A Brief Review of Nanomaterials for Aerospace Applications: Carbon Nanotube-Reinforced Polymer Composites

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1.0 Introduction

This report identifies some of the technical challenges and key research efforts in the area of nanomaterial composites for use in aerospace applications. Specifically, this report focuses on carbon nanotube-reinforced polymers. Also included are brief lists of US government-led or -sponsored research and research programs, useful publications and other reference materials, and contact information for those individuals who have made significant and continued contributions to this field.

2.0 Technical Issues Limiting Advancement of Nanotube-Reinforced Composites

The extraordinary stiffness and specific tensile strength of carbon nanotubes (CNTs) makes them well-suited for use as reinforcing elements in polymer composites. The incorporation of carbon nanotubes can greatly increase the strength and stiffness of a polymer matrix with minimal increases in weight. It also can augment the ability of a material to resist vibration and flame [1-2]. There are a number of technical challenges that must be overcome before carbon nanotube reinforced-polymer composites can become commercially viable.

Perhaps the most obvious obstacle is that of cost: pure, high quality carbon nanotubes can cost up to $1000/gram [3]. However, the price of nanotubes has dropped dramatically over the past several years as a result of several efforts focused on realizing the mass production of CNTs. This trend is expected to continue as nanotube synthesis techniques are refined and more manufacturing facilities are brought online.

A recent review article identified four critical requirements for effective fiber reinforcement of composite materials: large aspect ratio, interfacial stress transfer, good dispersion, and alignment [4]. While carbon nanotubes typically have very high aspect ratios, their absolute lengths still remain short, which makes them difficult to manipulate and process. Most CNTs are only on order of microns in length, while individual CNTs of some centimeters in length have been synthesized [5]. However, long nanotubes cannot be synthesized in bulk quantities, at present.

In order to increase the length of nanotube-based reinforcing fibers, a number of research groups are investigating methods for producing longer fibers from shorter nanotubes. Woven CNT composite fibers up to 100 meters in length have been demonstrated [6], as have thin, continuous, transparent sheets of nanotubes [7]. While much of this work has focused on the development of conductive fibers for wearable electronics, these materials also are well-suited for inclusion within composite materials. Nanotube sheets, in particular, have been used to fuse together thermally two polymer sheets in a transparent and seamless fashion [7].

Due to their unique electrical and structural properties, carbon nanotubes tend not to bond strongly with their host matrix or with each one another. As a result, the potential increases and improvements in the mechanical properties of a nanotube composite are limited by the degree of interfacial stress transfer that can be achieved. A great deal of research has focused on remedying this problem through chemical functionalization and surface modification of carbon nanotubes [8]. Ion beam irradiation has also been shown to promote crosslinking and improve binding within bundles of nanotubes [9].

CNT dispersion within the matrix is important to achieve efficient and effective load transfer to the nanotubes. This helps to ensure uniform stress distributions and minimizes the effect of stress concentration. The two primary difficulties associated with dispersion are separating individual CNTs from each other and then uniformly mixing them with the polymer matrix. Sonication of CNTs within a solvent is one of the most common methods [4] and addresses both difficulties simultaneously. Shear mixing and magnetic stirring are also commonly used to mix nanotubes within a polymer.

The alignment of CNTs within a matrix is probably the least critical of the four requirements for nanotube composites, as the alignment requirements are often dictated by the intended application. Highly-oriented fibers will provide the greatest increase in strength in the fiber direction, but little to no improvement in the transverse direction. In comparison, randomly-oriented fibers will result in isotropic mechanical properties, but at reduced levels of improvement [4].

3.0 Leading Researchers in Nanotube Fibers and Composites

Listed below and in Table 1 are several prominent researchers or research groups that are actively involved in the development of carbon nanotube-based fibers and composite materials. This list is not comprehensive, but instead attempts to identify

Table 1 - Summary of Notable Researchers Engaged in CNT-Reinforced Polymer R&D

Last	First	Affiliation	Email	Phone	Interests and Accomplishments
United States					
Baughman	Ray	UT Dallas	ray.baughman@utdallas.edu	972-883-6538	Baughman played a role in DARPA's Synthetic Multi-Functional Materials program, with the stated goal of demonstrating "that carbon nanotube composites can be simultaneously used as structural materials and for one or more other key functions. The program will provide the first available technology for spinning continuous fibers consisting entirely of single-wall carbon nanotubes."
Vaia	Richard	AFRL	Richard.Vaia@wpafb.af.mil	937-255-9184	Research Leader for the Polymer Core Technology Area and Lead of the NanoMaterials Strategy Group at AFRL's Materials and Manufacturing Directorate. His group focuses on polymer nanocomposites, photonic technologies and their impact on developing adaptive soft matter.
Kumar	Satish	Georgia Tech	satish.kumar@ptfe.gatech.edu	404-894-7550	Single-Walled Carbon Nanotube-Polymer Composites: films, fibers, and bulk composites
Wang	Ben	Florida State University	indwang1@eng.fsu.edu	850-410-6339	Carbon nanotube mats (buckypaper) for aerospace structures, lightweight armor, and other applications
Odegard	Greg	Michigan Technical University	gmodegar@mtu.edu	906-487-2329	Former post-doc at NASA Langley, where he authored and co-authored many papers on nanotube composites, with an eye for aerospace applications
Non-US					
Coleman	Jonathan	Trinity College Dublin, Ireland	coleman@tcd.ie		Has been involved in various aspects of CNT-composite research over the past several years, recently published a comprehensive review of the field.
Poulin	Phillipe	Université Bordeaux I	poulin@crpp.u-bordeaux.fr		Perhaps best known for creating "macroscopic fibers and ribbons of oriented carbon nanotubes," Poulin has been actively involved in nanotube fiber R&D.

those researchers and research groups within the US that have made consistent and significant contributions to the field. These groups and their lead investigators are:

- Ray Baughman, University of Texas at Dallas – Prof. Baughman's group has been responsible for a number of significant advances in the development of nanotube-based textiles. Their notable achievements include the synthesis of nanotube composite fibers stronger than spider silk, as well as the drawing and weaving of carbon nanotube yarns, sheets, and films. Baughman also participated in the Defense Advanced Research Projects Agency (DARPA) Synthetic Multi-Functional Materials Program.
- Satish Kumar, Georgia Tech – Satish Kumar has been investigating polymers and polymer composites since receiving his Ph.D. in Polymer and Fiber Science in 1979. Over the past several years, Dr. Kumar has focused on nanotube-polymer composites, with research in the processing and properties of SWNT/polymer composite fibers and the dispersion, functionalization, and orientation of nanotubes within a polymer matrix.
- Jonathan Coleman, Trinity College Dublin – Prof. Coleman and his group have been investigating nanotube-reinforced composites since 1999 and have performed both theoretical and experimental investigations into the strengthening mechanisms involved in such materials.
- Ben Wang, Florida State University/FAC2T – Buckypaper, a carbon nanotube mat, was developed at the Florida Advanced Center for Composite Technologies (FAC2T) by Prof. Wang and his group. In addition to the potential improvements in mechanical properties made possible by using such a material in composites, Wang points out that EM/radar shielding/deflection may also be realized.
- Pulickel Ajayan, Rensselaer Polytechnic Institute (RPI) – Prof. Ajayan leads a research team that has been involved in many areas of carbon nanotube research, with an important component of that work involving development of carbon nanotube nanofibers and composites.
- Rod Ruoff, Northwestern University – Prof. Ruoff, a mechanical engineer, leads a diversified group at Northwestern similar to Ajayan's at RPI, with research

investigating the physical and mechanical properties of many different nanostructures, including composites.

- Rodney Andrews, University of Kentucky – Prof. Andrews' research has been strongly focused on the alignment and dispersion of nanotubes within composite materials.
- Tsu-Wei Chou, University of Delaware – Prof. Chou heads the Nanomaterials Research Laboratory at UD, where experimental and theoretical research is performed in the areas of nanocomposite processing and characterization.
- Rice University/Carbon Nanotechnologies, Incorporated (CNI) – Richard Smalley's group at Rice University and its affiliated CNT synthesis company have long been involved in nanotube R&D. The Office of Naval Research (ONR) has funded a program called "Synthesis, Purification, and Assembly of Carbon Single Wall Nanotube Fibers" at Rice, and CNI holds several patents on the synthesis of CNT fibers.

In addition to university R&D efforts, there also are several government agencies actively involved in nanocomposite R&D, both in active research and in program management:

- At NASA Langley Research Center, Gregory M. Odegard, Sarah-Jane V. Frankland, Thomas S. Gates, Kristopher E. Wise, Harik M. Vasyl, John W. Connell, K. Janice Pawlowski, and others all have been actively involved in CNT composite modeling, experimentation, and characterization during the past several years. Odegard has since left NASA and is a professor at Michigan Technological University.
- At the Air Force Research Laboratory (AFRL), the following program managers are currently pursuing or have recently pursued R&D related to nanomaterial composites: David Curliss (Nanostructures for high performance composites), Benji Maruyama (Carbon-based nanotubes & nanofibers), Shawn Phillips (Nanocomposites), and Richard Vaia (Nanostructured materials, nanocomposites, polymeric nanofabrication). AFRL is also involved in a $1.5M joint venture with the National Composite Center (NCC) and the Wright Materials Research Company to produce

and commercialize new fabrication processes for carbon nanofibers, nanotube membranes, and buckypapers.

- There is a Multifunctional Carbon Nanotube Composites research program at Oak Ridge National Laboratory.
- There is currently a Small Business Technology Transfer (STTR) program through ONR entitled, "Functionalized Nanotubes for High Performance Composites" directed by Roger Crane.
- In November 2003, NASA awarded a Phase II Small Business Innovation Research (SBIR) grant to Zyvex Corporation for a program to develop "hierarchical composites comprising continuous carbon nanotube composite fibers in a nanotube-reinforced matrix." The goal of this program was to "to develop ultra-high-strength, low-weight composites for aerospace applications. Specifically, this work will enable the combination of continuous CNT fibers with a CNT-reinforced host polymer."

4.0 Foreign Efforts

The European Commission has published a 2006 document entitled, "Roadmap Report Concerning the Use of Nanomaterials in the Aeronautics Sector." This report identifies several areas of aerospace nanomaterial development, including polymers with carbon nanoparticles/fillers, and the level of technological readiness for each. Also included in the report are the projected cost and market evolution of each material technology, timelines of possible industrial applications, and a list of companies and institutes actively involved in aerospace nanomaterial R&D.

Notable foreign researchers include Jonathan Coleman of Trinity College Dublin and Phillipe Poulin of Université Bordeaux I. Coleman has authored over 40 papers on nanotubes and nanotube composites, while Poulin is actively involved in the R&D of carbon nanotube-based fiber and films for composite materials.

5.0 Publications and Conferences

Cientifica, an international nanotechnology consulting firm, recently published a report entitled, "Nanotubes for the Composites Market." This report addresses application areas of carbon nanotubes for composites, if and when nanotubes will replace carbon fiber, and why carbon nanotubes still remain prohibitively expensive. Also included are both market analysis and prospectus covering the years 2005 through 2010 and an extensive list of nanotube suppliers worldwide.

The NanoSPRINT Encyclopedia of Nanotechnology contains a section on Nanotube Composite Materials that profiles over 300 researchers, 150 patents, and 220 publications. This volume seems like it would be a valuable reference for identifying key researchers and publications within this field. See http://www.nanosprint.com/nanotubes_encyclopedia.html.

In 2003, the 1st annual Nano Materials for Aerospace Symposium was held in Corpus Christi, Texas. This conference series has since been renamed to Nanomaterials for Defense Applications, and the latest meeting was in Virginia Beach, Virginia, in May 2006. The next meeting will occur in May of 2007 in San Diego, CA.

6.0 Non-polymer Nanotube Composites

Although most nanotube composite research has investigated polymer matrix materials, some research has also been performed on non-polymer matrices. In 1998, a group at the University of Tokyo published an article on the processing and properties of nanotube-reinforced aluminum composites [10]. More recently, in 2005, a paper entitled, "Extraordinary Strengthening Effect of Carbon Nanotubes in Metal-Matrix Nanocomposites Processed by Molecular-Level Mixing" was published by Korean researchers [11].

7.0 Summary and Conclusions

There are many economic and technical issues currently preventing carbon nanotube-reinforced polymers from being applied to large-scale composite structures. The high cost and relatively short lengths of CNTs, combined with our inability to effectively disperse and align them within a host matrix, prevent us from developing composite structures that could supplement or replace conventional aerospace materials.

However, there are a number of research efforts underway that address these and other concerns. Investigators worldwide are in pursuit of advanced synthesis processes capable of large-scale production of CNTs of macroscopic lengths, while others are focusing on combining shorter CNTs into longer and more useable composite fibers. Functionalization and irradiation of polymer-embedded nanotubes and nanotube fibers also have been shown to enhance dispersion and strengthen nanotube-matrix interactions, allowing us to improve further the mechanical properties of CNT-reinforced composites. Despite these efforts, much additional R&D is still needed before the full potential of these advanced composites can be realized and implemented.

8.0 References

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