticles thus minimizing health concerns with nanotechnology, while providing nanoporosity throughout the entirety of the composite system. Nanobridization may be viewed as a density system transformation of material heterogeneity utilizing a unified class of materials such as Polyanomers and in developing next generation structures such as Featherweight Carbon Fiber Reinforced Polymers (CFRP). Polyanomers are further defined by the incorporation of hollow carbon fibers, electrospun nano-fibers, nano-pores and carbon nanotubes (CNT) into this newly established type of matrix. Nanobridization involves fractal structural design and constitutes a scalable structure from the nano- to the macro- scale and vice versa, resulting in a spatial density with significant overall weight reduction.

Featherweight composites are a characteristic example product of nanobridization process, as they include novel bio-inspired fractal structures which are combined with unprecedented mechanical and transport properties. Porosity is designed both at the macro- (honeycomb/foam type) and micro- (hollow carbon fiber foamed matrix and interphase) scales and can find immediate applications such as tooling and nonstructural or failure critical applications. Featherweight composite manufacturing introduces a new production process which includes novel steps, such as electrospinning of carbon fibers and aligned CNT incorporation into the novel polyanomeric matrix system, and an innovative, integrated, roll-to-roll (R2R) process sequence.

The main objective of this work is to discuss the manufacturing scalability of polyanomeric composites through nanobridization and to highlight potential relevant uses for this technology in the automotive industry. This type of material establishes a unique framework for creating the next-generation of composites technology that will be 25 to 40% lighter, while maintaining structural load-bearing characteristics such as stiffness and strength. Various polyanomers have been investigated in the Polymeric Composites Laboratory and will be discussed in this article.

CITATION: Kamp, C., Seferis, J., Arnold, M., and Drakonakis, V., "Featherweight Composites Manufactured by Selective Nanobridization with Potential Applications in the Automotive Industry," *SAE Int. J. Mater. Manf.* 7(3):2014, doi:10.4271/2014-01-1061.

INTRODUCTION

After several decades of attempting to standardize different composite material systems, it has become apparent that it is unattainable for many practical applications due to stringent properties regulations. This is especially true in the aviation industry, where strict qualification and certification protocols are

in many cases impassible barriers to the introduction of new technologies. These confined regulations have become a major obstacle for introducing new material and process technologies industry-wide and have been a driving force for some time. However, with the promise of wide utilization in the automotive industry, the capacity for carbon fiber reinforced and CFRP's is set to greatly increase at a global scale. This

article will demonstrate how such a system of integrated testing and transformative research and development can be achieved by considering the concept of porosity in CFRP's at the macro-, micro- and nano-scales utilizing the examples of honeycomb systems, and especially featherweight composites and nanoporosity. Nanobridization may be viewed as a macromolecular transformation of material heterogeneity utilizing a unified class of matrix materials as Polyanomers and in developing next generation structures such as Featherweight Carbon Fiber Reinforced Polymers.

Numerous methods exist for creating heterogeneous multilayer structures, which in some cases introduce porosity into the CFRP systems at different size scales. For example, honeycomb intermediate layers introduce porosity on the macro-scale, while foamed resin and hollow carbon fibers introduce porosity on the micro-scale and nanoparticle reinforcement such as carbon nanotubes introduce porosity on the nano-scale. It has been shown that in simple heterogeneous systems that modifier particles, such as nylon, can be sprinkled onto the prepreg surface or premixed with the resin applied in the prepreg process [1, 2, 3]. The modifier size and shape can have an effect on the amount of resin applied in each impregnation step since the goal of a prepreg resin impregnation step is to end up with a uniform resin/modifier surface and to maintain the carbon fiber volume fraction at 60%. Significant increases in fracture toughness (modes I & II) have been observed in CFRP composites with micron-sized nylon modifier particles, as well as other plastic types and even some metals [4,5] where the toughness is also significantly improved [6,7].

Interestingly, CFRPs with designed porosity and smart structures can be produced with control of specific materials properties. For example, the modulus increases with density in most materials, including metals, ceramics, fiber-reinforced plastics (FRPs). However, polymer nano-composites may exhibit an opposite behavior (over a certain range) where the modulus increases with decreasing density. This is true in the case of nanoparticle modifiers such as carbon nanotubes (CNTs) where an increasing CNT volume fraction results in a density decrease with a modulus increase [8]. In general, it is thought that nanocomposites have improved materials properties due to the extremely high interaction surface area of the nano-inclusion. Figure 1 depicts the elastic modulus vs. material bulk density relationship where several nanocomposites with different CNT distribution characteristics show opposite behavior to most common materials [8].

By controlling the induced intra- and inter-layer porosity within carbon fiber reinforced polymers, nano-scale porosity can be connected directly to the polymer matrix free volume and can have a major impact on both relative material weight and strength, among other properties. This work shows that while proper use of continuous fiber reinforced composites can result in a nominal 40% reduction in weight over aluminum, the

concept of nanobridization in CFRPs can lead to an additional 40% reduction in weight while maintaining the same mechanical/structural properties. It is worth mentioning that although on a materials basis CFRP is approximately 40% lighter than aluminum, in aerospace applications the actual weight reduction is usually below 20% due to the insecurity feeling of design engineers, which itself is caused by CFRP inherent anisotropy and heterogeneity, and most importantly its unstable interfacial adhesion to other materials, leading to the "black aluminum" phenomenon. The Boeing 787 Dreamliner and the soon to be certified Airbus 350XWB are interesting examples of this fact since the actual weight reduction is significantly less than 40% with the implementation of CFRPs as a replacement for aluminum in load bearing structures [9].

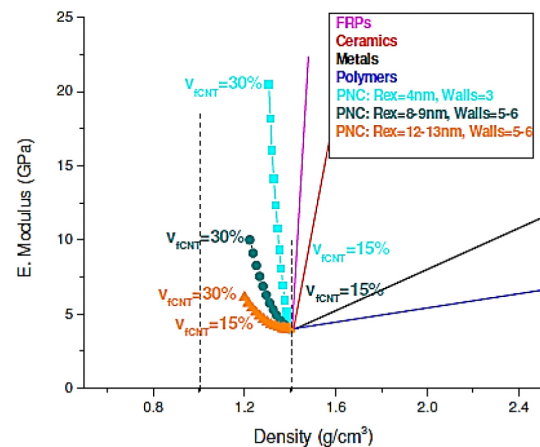


Figure 1. Elastic modulus vs. bulk density for a range of materials. The 3 polymer nanocomposites show opposite behavior to the other common materials. Adapted from [8].

Part of the motivation for featherweight composites comes from nature in the way of bird feathers and bones. Especially feathers have scalable hollowness and porosity from the nano- to macro-scales. The weight of a feather is systematically reduced by this hollowness in all parts including the rachis, barb and hamuli. In addition, the structure of feathers have been described as fractal or self-similar over many scales to optimize lift (bending moments), drag (shear stress), thermal conduction, radiation reflection, boundary layer conduction, electrical dissipation and wetting [10]. The featherweight CFRPs aim to be fractal structures in the macro-, micro- and nano-scales similar to that of the bird feather example.

Through the introduction of controlled porosity, featherweight CFRPs aim to replace conventional CFRPs for situations where specific material properties such as density and weight can be controlled without sacrificing strength. More specifically, featherweight CFRPs have a maximum strength to weight ratio and are therefore interesting alternatives to materials typically used in applications where weight savings result in increased efficiency such as in the case of automobiles. Out-of-autoclave production is possible for featherweight composite production

and is further discussed in [42] where material pre-heating combined with a fast cure technique allows for production time under one hour, thus making the material discussed in this article relevant for large-scale automotive production applications.

It is in the author's opinion that the internal combustion engine is quickly approaching the maximum efficiency possible within the thermodynamic limits. As international regulations get increasingly stringent not only for emissions but for efficiency and fuel economy, weight reduction, especially in passenger trucks and automobiles, seems to be a practical goal for large-scale improvement. As an approximate 'rule of thumb', a 10% weight reduction in an automobile can result in up to a 7% gain in fuel economy, while the weight reduction also results proportionally in over an order of magnitude reduction in CO₂ production. In the U.S., the Partnership for a New Generation of Vehicles (PNGV) is an example of an infrastructure push towards increased efficiency with the ultimate goal of 80 miles per gallon passenger automobiles, while a large European project exists with the goal of including more composites in automobiles called HIVOCOMP. For these reasons, novel materials such as featherweight CFRPs with significantly reduced weight and uncompromised strength are of great interest to the automotive industry.

The featherweight concept discussed in this article includes a laminate structure with porous regions sandwiched between carbon fiber layers, where the laminas are assumed to behave as homogeneous structures with uniform stress throughout the material thickness. The porous interlayers will be discussed further and consist either of an epoxy nanofoam or a cellulose acetate electrospun nano-fiber bed. Other featherweight possibilities which are not discussed in this article include hollow carbon fibers and honeycomb cross sectional inserts.

EXPERIMENTAL

In general, foams are either expanded, such as in the case of polystyrene foam, or created, such as in epoxy foam. Epoxy foams have proven useful in the composite industry due to their high adherent strength, low water adsorption, dimensional stability, heat resistance and that they are relatively chemically inert, as shown in various commercial epoxy foam systems [41]. Foams have a tendency to inhibit crack propagation and for that reason have been utilized in part of this study as CFRP interlayer materials. Previous studies have shown that foams with nano-sized pores, or nano-foams, can be reinforced with nanoparticles for bulk property manipulation [11, 12, 13, 14, 15, 16]. In addition, it has been shown in literature that there are numerous means by which to control the pore size in nano-foams while reinforcing the pore integrity [17, 18, 19, 20, 21, 22, 23, 24, 25, 26].

Nanoparticle reinforcements, when added to the production of nano-foams (bubble formation), tend to get transported to the

pore surfaces due to the surface free energy of the bubble. More specifically, the isomorphic substitution of nanoparticle reinforcements are generally charged, which in turn makes the bubble surface charged, creating an electrical double layer (EDL) [27]. The EDL generates electrostatic forces, which are repulsive, that electrically and mechanically stabilize the pores resulting in lightweight, and high-performance composite foam structures. It is important to mention that the anisotropic alignment control of the nano- and micro-sized pore reinforcement materials is crucial to the mechanical and electrical integrity of the foam reinforcement.

In addition to porous foams, electrospun fibers have also been used as CFRP interlayers. Such fibers increase the consistency of the fractal interlayer architecture which decreases the weight and increases the stiffness. Electrospun fibers, as discussed in [28-29], utilize a formation mechanism which allows for continuous nano- to micro-sized fibers based on the uniaxial stretching of a viscoelastic solution [30-31]. Essentially, an electric field is applied between a conductive (i.e. metal) collection target, which in this case was the carbon fiber bed, and a metallic syringe tip (spinneret) where a droplet of the solution is held in place by its own surface tension as the nano-fibers are extruded [32-33]. Nanoparticle reinforcements can also be utilized with electrospun fibers for increased strength and can be added to the polymer precursor prior to electrospinning. High-quality, low-cost commercial scale electrospinning techniques are currently commercially available, where electrospinning instruments without nozzles would allow for roll-to-roll production in the pre-impregnation zone of the prepreg process [40].

Featherweight CFRP sample properties have been measured in this study by Dynamic Mechanical Analysis (DMA) standard flexural and tensional testing methods, and visualized via Scanning Electron Microscopy (SEM). The experimental measurements of interest include storage modulus, glass transition temperature, $\tan\delta$, flexural modulus, flexural strength, stiffness and fracture toughness.

Dynamic Mechanical Analysis (DMA) is a key technique for measuring the viscoelastic behavior of the matrix systems utilized in featherweight CFRPs which are described in this article. DMA is commonly used in the composites industry to investigate and optimize manufacturing methods and is sensitive to several relevant composite properties such as fiber orientation and inhomogeneity in thermoset matrix cross-linking [34]. In addition, DMA can elucidate properties related to the interphase used in glass and carbon fiber reinforced polymers [34, 35, 36].

DMA takes advantage of the fact that for viscoelastic materials, strain is not in phase with stress in an applied sinusoidal stress pattern. The dynamic modulus, M^* , is defined as the ratio of an applied sinusoidal stress, σ^* , and the resulting sinusoidal strain, ϵ^* . If the sample is linearly viscoelastic, the frequency of