CARBON FIBERS
AND THEIR COMPOSITES

An American Carbon Society Workshop

SHORT ABSTRACTS

April 16-17, 2015

Double Tree Hotel, Oak Ridge, TN

The American Carbon Society

GRAFTech International | Redefining limits

Invited Lecture 1 Thursday @ 8:45 AM

Carbon Fiber Overview with an Emphasis on Spinning PAN Precursor (White Fiber)

Matthew C. Weisenberger, E. Ashley Morris, G. Wilson Rice, T. Rantell

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2540 Research Park Dr., Lexington, KY 40511 (US)

Carbon fiber and their composites have attracted a new level of broad interest with their increasing incorporation into commercial aerospace, and particularly automotive structures, for lightweighting. This talk will review a bit of the history of carbon fiber, and give a general overview of carbon fiber processing for rayon, pitch and PAN-based carbon fiber. Second, with the vast majority of carbon fiber derived from PAN, a more in-depth look at PAN precursor (or white fiber spinning) will be discussed. Here, topics will range from polymer solution (or dope) formulation & preparation to solution spinning processing & fiber morphology development. Finally, work with high molecular weight PAN, and with co-spun PAN precursor (dispersed carbon nanotubes, and co-solubilized lignin) will be discussed.

Invited Lecture 2 Thursday @ 9:30 AM

Alternative Precursor Chemistries and Conversion Technologies for Carbon Fiber Manufacturing

Amit K Naskar

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6053

Carbon fibers are low-density, high performance materials used in a variety of structural composite applications. Historically, carbon fiber usage was limited to high end specialty applications. A lower end, high volume utilization, such as widespread use in passenger vehicles, will require significant cost reduction and new technology development. This presentation will give an overview of research approaches that are being considered globally.

Identifying suitable lower-cost precursors is a major objective to enable the widespread commercialization of carbon fibers. Inexpensive precursors that were considered include polyolefins, textile grade PAN, lignin, and melt-processible PAN. This presentation will focus on melt-processible precursors. Melt-processibility, however, precludes direct thermal stabilization of these polymeric fibers. To enhance the production rate, radiation assisted crosslinking and chemical functionalization routes have been adopted. A generalized structure-property relationship of carbonized fibers will be presented.

Invited Lecture 3 Friday @ 8:30 AM

Designing Research Systems for Scale Up

Renee Bagwell

Harper International, Buffalo, NY

Thoughtful decisions are required in the configuration of a research scale carbon fiber process system that will ensure a correlation of the results to successful commercial scale production. Many research systems solely consider research program goals, however this objective must also be coupled with the requirement to output relevant data to make a successful stepwise progression to a next level of production capacity while minimizing the number of future process and design tweaks. The presentation will discuss several technical areas relevant for scale-up that are often overlooked including air flow regime, catenary, application of and assessment of PAN finishes, and analysis of the off-gas composition.

Invited Lecture 4 Friday @ 10:55 AM

Advanced and Multifunctional Composite Structures: Challenges and Opportunities

Jeffery W. Baur

Material and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, OH

Advanced and multifunctional composites offer tremendous potential for light-weight aerospace structures and the integration of properties or device-like functions not typically associated with traditional polymer composites. This presentation will review technical efforts by the Organic Matrix Composites Materials and Processing Research Team within the Air Force's Materials and Manufacturing Directorate. It will include integrated computational methods for prediction of distortion and strength from processing residual stress, additive processing of advanced polymers and their composites, and enhanced multiphysics properties from nanotailored composites. The multiscale coupling of thermal, electrical, electromagnetic and/or mechanical properties for these multiphase structures is a key challenge to create novel multifunctional composites of interest to the Air Force. Specific examples include carbon nanotube composites, adaptive RF structures based on microvascular composites of liquid metal, composites with integrated sensing, and composites with a tailored response to rapid heating.

Invited Lecture 5 Friday @ 1:00 PM

Carbon fiber Composites in Aeronautic and Astronautic Applications

Wesley Hoffman

Air Force research Laboratory, Edwards, CA

Keynote Lecture 1 Thursday @ 10:35 AM

Surface Treatment of Carbon Fibers by the UVO Process: Effect on Fiber Surface Properties, Interfacial Adhesion, and Composite Mechanical Properties

Lawrence Drzal and Michael Rich

Department of Chemical Engineering and Materials Science, Composite Materials and Structures Center, Michigan State University

A robust carbon fiber surface treatment system has been developed using high intensity ultraviolet light in an ambient atmosphere augmented with small amounts of ozone, known as UVO. The UVO system has the desirable features of operating at room temperature and pressures, requiring short treatment times and capable of operating at speeds consistent with carbon fiber production rates. This method has been successfully applied to low and intermediate modulus PAN fibers and ultrahigh modulus Pitch fibers. Surface chemical and topographical changes on PAN and Pitch carbon fibers have been quantified as a function of UVO treatment time with X-ray photoelectron spectroscopy, scanning probe microscopy, and Raman spectroscopy. Measurement of the fiber tensile strength confirmed that tensile strength was not adversely affected and in some cases, the fiber tensile strength was improved following this UVO treatment. Interfacial adhesion, as measured by the single fiber fragmentation test, found that the UVO surface treatment was as or more effective as contemporary electrochemical-anodic treatments of commercially produced carbon fibers. Additionally unidirectional composites made of UVO surface treated fibers had mechanical properties of equal or greater value compared to commercially treated fibers. We report the effects of UVO treatment starting with fiber surface chemistry, its effects on fiber topography and structure, followed by interfacial adhesion, and finally, its effect on composite properties to gain a comprehensive understanding of surface treatments using the UVO process.

Keynote Lecture 2 Thursday @ 7:00 PM

Overview of Institute for Advanced Composites Manufacturing Innovation

Cliff Eberle

Oak Ridge National Laboratory, Oak Ridge, TN

The Institute for Advanced Composites Manufacturing Innovation (IACMI) is the newest Institute within the National Network for Manufacturing Innovation. Funded by the U.S. Department of Energy, IACMI was announced by President Obama in January. IACMI's primary focus is the deployment of emerging structural polymer composites technologies in high volume energy industries, with a major emphasis on carbon fiber reinforcement. This talk will describe the background, mission, objectives, and design of the Institute as well as how to become engaged in its execution.

Oral Presentation 1 Thursday @ 11:05 AM

The Role of Microstructure and Voids in Carbon fiber Mechanical Properties

Soydan Ozcan

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN

Although carbon fibers are produced using similar process steps, formation of thermoplastic fibers, stabilization, and carbonization, their final structures that govern the end properties may be significantly different. The final structure strongly depends on the starting polymer precursor and carbon fiber process parameters. Polyacrylonitrile (PAN) and Pitch are the most predominant polymer precursors used in the production of carbon fibers. PAN-based carbon fibers consist of nanocrystalline graphitic domains typically 1.5 – 5 nm in size surrounded by amorphous carbon; instead pitch-based carbon fibers are 10 to 50 nm crystallites where the graphitic (002) planes (d = ~0.334 nm) are mostly aligned parallel to the fiber axis. These fibers typically show a difference in nanostructure between the skin and core of the fiber. It has been seen that the skin-core structure plays significant role on mechanical properties. Design of more homogenous carbon fiber microstructure by controlling the starting polymer and process parameters resulted in different set of tensile strength and elastic modulus properties, which have not been observed in skin-core structure of PAN carbon fibers. The microstructural defect distribution (0.1nm to 200nm) measured by small angle X-Ray scattering also showed direct relationships with tensile strength of carbon fibers. Therefore, research into understanding the formation of carbon structures from various polymer precursors offers opportunity for designing microstructures leading to improved properties and reduced cost carbon fiber.

Oral Presentation 2 Thursday @11:25 AM

Overview of Carbon Fiber Technology Facility (CFTF) and Manufacturing Demonstration Facility (MDF)

Ron Ott

Oak Ridge National Laboratory, Oak Ridge, TN

Oral Presentation 3 Friday @ 9:15 AM

Treatment of Lignin Precursors to Improve their Suitability for Carbon Fibers: A Literature Review

Ryan Paul, [1]-Xuliang Dai,[1] Andrew Hausner,[1]. Amit Naskar,[2] Nidia Gallego[2]

[1] GrafTech International Holdings Inc.
[2] Oak Ridge National Laboratory

Lignin has been investigated as a carbon fiber precursor since the 1960s. Although there have been a number of reports of successful lignin-based carbon fiber production at the lab scale, lignin-based carbon fibers are not currently commercially available. This review will highlight some of the known challenges, and also the reported methods for purifying and modifying lignin to improve it as a precursor. Lignin can come from different sources (e.g. hardwood, softwood, grasses) and extraction methods (e.g. organosolv, kraft), meaning that lignin can be found with a diversity of purity and structure. The implication of these conditions on lignin as carbon fiber precursor is not comprehensively known, especially as the lignin landscape is evolving. The work presented in this review will help guide the direction of a project between GrafTech and ORNL to develop lignin carbon fiber technology, as part of a cooperative agreement with the DOE Advanced Manufacturing Office.

Oral Presentation 4 Friday @ 9:35 AM

Effect of Processing Conditions on the Structure and Properties of Cellulosic Precursor-Based Carbon Fibers

Gajanan Bhat[1,] K. Akato[1], N. Hiremath[1], Wesley Hoffman[2] and Farhad Mohammadi[3]

[1]The University of Tennessee, Knoxville, TN
[2]AFRL, Edwards Air Force Base, CA
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Carbon fibers are predominantly produced from polyacrylonitrile (PAN) or pitch precursors. Rayon was the first precursor investigated for high modulus carbon fibers, and rayon-based carbon fibers have some unique properties. Only a handful of companies produce rayon-based carbon fibers in the world, and no rayon is commercially produced in the US. Experimental studies are being conducted to optimize the processing conditions for conversion of a new domestically produced rayon precursor into carbon fibers with useful performance properties. Results from this ongoing investigation will be discussed. Also, earlier work on other precursors such as polyethylene and polyimide as carbon fiber precursors will be presented.

Oral Presentation 5 Friday @ 11:40 AM

Computational Modeling and Experimental Characterization of Macroscale Piezoresistivity in Aligned Carbon Nanotube and Fuzzy Fiber Nanocomposites

Adarsh K. Chaurasia, Xiang Ren, Yumeng Li, Engin C. Sengezer, Josh Burton and Gary. D. Seidel

Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061-0203, USA

In this study, a multiscale computational micromechanics based approach is developed to study the effect of applied strains on the effective macroscale piezoresistivity of carbon nanotube (CNT)-polymer and fuzzy fiber-polymer nanocomposites. The computational models developed in this study allow for electron hopping and inherent CNT piezoresistivity at the nanoscale in addition to interfacial damage at the CNT-polymer interface. The CNT-polymer nanocomposite is studied at the nanoscale allowing for interfacial damage at the CNT-polymer interface using electromechanical cohesive zones. For fuzzy fiber-polymer nanocomposites, a 3-scale computational model is developed allowing for concurrent coupling of the microscale and nanoscale. The electromechanical boundary value problem is solved using finite elements at each of the scales and the effective electrostatic properties are obtained by using electrostatic energy

equivalence. The effective electrostatic properties are used to evaluate the relative change in effective resistivity and the macroscale effective gauge factors for the nanocomposites. In addition, the piezoresistive response of aligned CNT-polymer and fuzzy fiber-polymer nanocomposites is investigated experimentally. The results obtained from the computational models are compared to the experimentally observed change in resistance with applied strains and associated gauge factors.

Oral Presentation 6 Friday @ 1:45 AM

An Overview of Modern Carbon Fiber Characterization Techniques

<u>Carlos A. Leon y Leon</u>
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Throughout their manufacturing processes, carbon fibers and their precursor materials undergo a wide variety of physical and chemical changes that are known to impact their end use. This overview focuses on many established and some emerging techniques for the physical and chemical characterization of carbon fibers. Methods already available for the evaluation of carbon surface heterogeneity, and the use of modern catalysis research techniques, are emphasized. In particular, the impact of surface heterogeneity on pore size distribution estimates is considered in view of new IUPAC-led discussions highlighting the use of argon at 87K (vs. the standard N_2 at 77K) for pore size evaluations, along with the virtues and limitations of density functional theories based on non-local (NLDFT) and quenched solid (QSDFT) modeling approaches. These considerations are complemented by a brief overview of the use of chemisorption and temperature programming techniques to characterize carbon fiber chemical heterogeneity.

Oral Presentation 7 Friday @ 2:05 PM

Elucidation of Stabilization Pathways of Polyacrylonitrile by ^{13}C-^{13}C and ^{1}11-^{13}C Two-Dimensional Solid-State NMR Spectroscopy

Xiaoran Liu and <u>Toshikazu Miyoshi</u>

Department of'Polymer Science, The University of Akron, Akron. OH. 44325-3909

Polyacrylonitrile (PAN) is used as major precursor to produce carbon fiber. From PAN to carbon fibers, several heat treatment processes including stabilization, carbonization and graphitization are involved.[1] During stabilization, linear polymer structure is believed to convert to ladder structure, which makes it a b l e to survive during further heat treatment at even higher temperature. For the past decades, several experimental approaches including FT-IR., DTA, TGA, etc. have been applied to characterize chemical structures of stabilized PAN.[1,2] However, due to experimental limitations, stabilization process was still not well understood at the molecular level. In this talk, we report a novel strategy to characterize PAN stabilized at various temperatures *(Ts)* by two dimensional ^{13}C-^{13}C and ^{1}H-^{13}C correlation NMR techniques combined with selectively ^{13}C isotopic labeling. Through-bond correlations of stabilized PAN was successfully characterized to identify different chemical structures

depending on *Ts*. Improved spectral resolutions of 1- and 2D- NMR data for the first time will reveal different stabilization pathways for PAN stabilized under air and nitrogen, respectively.

1. Rahaman. A. F.; Ismail A. F.: Mustafa, A. *Polym. Degrad. Stab.* **2007**. *92*, 1421-1432.
2. Nguyen-Thai, N. U.; Hong. S. C. *Macromolecules* **2013**, *46*, 5882-5889.

Oral Presentation 8 Friday @ 2:25 PM

Three-Dimensional Multi-Reinforced Ceramic Composites with Enhanced Mechanical/Thermal/Electrical Property

Cheryl Xu

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Traditional fiber reinforced ceramic matrix composites have demonstrated excellent in-plane mechanical properties however bearing considerate weak inter-laminar fracture toughness which significantly limit their broader application when out-of-plane properties are needed. In this paper, we proposed a new manufacturing method to fabricate one kind of three-dimensional (3D) multi-reinforced ceramic matrix composites where carbon nanotubes are embedded within the orthogonal direction's inter-bundle of each carbon fiber sheet and also are infiltrated in between each two adjacent carbon fiber sheets. This manufacturing method is low cost, does not involve any chemical reaction, and materializes a true three-dimensional (3D) composite structure without necessity of altering anything to carbon fiber sheet. The fabricated ceramic matrix composites demonstrate enhanced mechanical property, thermal and electrical conductivity: the strength increases 26%, and electrical conductivity increases 2000% along the through thickness direction. Furthermore, the matrix exhibits an anomalously high resistance to oxidation and hot-corrosion.

Oral Presentation 9 Friday @ 2:45 PM

Fluorescent Carbon Dots and Nanodiamonds as Optical Additives in Polymeric Fibers for Biological Imaging Applications

Li Cao, Yanwen Hou, and Khalid Lafdi

Department of Chemical and Materials Engineering, University of Dayton, Dayton, Ohio 45469

Fluorescence labeling is considered to be an indispensible technique for biomedical applications. Cadmium-based semiconductor quantum dots (QDs) have been widely investigated for biomedical optical labeling research. However the heavy metal elements in these QDs are one of the drawbacks for clinical application due to the potential health concern. Carbon dots and nanodiamonds are two kinds of carbon based nanoparticles that have excellent optical properties. Their superb stability in aqueous solution, excellent fluorescent behavior and biocompatibility have recently drawn tremendous attention for biological optical imaging research. In this presentation, a comparison of fluorescent carbon dots and nanodiamonds are briefly reviewed, as well as their biological imaging studies. In particular, our recent research on fluorescent nanodiamonds as optical additives in polycaprolactone fibrous scaffolds has demonstrated their possibilities to serve as a promising optical probe for tissue engineering applications

Poster 1 Thursday @ 5:30 PM

The Effects of Coagulation Bath Concentration on PAN Precursor Fiber Morphology

Wilson Rice, E. Ashley Morris, Matthew Weisenberger

Center for Applied Energy Research, University of Kentucky, Lexington, KY, USA

For the purpose of improving the quality of PAN-based precursor, it is necessary to better understand the process of coagulation. It has been hypothesized that the initial step of coagulation into nascent fibers greatly impacts the final structure of the fiber. Here, the effects of bath concentration on precursor fiber structure were examined. By cross sectional analysis of SEM micrographs of the freeze-dried fiber immediately after coagulation. These micrographs present information on fiber shape and surface morphology. Further tests to characterize the fiber's density and swelling degree, a measure of porosity, were also conducted in order to provide a better understanding of the effects of coagulation bath concentration on fiber morphology.

Poster 2 Thursday @ 5:30 PM

The Effects of Lignin Addition on the Properties of PAN Based Carbon Fiber

E. Ashley Morris, Matthew C. Weisenberger, and Sarah E. Edrington

University of Kentucky, Center for Applied Energy Research, Lexington, KY 40511, USA

Carbon fiber is a material known for possessing a high strength to weight ratio but at a high cost to manufacture. By reducing the cost of the carbon fiber precursor, manufacturing costs can be reduced significantly and the integration of carbon fiber composite materials into industry can be facilitated. In this study, lignin, an inexpensive renewable resource, was used as a partial replacement for polyacrylonitrile (PAN) in spinning precursor carbon fibers. Two precursor fiber samples were spun for this experiment, a baseline composed of only PAN and a lignin/PAN hybrid. The resulting batch-oxidized and carbonized fibers were tensile tested and the diameters as well as surface and cross sectional morphology were examined under SEM. A comparison of the PAN and lignin/PAN carbon fiber tensile properties and surface and cross sectional morphology will be discussed.

Poster 3 Thursday @ 5:30 PM

Development of Carbon Materials from Low Grade Petroleum Resources

Chul Wee Lee, Ji Sun Im, Young-Pyo Jeon

Center for C-Industry Incubation, Korea Research Institute of Chemical Technology (KRICT), University of Science and Technology (UST), Daejeon 305-333, Republic of Korea

Carbon technology is a core technology applied to basic industries ranging from sporting goods, electronics, automobiles, and steel mills to aerospace industry. Carbon materials ranging from carbon fiber, artificial graphite, carbon black, and etc., can be derived from low grade petroleum resources; pyrolysis fuel oil (PFO), fluid catalytic cracking decant-oil (FCC-DO), and vacuum residue (VR). With the aid of inherent low impurity, petroleum derived carbon materials can have relatively higher value than those from coal resources. Depending upon the technology to upgrade low grade petroleum residues, applications can be extended; a) intensified road construction based on cost-competitive low performance carbon fiber, b) artificial graphite derived from low grade isotropic or needle cokes, and c) air and water purification by utilizing activated carbon fibers. Overall, low grade petroleum residues can be cost-competitive if processed into carbon materials.

Poster 4 Thursday @ 5:30 PM

Nanofiber-by-Gas Jet Carbon Nanofiber Derivation Method and Numerical Simulation

Darrell H. Reneker, Maxim Mikhaylenko, Alex Povitsky,

The University of Akron, Akron, OH

A novel Nanofiber-by-Gas Jet (NGJ) method of carbon sub-micron scale fiber derivation from mesophase pitch has been developed by College of Polymer Science and Polymer Engineering of The University of Akron. Similar to meltblowing, this method features non-spinning fiber production, where molten resin is exposed to a hot air jet at a close temperature. A rectangular slit dye nozzle showed satisfactory productivity for polypropylene, Mitsubishi ARA24 and other low melting temperature (230 – 290℃) resins. However, the fiber output dropped for high temperature (350 - 370℃) melting mesophase pitches exhibiting rheological properties at lower temperatures due to their liquid crystal character. For the latter materials, a specially designed concentric nozzle and its' further modifications were used to achieve higher production rate

The multiscale numerical simulation approach was used to model multiphase flow of a hot air stream over a molten viscoelastic pitch surface, to predict deformation profiles of its' characteristic rippling due to the drag induced by air flow at the phase of nanofibers embryos formation and growth.

Finite Volume Method was used to determine initial flow field inside the nozzle and then one of the Boundary Element Methods – Boundary Singularity Method – was adopted for solving quasi-steady problems of viscoelastic pitch surface deformation due to impinging low-Reynolds number flows at microscopic pitch rippled surface inside NGJ nozzle.

Poster 5 Thursday @ 5:30 PM

Tensile Properties and Supranano Structure of Carbon Nanotube Yarns

Nitilaksha Hiremath [a], Gajanan Bhat[a], Amit Naskar[b], Jimmy Mays[a, b]

[a] The University of Tennessee at Knoxville TN
[b] Oak Ridge National Laboratory, Oak Ridge TN

A systematic characterization of carbon nanotubes (CNT) based yarns has been conducted to elucidate their structural integrity and mechanical properties. Electron microscopy studies with focused ion beam (FIB) were carried out to investigate the structure of CNT yarns, especially the cross section. TEM was also carried out to examine the nanotubes and their arrangements within the yarns. Tensile properties of the yarns, as well as to the failure mechanism were also thoroughly investigated. Whereas these yarns are relatively strong, the evidence of poor packing and orientation of CNT within the yarns suggests that by appropriate improvement to the structure, tensile properties can be further improved.

Poster 6 Thursday @ 5:30 PM

Tensile and Interfacial Characterization of Lignin Carbon Fibers

Nathan Meek,[1] Dayakar Penumadu,[1] Omid Hosseinaei,[2] David Harper[2]

[1] Civil and Environmental Engineering, University of Tennessee, Knoxville, TN
[2] Center for Renewable Carbon, Material Science & Technology Unit, University of Tennessee, Knoxville, TN

In this study, we are characterizing produced lignin carbon fibers from the Center for Renewable Carbon (CRC). The lignin carbon fibers are manufactured from softwood and hardwood feedstocks. Mechanical and interfacial properties are analyzed to identify various feedstocks and processing techniques that produce the highest quality carbon fiber for composites. Single fiber mechanical characterization is performed on a unique MTS Nano-Universal Testing Machine (UTM) that is specifically designed to test single fibers due to it nano-scale load and displacement resolution. Single fibers are tested in lieu of tow testing to isolate the fiber mechanical properties and eliminate intra-tow effects. Interfacial properties are determined using single fiber fragmentation testing (SFFT). Critical fiber lengths, delamination zones, and carbon fiber surface features are studied through SFFT. Once characterization is complete, lignin carbon fibers that performed the best are targeted for scale up and additional studies. Carbon fiber samples are also analyzed using optical microscopy and scanning electron microscopy.

Poster 7 Thursday @ 5:30 PM

Melt Spun and Electrospun Carbon Fibers from Different Lignin Precursors

Omid Hosseinaei, David Harper, Joseph Bozell, Timothy Rials

Center for Renewable Carbon, University of Tennessee, 2506 Jacob Dr., Knoxville, TN 37996.

Lignin is the second most abundant natural polymer on the planet and considered as a renewable and sustainable source for making value added products. One of the potential products from lignin is carbon fiber. Lignin has potential as a carbon fiber precursor due to its low price, high carbon content, and

renewability. Melt spinning and electrospinning are two common methods for making fibers with different characteristic and applications. While melt spun fibers manly use in structural and composite applications, electrospun fibers have potential applications in energy storage and filtration. Lignin has been shown potential for usage in both process. Different lignin precursors, softwood kraft, organosolv hardwood and organsolv lignin from grasses (switchgrass), were used for making meltspun and electrospun fibers. Organoslv hardwood had the best fusibility and spinnabiltyin for melt spinning process. Organosolv switchgrass was spinnable, but continuous spinning was not possible and possessed poor properties. However, spinning significantly improved with sequential solvent fractionation of lignin. Softwood kraft also required sequential solvent fractionation to be fusible and spinnable. Organosolv hardwood can directly dissolve in electrospinning solution and form electrospun mats. Organoslv switchgrass and softwood kraft need processing to be soluble in an electrospinning solvent.

Poster 8 Thursday @ 5:30 PM

Influence of Organosolv Fractionation Time on Thermal and Chemical Properties of Lignins

Jingming Tao,Omid Hosseinaei,Pyoungchung Kim, David Harpcr, Joseph Bozell,Timothy Rials and Nicole Labbé

University of Tennessee Center for Renewable Carbon, 2506 Jacob Drive, Knoxville, TN, 37996, USA

Lignin holds promise as precursor for producing low-cost carbon fibers. Compared to other methods, organosolv fractionation produces a lignin with high purity. Nevertheless, organosolv lignins need further refinement to be a reliable fiber feedstock. We hypothesize that purer and more suitable lignin can be obtained under an optimal time as fractionation progresses. In this study we test this hypothesis by fractionating yellow poplar *(Uriodemlron rulipera)* using a mixture of methyl isobutyl ketone, ethanol, and H_20 with sulfuric acid as catalyst at 140°C over a two-hour period. Black liquor was collected every 15 min during the fractionation to generate a series of lignins. With the increase in time, lignin purity improved from 90.3% to 94.6%, the glass transition temperature increased from 117.3 to 137.1°C. Overall, this study demonstrates that thermal and chemical properties of lignin can be controlled to some extent by the fractionation time to produce lignins with desired properties.

Poster 9 Thursday @ 5:30 PM

Understanding of Polyacrylonitrile Stabilization by Solid-State NMR

Xiaoran Liu and Toshikazu Miyoshi

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Polyacrylonitrile (PAN) is used as major precursor to produce carbon fiber. From PAN to carbon fibers, several heat treatment processes including stabilization, carbonization and graphitization are involved.[1] During stabilization, linear polymer structure is believed to convert to ladder structure, which makes it able to survive during further heat treatment at even higher temperature. For the past decades, several experimental approaches including FT-IR, DTA, TGA, etc., have been applied to characterize chemical structures of stabilized PAN.[1, 2] However, due to experimental limitations, stabilization process was still not well understood at the molecular level.

In this poster, we report a novel strategy to characterize PAN stabilized at various temperatures *(Ts)* by two dimensional ^{13}C-^{13}C and ^{1}H-^{13}C correlation NMR techniques combined with selectively ^{13}C isotopic

labeling. Through-bond correlations of stabilized PAN was successfully characterized to identify different chemical structures depending on *Ts*. Improved spectral resolutions of I and 2D NMR data for the first time will reveal different stabilization pathways for PAN stabilized under air and nitrogen, respectively.

I. Rahaman, A. F.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stab.* 2007, *92,* 1421-1432.
2. Fu, Z.; Gui, Y.; Cao, C.; Liu, B.; Zhou, C.; Zhang, H. *J. Mater. Sci.* 2014, *49(7),* 2864-2874.

Poster 10 Thursday @ 5:30 PM

High Yield Process for Lignin-Based Activated Carbon Fibers

Nidia C Gallego, Yanfeng Yue, Cristian I Contescu

Oak Ridge National Laboratory, Oak Ridge, TN

Lignin is a component of wood, and second (after cellulose) most widely encountered natural polymer. It is available in large amounts as a byproduct of pulp and paper industries or from biorefineries. Attempts of producing carbon fibers from lignin have been limited, partly because the carbon fibers obtained did not have the mechanical properties comparable to those obtained from PAN or pitch. However, lignin-derived carbon fibers can be physically activated to produce activated carbon fibers with remarkable properties. Physical activation is accompanied by high carbon losses during controlled carbon oxidation, which cause higher production costs. An alternate method to induce porosity is chemical activation, which is accompanied by lower weight losses and requires lower temperatures and shorter processing times than physical activation. We will present recent results obtained at ORNL in direct chemical activation of lignin-derived carbon fibers treated with phosphoric acid. The microstructural properties of lignin-derived activated carbon fibers show that chemical activation with phosphoric acid can be successfully used to produce activated carbon fibers with high surface area and porosity

Poster 11 Thursday @ 5:30 PM

Effect of CNT Additives on Electrospun Fibers Properties

Chang Liu, Jean-Baptiste Dumuids, Nuha Al Habis, Yuhan Liao, Li Cao, Khalid Lafdi

Department of Chemical & Material Engineering, University of Dayton

The relationship between processing and physical properties of two basic systems such as polyacrylonitrile (PAN)/carbon nanotube (CNT) and polycarbolactone PCL/CNT nanocomposites were investigated. PAN based materials will be used a conductive sensor for a structural health monitoring and the second system will be used to fabricate a biomimetic nanofibrous extracellular matrix for tissue engineering

In this study, electrospinning and spin coating processes are used to manufacture two kinds of nanofibers based membranes. Physical properties of these materials were measured as function of processing method and CNT concentration. In the PAN based system the maximum value for modulus and yield stress are found in electrospinning membranes with a 5% concentration of CNT, however, for spin coating film, moduli kept increasing with the addition of CNT. However the yield stresses (maximum stress) kept constant. The addition of CNT for electrospinning membrane led to a higher value of elongation.

Conversely, in both PAN and PCL based systems, a maximum increase of 400% was recorded. However, in the PAN system the increase was occurred at 5% of CNT concentration and in the PCL case the increase occurred at 1% CNT concentration. This result let to believe that there is an intimate interaction between CNT and host matrix.

Poster 12 Friday @ 10:00 AM

3D-Printed Carbon Fiber Reinforced Polymer Composites

Halil L. Tekinalp[a], Vlastimil Kunc[b], Gregorio M. Velez-Garcia[a], Chad E. Duty[b], Lonnie J. Love[b], Amit K. Naskar[a], Craig A. Blue[b], Soydan Ozcan[a]*

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[b]Manufacturing Demonstration Facility, NTRC II, Oak Ridge National Laboratory, Knoxville, TN 37932

Additive manufacturing technique has been mainly used for rapid prototyping; however, recently there has been a growing interest in direct manufacture of actual parts using this technique. In order to render this technology suitable for the manufacture of actual load-bearing components, improvements in both the printing technique and the mechanical properties of the feedstock materials are required. In this study, short fiber (0.2 mm to 0.4 mm) reinforced acrylonitrile-butadiene-styrene composites as a feedstock for 3D-printing were investigated in terms of processibility, microstructure and mechanical performance in comparison to traditional compression-molded counterparts. 3D-printing yielded samples with dramatically high fiber orientation (up to 91.5 % in the printing direction), and significantly improved tensile strength and modulus (i.e., ~115% and ~700% increase, respectively). The differences in the mechanical properties of the 3D-printed and the compression-molded composites were explained based on their microstructure (i.e., fiber orientation, dispersion and void formation).

Poster 13 Friday @ 10:00 AM’

Negative Permittivity Discovered in Continuous Carbon Fiber Epoxy-Matrix Structural Composites

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Composite Materials Research Laboratory, University at Buffalo, State University of New York, Buffalo, NY 14260-4400, USA.

Negative permittivity (real part) has been discovered in continuous carbon fiber epoxy-matrix composites in the through-thickness direction. The permittivity is down to -550 (up to 1 MHz) when a 35-μm thick cellulose fiber paper interlayer is present at every interlaminar interface. The greater is the moisture content in the paper prior to incorporation, the more negative is the permittivity. The moisture is introduced by wetting the paper with tap water, though the moisture evaporates during the subsequent curing at 177°C. The use of deionized water gives positive permittivity. When the 35-μm thick paper has been dried at 110°C prior to incorporation, the permittivity is positive. When the paper is 60-μm thick, the permittivity is positive. Thus, the negative permittivity requires close proximity between adjacent lamellae, in addition to the ions in the tap water. It is attributed to the interaction of the fiber surface functional groups with these residual ions.

Poster 14 Friday @ 10:00 AM

Lignin-Based Novel Carbon Foams

Rohit Uppal and David Harper

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Carbon foams (CFs) are low-density porous next-generation materials. Mesophase pitch based carbon foams are proving to be popular. CFs using mesophase pitch (MPP) costs $9/lb, and thus precludes their use in commodity applications. Lignin has great potential to be a precursor for the manufacture of commodity CFs as it has low cost (<$0.50/lb). We developed a rapid process for making lignin-based inexpensive rigid CFs, which can be used for non-load bearing applications such as thermal and acoustic insulation, catalyst support, porous electrodes, filtration, batteries, etc. Chemically fractionated Indulin AT Kraft lignin blended with azodicarbonamide and without were formed into foams under high temperature and pressure. Both types of foams were pyrolyzed into CFs at 1000 °C in nitrogen environment. The CFs from pure lignin had a density in the range of 0.46 to 0.48 g/cc, whereas CFs from blended lignin had a density in the range of 0.25 to 0.31 g/cc. The compressive moduli of CFs were significantly higher than that of lignin foams.

Poster 15 Friday @ 10:00 AM

Thermal Management in Carbon Fiber Composites

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Carbon fiber/epoxy composites are burdened by poor transverse thermal transport, which continues to be a significant problem for many electronics applications. In order for the electronics to remain functional, the heat must be dissipated from the system. Our research has attempted to solve this problem through the integration of heat spreaders into carbon fiber composites. The optimum in-plane thermal diffusivity can be determined by testing composite layup orientation, spreader properties, and spreader location, through the use of a laser flash apparatus (Netzsch LFA 427). The results show that composite layup orientation and heat spreader quality contribute significantly to in-plane diffusivity.

Poster 16 Friday @ 10:00 AM

Carbonization of Microfibril Cellulose Aerogel: Surface, Structural and Oil Absorption Properties

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Carbon aerogel derived from cellulose, a widely abundant biomass, was synthesized with high porosity, extremely low density, hydrophobic and oleophilic properties. The oil sorption capacity of carbon aerogel is up to 64 times of its own weight. Research on surface and structural properties indicate that (1) the porosity of microfibril cellulose (MFC) aerogel is 97.8% and up to 99% for carbon aerogel; (2) A combination of micropores and open surface is formed in carbon aerogel. Macroporous 3D network structure of carbon aerogel make oil easy to permeate into the structure and is beneficial for oil absorption; (3) Total surface area of MFC aerogel heat treated at 700°C is 521 m²/g, which is much higher than that of samples heat treated at 950°C (145 m²/g). Pore size distribution of carbon aerogel heat treated at two different temperatures shows some discrepancy. Graphite structure was observed for MFC aerogel carbonized at 950°C by HR-TEM technique. Thermogravimetric analysis (TGA) was conducted and confirmed an optimal carbon yield of 13.9% when heating rate was 2°C/min during the rapid mass loss processes. A hydrophilic character was observed from MFC carbon aerogel. The findings of this research offer a promising product for fast and selective removal of spilled oil and purification of industrial oily wastewater with excellent recyclability.

Poster 17 Friday @ 10:00 AM'

Carbon Fiber Composites with Lignin-Extended Thermoplastics

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Lignin, a biomass-derived macromolecular material, was used as an extender of Acrylonitrile-Butadiene-Styrene (ABS), a common industrial thermoplastic resin. Solvent fractionated Kraft lignin was incorporated in ABS matrix by melt-blending technique. The effects of lignin incorporation on thermal stability, morphological, mechanical and rheological properties were investigated. The lignin-extended partially renewable ABS resins were subsequently reinforced with chopped carbon fibers for composites fabrication and testing. The mechanical performances of the composites are equivalent to those of reinforced ABS materials reportedly used in automotive applications.

Poster 18 Friday @ 10:00 AM

In-situ Raman and Piezoresistive Characterization of Aligned Carbon Nanotube-Polymer Nanocomposites

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The potential use of carbon nanotube (CNT)-polymer nanocompositcs currently being considered for use as structural health monitoring (SHM) sensors is an area of rapidly growing interest. Current observations provide real-time structural health monitoring capabilities and self-diagnostic functionalities of CNTs in SHM sensors with doping the polymer matrix of structural composites with CNTs either close to percolation concentration or just above percolation concentration to provide strain sensing capabilities to structural members. Of particular interest to the present work is investigating the local and global strain sensing capabilities of aligned CNT·polymer nanocomposites at a concentration below percolation threshold in nanocomposite SHM sensors via in·situ Raman spectroscopy and piczoresistivity measurements. Dielcctrophoresis under the application of AC electric fields is one of the primary fabrication techniques for obtaining aligned CNT-polymer nanocomposites, and is used to generate long range structure/architecture control at the structural level. Excellent piezoresistive capabilities having the potential to provide real-time structural SHM and self-diagnostic functionalities are obtained at a concentration below percolation threshold for aligned specimens.

Poster 19 Friday @ 10:00 AM

Progress on the Development of Low Cost Environmental Barrier Coatings

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Carbon reactions with metals limits the application uses for carbon-carbon composites in powdered metal sintering and heat treating environments. Early stage investigations into aqueous, paint based and plasma-spray coatings used as barriers to reduce reaction with common metals used in powder metallurgy are presented. Applicability of the coatings was investigated through a series of reaction tests in flowing N_2-5%H_2 at 1175 to 1315C. Four coatings displayed encouraging performance and warrant further development in terms of their application to C-C materials, cost, and life in sintering and heat treating environments.

Poster 20 Friday @ 10:00 AM

Engineered Carbon-based Materials for Hard and Soft Tissue Repair and Reconstruction

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Carbon-based materials are considered to be promising as implants because of their unique mechanical and biocompatibility properties. This article investigates the use of carbon-based materials as a functional interface for tissue scaffolds and medical implants. Three basic parameters were explored: graphene orientation, crystallinity, and surface interaction. These parameters were measured using optical microscopy, x-ray diffraction, and atomic force microscopy. To explore the effect of the orientation, samples were made with and without a preferred carbon orientation. Conversely, the crystallinity was studied using graphitic and carbonaceous matrices. Finally, the surface interaction study was carried out using oxygen surface functionalized and non-functionalized carbon fibers. Fluorescent, confocal, and environmental scanning microscopy were used to visualize cell response. The cell attachment, proliferation, and elongation were prevalent on the unidirectional carbon preform. Cells tended to orient parallel to the fiber axis (parallel to the 002 graphene plane) and proliferate as a function of higher crystallinity, although the addition of oxygen or other functional groups disrupted the interaction between cells and graphene surface and inhibited the growth. In conclusion, osteoblast (bone-forming cells) attachment and overall growth is a function of crystallite size, graphene orientation, and carbon graphitization.

Poster 21 Friday @ 10:00 AM

Structural Characterization of Lignin-based Composite Anodes for Lithium-ion Batteries

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Novel lignin-based carbon composite materials consisting of nanocrystalline and amorphous domains are promising candidates for low-cost, high-performance anodes in next-generation lithium-ion batteries. These materials are manufactured through a pyrolyzation process, in which structural characteristics at the nanoscale and mesoscale can be controlled, including nanocrystallite size, volume fraction of crystalline material, and composite density. Pair distribution functions (PDFs) for these materials obtained from the NOMAD diffractometer at the Spallation Neutron Source are compared to data developed from a computational study. The study is designed to understand how the structural characteristics of the composite materials impact performance properties, including ion capacity and ion mobility. Classical molecular dynamics simulations are utilized to determine d-spacing in the nanocrystallites, preferential ion binding sites, and structural response of the anode as a function of ion loading. This model is validated using the PDFs from neutron diffraction. Decomposition of the simulated PDFs provides an atomistic explanation for each feature in the experimental spectra. The model systems are thus used to develop a mechanistic understanding of the aforementioned structure-property relationships.