## 14. ABSTRACT
The goals of this research were to establish feasibility of manufacturing and to evaluate performance of novel continuous polyimide nanofibers and their nanocomposites. The specific objectives were: (1) demonstrate feasibility of fabrication of continuous nanofibers from a range of specially synthesized soluble polyimides; (2) characterize their mechanical behavior and properties; and (3) fabricate and characterize polyimide nanofiber-reinforced composites. Continuous nanofibers were successfully manufactured from several specially designed polyimides and tested in the broad range of diameters. Significant simultaneous improvements in strength and toughness with the reduction of diameter were observed and analyzed. The best nanofibers were as strong as advanced conventional fibers while maintaining higher toughness. It was shown that chemical structure and processing control nanofiber properties and toughness. Polyimide nanofibers were also successfully incorporated into nanocomposites. It was demonstrated that continuous nanofibers may provide unique advantages for future structural nanocomposites.

## 15. SUBJECT TERMS
Continuous nanofibers, polyimides, electrospinning, nanocomposites

## 16. SECURITY CLASSIFICATION OF:

<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNCLASSIFIED</td>
<td>UNCLASSIFIED</td>
<td>UNCLASSIFIED</td>
</tr>
</tbody>
</table>

## 17. LIMITATION OF ABSTRACT
UL

## 18. NUMBER OF PAGES
35
# Advanced Single-Polymer Nanofiber-Reinforced Composite Towards Next Generation Ultralight Superstrong/Tough Structural Material

## Abstract
The goals of this research were to establish feasibility of manufacturing and to evaluate performance of novel continuous polyimide nanofibers and their nanocomposites. The specific objectives were: (1) demonstrate feasibility of fabrication of continuous nanofibers from a range of specially synthesized soluble polyimides; (2) characterize their mechanical behavior and properties; and (3) fabricate and characterize polyimide nanofiber-reinforced composites. Continuous nanofibers were successfully manufactured from several specially designed polyimides and tested in the broad range of diameters. Significant simultaneous improvements in strength and toughness with the reduction of diameter were observed and analyzed. The best nanofibers were as strong as advanced conventional fibers while maintaining higher toughness. It was shown that chemical structure and processing control nanofiber properties and toughness. Polyimide nanofibers were also successfully incorporated into nanocomposites. It was demonstrated that continuous nanofibers may provide unique advantages for future structural nanocomposites.

## Subject Terms
- Continuous nanofibers, polyimides, electrospinning, nanocomposites

## Security Classification of:
- a. Report: UNCLASSIFIED
- b. Abstract: UNCLASSIFIED
- c. This Page: UNCLASSIFIED

## Limitation of Abstract
- UL

## Number of Pages
- 35
AFOSR GRANT FA9550-11-1-0204
FINAL REPORT 08/15/11-04/15/15

GRANT DATA

AFOSR Grant No. FA9550-11-1-0204

“ADVANCED SINGLE-POLYMER NANOFIBER-REINFORCED COMPOSITE - TOWARDS NEXT GENERATION ULTRALIGHT SUPERSTRONG/TOUGH STRUCTURAL MATERIAL”

Principal Investigators:

Yuris Dzenis
Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln

Stephen Z.D. Cheng
College of Polymer Science and Polymer Engineering, The University of Akron

Frank Harris
College of Polymer Science and Polymer Engineering, The University of Akron

AFOSR Program: Low Density Materials
Program Manager: Dr. Joycelyn Harrison
EXECUTIVE SUMMARY

A strategic goal of the U.S. Air Force is to be able to deliver munitions to targets anywhere around the globe in less than an hour. This will require very high speeds and novel lightweight and temperature resistant materials. Nanocomposites are promising emerging materials for structural and functional applications due to unique properties of their nanoscale constituents. However, the currently available nanocomposites based mostly on nanoparticles lack the high strength and stiffness required for structural applications. The advent of high-performance fibers and their introduction to advanced composites produced a revolution in the area of lightweight structural materials in the last decades. However, the current advanced fibers are brittle, i.e. they fail at low strains to failure of only a few percent. Continuous nanofibers can overcome the above problems and lead to new, revolutionary levels of performance in composites.

In this project, a new class of nanoscale reinforcement, i.e. continuous polyimide nanofibers was explored and developed for the first time. An emerging nanomanufacturing technology based on the electrospinning process was utilized. Continuous nanofibers were produced from a range of specially designed and synthesized polyimides (PI). Methods of control of nanofiber diameters were utilized. Novel specimen preparation and testing protocols were developed and utilized for mechanical testing of individual nanofibers in the broad range of diameters. Extraordinary simultaneous improvements in strength and toughness of PI nanofibers with the reduction of diameter were observed and analyzed for the first time. Best nanofibers were as strong as advanced conventional fibers while maintaining much higher toughness. It was shown that chemical structure and processing conditions control nanofiber properties and toughness. The developed novel polyimide nanofibers were successfully incorporated into nanocomposites.

This project provides an initial body of knowledge for the development of a new family of advanced nanoreinforcing materials, i.e. ultrahigh-performance continuous nanofibers for the next generation lightweight structural nanocomposites. Continuous polyimide nanofibers (PI NFs) from soluble polyimides demonstrated in this project for the first time have shown the strength levels of carbon fibers (CFs). However unlike CFs, these nanofibers were produced in a single step scalable room temperature process. Elimination of high-temperature oxidation and carbonization promises low cost nanofibers. In addition, PI NFs were 25-30% lighter than CFs. Most importantly and uniquely, the high-strength PI nanofibers exhibited ultrahigh strain to failure of up to 50% (depending on the chemical structure and processing). This led to superhigh levels of energy to failure (toughness) that exceeded the toughness of CFs and all other high-performance fibers. The demonstrated simultaneously ultrahigh toughness and strength of the PI NFs can be beneficial to structural composites. Such composites can have strength comparable to the strength of existing CF-epoxy composites while having significantly higher toughness and lower density. High toughness would allow for significantly lower factors of safety, thus further reducing the weight of composite structures. Once developed, such next generation ultratough strong and lightweight composites will be broadly applicable in DoD and civilian structures and will be especially beneficial in safety-critical applications such as primary aircraft structures and structural space components.
STATEMENT OF THE PROBLEM STUDIED

The goals of this research were to establish feasibility of manufacturing and to evaluate performance of novel continuous polyimide nanofibers and their nanocomposites. The main objectives of this project were: (1) demonstrate feasibility of fabrication of continuous nanofibers from a range of specially synthesized soluble polyimides; (2) characterize their mechanical behavior and properties; and (3) fabricate and characterize polyimide nanofiber-reinforced composites.

SUMMARY OF SIGNIFICANT RESULTS

*Simultaneously Strong and Tough Nanofibers: First Observation and Proposed Structural Mechanisms*

Strength of structural materials and fibers is usually increased at the expense of strain at failure and toughness. Recent experimental studies have demonstrated improvements in modulus and strength of electrospun polymer nanofibers with reduction of their diameter. Nanofiber toughness has not been analyzed; however, from the classical materials property trade-off one can expect it to decrease. By analyzing long (5-10 mm) individual polyacrylonitrile (PAN) nanofibers, we showed for the first time that nanofiber toughness also dramatically improved. Reduction of fiber diameter from 2.8 micrometers to ~100 nanometers resulted in simultaneous increases in elastic modulus from 0.36-48 GPa, true strength from 15-1750 MPa, and toughness from 0.25-605 MPa with the largest increases recorded for the ultrafine nanofibers smaller than 250 nanometers. The observed size effects showed no sign of saturation. Structural investigations and comparisons with mechanical behavior of annealed nanofibers allowed us to attribute ultrahigh ductility (average failure strain stayed over 50%) and toughness to low nanofiber crystallinity resulting from rapid solidification of ultrafine electrospun jets.

The observed decrease in polymer crystallinity with electrospun nanofiber diameter needs to be further studied and may not be universal. Polymer crystallization is a complex process that depends on a large number of parameters and processing conditions and the atactic polyacrylonitrile may be prone to produce lower crystallinity. Recent publications point to some examples showing increased nanofiber crystallinity with diameter decrease. However, other studies and our own preliminary analysis of several other nanofiber families indicate that other polymer systems may exhibit behaviors similar to PAN. Peculiarities of crystallization during complex coupled electrospinning process (this technique combines electrical, mechanical, mass transfer, and thermal phenomena in a single multiphysics process) are yet to be studied and methods of control to be developed. Models of polymer jets incorporating solvent evaporation and polymer solidification are expected to provide insights. Chemical structure of macromolecules is expected to play a key role along with processing parameters.
Novel Soluble Polyimides for High-Performance Nanofibers

Several families of soluble polyimides suitable for electrospinning were produced. The focus was on chemical control of solubility that is essential for control of both polyimide synthesis and subsequent electrospinning of continuous nanofibers from solutions. Control of nanofiber structure formation during electrospinning via altering liquid crystalline state of the solution was also addressed.

Aromatic polyimides have been classified as being insoluble or only soluble under extremely rigorous conditions. This chemical resistance is a useful feature for polyimide applications in harsh environmental conditions. There are several main factors influencing the solubility of polyimides. The insolubility originates from the high aromaticity, the rigid imide structure in the polymer backbone, the formation of inter- and intramolecular charge transfer complexes, and the ordered structures resulting from chain packing of the molecules. In order to enhance their solubility, one or a combination of the following structural modifications can be used: 1) The incorporation of one or more large pendant groups; 2) The incorporation of flexible or non-symmetrical linkages; 3) The introduction of polar groups, which have strong interactions with solvents; 4) Disrupting the symmetry and recurrence regularity through copolymerization; and 5) The introduction of non-coplanar structures.

In the past three years under this research grant support, we used the above strategies to produce versatile organo-soluble polyimides enabling precise one-step processing into nano-fibers and nano-fiber assemblies. The specific attention was paid to modification of the structure of aromatic polyimides for the purpose of controlling solubility in common organic solvents, retaining high molecular weight and tuning their physical properties such as glass transition temperature, crystallinity and molecular orientation.

Polymerizations were conducted at Akron. Six new polyimide and copolyimide samples were successfully synthesized via one-step polymerization reactions carried out in refluxing m-cresol or p-chlorophenol containing a catalytic amount of isoquinoline at a range of reaction temperatures. They were:

1. BisADA / OTOL $T = 263 \, ^{\circ}C$
2. PFMB
6FDA/PFMB/6FOBDA = 100/80/20 (LS-13-82B) $T = 285 ^\circ C$

$6FDA + 0.8 \cdot H_2N-\text{PFMB} + 0.2 \cdot H_2N-\text{9FOBDA} \xrightarrow{\text{Polycondensation}} \text{Phenolic Solvent}$

$6FDA/BPDA/PFMB = 50/50/100$ $T = 268 ^\circ C$

$0.5 \cdot 6FDA + 0.5 \cdot \text{BPDA} + H_2N-\text{PFMB} \xrightarrow{\text{Polycondensation}} \text{Phenolic Solvent}$

$B_{12}\text{ADA} : \text{PFMB} : C_{6}BP = 100 : 80 : 20$ $T_g = 155 ^\circ C$
Molecular characterizations of the resulting polymers have been performed including $^1$H NMR, FTIR, intrinsic viscosity, etc. to establish the relative molecular weight and molecular structure of the polymer backbone. The physical characterization of the polyimides and copolyimides included glass transition temperature (Tg), thermal stability and structure orders developed during the nano-fiber spinning. The relationship between chemical structures, fiber morphologies and nano-fiber properties were established and formed a feedback loop to guide the synthetic efforts enabling continuous improvement of the polyimide systems.

From structure point of view, compounds 1-4 are in linear backbone in nature with high glass transition temperatures and high thermal stabilities. Among them, 1 and 2 possess fewer kinks in the backbones and better ordered structure and thus, can generate more crystallinity. On the other hand, 3 and 4 are more or less random copolymers and therefore, backbone is less prone to crystallize. All of 1 to 4 compounds can generate high degree of molecular orientation under tension. On the other hand, in compound 5 we introduce side chain liquid crystals. It leads to lower glass transition temperature, yet the liquid crystalline moiety may assist the backbone orientation. The existence of the side chains may also help to improve the fracture energy of the nano-fibers. This polyimide can also serve as a polyimide matrix material. Compound 6 is a combination of compound 1 to 4 and 5. This compound is expected to exhibit combined properties between these two types of polyimides. Overall, the synthesized polyimides were organo-soluble, rigid enough to possess high mechanical properties, possessed high degradation temperatures, and could be used to tune crystallinity and chain orientation during the fiber spinning.
Controlled Nanomanufacturing and Structural Evaluation of Nanofibers from Soluble Polyimides

Polyimide nanofilaments were produced from soluble polyimides developed at UA by controlled solution electrospinning in Nebraska. Modeling-based approaches to control nanofiber diameter, deposition, and alignment were utilized. Samples of individual nanofilaments and aligned sheets of nanofibers were fabricated. By modifying the conditions of electrospinning, we were able to modulate nanofiber diameter in a very broad range. New insights into the jet motion and polymer structure formation obtained by the newly developed at UNL 3D continuum modeling in presence of solvent evaporation allowed further refinement of the process. In addition, this new coupled 3D continuum model of the process provided better understanding of macromolecular orientation within the nanofibers.

Nanofiber molecular-level structure was characterized using SEM, soft polymer TEM, DSC, TGA, NMR, IR and Raman spectroscopy, and electron and X-ray diffraction. The resulting nanofibers were mechanically tested at UNL. Mechanical properties of individual nanofilaments were evaluated using unique testing system allowing tensile tests of high accuracy on aligned individual nanofilaments. We developed and implemented tensile test protocol for single long electrospun nanofilaments. Specimens were produced and mounted using precision deposition methods developed in our laboratory. Sample alignment, diameter, and surface morphology were measured by SEM, environmental SEM (ESEM), high-resolution optical microscopy. Individual fibers were mechanically tested in a NANO UTM testing system under a constant strain rate of 0.001 s\(^{-1}\). Fibers of 4-5 cm in length were electrospun as free-standing filaments. A 5-10 mm section of the fiber (the gauge length in this study) was transferred and glued to the grips of the testing machine with an epoxy adhesive. An adjacent section of the same fiber was examined using a Quanta 200 FEG SEM (FEI). Its diameter was measured in at least three places and averaged for the purpose of calculating the mechanical properties. Specimens were tested through failure and full stress-strain diagrams were recorded and analyzed. As-spun PI fibers exhibited elasto-plastic behavior with large deformations to failure. Measured load and displacement variations were converted to engineering and true stresses and strains and plotted as stress-strain diagrams. True stress and strain are often used to describe material behavior at large deformations. Nanofiber modulus, failure stress (strength), strain at failure, and toughness (area under the curve) were calculated from the obtained stress-strain diagrams. Modulus and toughness were computed using engineering stress-strain diagrams.

Based on prior investigations, special attention was paid to scaling nanostructured fiber properties with nanofilament diameter. Size effects similar to the ones observed in PAN were observed for PI and evaluated with sufficient statistics. Several group members in Nebraska have been trained to use the developed nanomechanics testing system and protocol to achieve higher throughput. As a result, solid statistics was obtained for nanofibers manufactured from several precursors developed at UA and/or using different process parameters at UNL. The latter is especially important in experimental fiber studies due typical high scatter.
Variations of the measured strength, modulus, strain at failure, and toughness with diameter of individual as-spun PI nanofibers were plotted and analyzed. The results showed extraordinary increases in strength and modulus as nanofiber diameter decreased. The highest strength and modulus values measured in this study were on par with strengths and moduli of commercial carbon fibers. Such high values of modulus and strength in polymers are usually achieved at the expense of strain at failure. Remarkably, the high strength of the ultrafine PI nanofibers was achieved without statistically noticeable reduction of their failure strain. These unique simultaneous increases in modulus, strength, and strain at failure led to a dramatic increase of toughness. The highest recorded toughness was an order of magnitude higher than toughness of the best existing advanced fibers and exceeded toughness of spider silk. Mechanisms of this unusual behavior need to be better understood but the current results show promise.

The magnitudes of the mechanical improvements in the current study are among the strongest size effects recorded for any material. While most fibrous materials exhibit increases in strength with diameter decrease (observation of diameter-dependence of strength in glass fibers triggered the development of modern fracture mechanics theory), these increases usually are moderate. The relative increases in modulus and strength of PI nanofibers far exceed these size effects reported previously. Size effects on toughness have not been previously reported and have been studied here for the first time. Comparison of as-spun PI nanofibers with commercial and developmental fibers and structural materials indicate that these nanofibers may help circumvent the classical strength-toughness trade-off. Properties of most existing structural materials and fibers are within the shaded area of the strength-toughness diagram, demonstrating classical trade-off. Spider silk is one natural material providing exceptionally high toughness at high strength. In addition, several recent carbon nanotube (CNT)-based fibers and yarns showed promising combinations of specific strength and energy-to-failure. Analysis of new PI data showed that fine continuous nanofibers in this study outperformed most existing and developmental carbon nanotube-based fibers in terms of toughness. The best recorded strengths of nanofibers equaled or exceeded the strengths of most conventional advanced fibers such as carbon fiber while exhibiting 6-10 fold higher toughness. The best recorded strengths of as-spun PI nanofibers were 2-3 times higher than the strength of spider silk while showing several times higher toughness (spider silk is regarded as the toughest strong material known). Finally, best as-spun PI nanofibers outperformed all published developmental CNT fibers while approaching the level of performance of the toughest CNT fibers reported to date. Encouragingly, all trends analyzed in this study did not show signs of saturation, indicating a strong possibility of further performance improvements.

Fabrication and Characterization of PI Nanofiber Composites

We performed extensive exploratory studies on incorporation of the novel PI nanofibers into composites. First, we used our recently developed 3D nanofiber deposition simulation
models to further optimize nanofiber deposition on substrates. The modified processing techniques were used to produce aligned nanofiber sheets and other structures with controlled nanoarchitectures. Unidirectional nanofiber sheets were impregnated with the epoxy resin, cured, and tested at UNL. For comparison, nanocomposites were also produced from random nanofiber mats. High quality of nanocomposite impregnation and consolidation was verified by SEM. The microscopic evaluation and analysis of fracture surfaces also showed good nanofiber – matrix interfacial bonding in the studied systems.

The resulting nanocomposites were tested using several quasistatic testing methods including a unique method of composite fracture toughness evaluation developed earlier by Dzenis in collaboration with AFRL. Anisotropic mechanical properties of resulting unidirectional nanocomposites were evaluated for the first time and compared to random nanocomposite properties. Exploratory incorporation of as-spun PI nanofibers as nanoreinforcement at interlaminar interfaces to suppress delamination in advanced laminated composites was also performed. The obtained results show the applicability of the developed PI NFs in advanced structural composites and provide valuable initial information for further development of such composites.

**Development of PI Matrix and Fabrication and Characterization of Single-Polymer Nanocomposites**

Proper matrix is very important for composite mechanical performance. Matrix should be able to infiltrate nanofiber constructs and establish proper load transfer to reinforcement. In this project, we explored the feasibility of use of polyimide matrix to build a unique single-polymer nanocomposite. This approach was enabled by the versatility of polyimide chemistry. In addition to very good material compatibility and interfacial stress transfer, the single-polymer polyimide nanocomposite is expected to have superior thermal stability.

Several routes were explored to develop a polyimide matrix for single-polymer composite. The matrix resins considered were thermoset such as polyimide based epoxies or thermoplastic such as recently developed 3,3',4,4'-benzophenonecarboxylic dianhydride (BTDA) and 2,2'-dimenthyl-1,3-(4-aminophenoxy)propane (DMDA) and polyetherimide (Ultem®) produced by GE, or combined thermoset and thermoplastic resin such as PMR-15 developed by NASA. Among these, BTDA-DMDA was a new resin developed with high fracture energy (4.28 kJm⁻² measured via double torsion), that was double of the fracture energy of other polymers. This significant increase of the fracture energy has been explained by multiple relaxation process and unique crystal morphology. Use of BTDA-DMDA as a matrix resin with carbon or polyimide conventional fibers was previously explored and it was shown that the fiber-matrix bonding was substantially improved in the single-polymer composite.

Several polyimides potentially suitable as a matrix in the novel PI NF/PI nanocomposite were synthesized and evaluated. Polyetheramide (PEI) was chosen for the initial
exploratory studies in this project. This polymer is non-crystalline, easy to process, heat resistant, yet with relatively low Tg of 215 degree C that allows both liquid and dry processing. Both matrix infiltration from solution (liquid route) and dry film pressing at intermediate temperatures were explored. Experiments on liquid infiltration of the PI nanofiber sheets produced by the classical 2-step route showed generally poor infiltration and mechanical properties. These nanofibers were fused and the resulting nanocomposites were not transparent. The liquid route experiments on the single step PI NFs were conducted using a range of solvents for the PEI in the hope to find a solvent that would not dissolve the nanofibers. At least one combination of the explored 5 solvents showed promise but the results need to be further confirmed and optimized. However, dry film pressing at intermediate temperatures produced positive outcomes. When properly optimized, this procedure demonstrated feasibility of building well-impregnated single-polymer nanocomposite with nanofibers surviving the nanocomposite manufacturing process intact. This first demonstrated single polymer nanocomposite shows high promise for translation of the unique discovered properties of PI nanofibers into macroscopic structural applications.

Other Relevant Work and Accomplishments

- **Ballistic potential of continuous PI nanofibers:** We have analyzed and confirmed high ballistic potential of the continuous PI nanofibers by calculating extraordinary high ballistic parameter (Omega) and simultaneously high specific strain energy and strain wave velocity in nanofibers. This will be especially beneficial for composites designed to withstand impact loadings and for safety-critical structures.

- **Further improvement of properties in nanofiber yarns:** We have developed novel numerical models of nanofiber networks and yarns with explicit representation of individual nanofibers and their contacts. Preliminary analysis showed that the observed size effects in individual NFs can be further significantly enhanced (up to 300%) in the dense nanofiber yarns. This provides an attractive route to bridge scales and to utilize unique nano properties in conventional macro materials.

- **Polyimide-derived carbon nanofibers:** We have explored carbonization of PI nanofilaments and compared their structure to the structure of conventional PAN based carbon nanofibers. The results show a possibility of further significantly improved toughness of carbon nanofibers.

- **Polyimide NF separators for Li-ion batteries:** We have developed eletrospun PI NFs for application as separation membranes in Li batteries. The quality of the membranes was better than any commercialized separators yet the temperature resistance was 100 degree C higher. The latter is especially promising for battery safety.
OVERALL CONCLUSIONS AND IMPACT

Demonstrated superior mechanical performance coupled with the unique macro-nano nature of continuous nanofibers make them readily available for macroscopic materials and composites that can be used in a variety of applications. This project produced significant fundamental advances and several “world’s firsts” in the following areas:

- Polyimide nanofibers from a range of soluble polyimides were produced and analyzed for the first time. Feasibility of their incorporation into composites was also demonstrated for the first time.

- The reported size effects on toughness are pioneering. Size effects on strength and modulus are not unusual and have been reported for fibers as well as nanofibers. However, strain to failure inevitably decreases when strength and modulus increase, leading to toughness decrease. Ours are the first observations of simultaneous increases in strength, modulus, and toughness with nanofiber diameter decrease.

- The magnitudes of the size effects reported in this paper are also pioneering. They show largest increases in strength and toughness reported for any material or fiber (more than 2 orders of magnitude). The highest recorded nanofiber strengths rival commercial and developmental advanced fibers and spider silk while showing significantly higher toughness. Lack of observed signs of saturation suggests possible further improvements with continuing reduction of nanofiber diameter.

- Our discovered nanofibers adds a new material class to the very select current family of materials with demonstrated simultaneously high strength and toughness. Such materials are being actively sought for the safety-critical applications. While analysis of our new systems is still in progress, the obtained preliminary results indicate that the mechanism might be a combination of classical size effects on strength with high failure strains caused by a degree of disorder (such as low or no crystallinity in polymer fibers). We believe the unifying feature of low order is caused by ultrafast solidification of fine jets in the electrospinning process (the reason simultaneously high strength and toughness have not been observed in fibers produced by other methods). This is the first comprehensive analysis of this unusual mechanical behavior of electrospun nanofibers.

- The diameter range exhibiting most significant mechanical improvements in this study (< 250 nm) is biomimetic and overlaps with the range of diameters of biological fibers, such as collagen fibrils. Polymer fibers are ubiquitous in biological materials and tissues and are commonly thought to be responsible for their superior mechanical properties and toughness. Silk fibers have been shown to possess nanofibrillar structure with nanofibrills ranging from 25-170 nm. Further studies of molecular mechanisms of mechanical behavior of continuous nanofibers may shed light on the nature of strength and toughness in biological materials, which could lead to novel biomimetic structural materials with unusual properties.
Our results and analysis challenge the prevailing paradigm of advanced polymer fiber development calling for high polymer crystallinity. LC and gel spinning processes were developed in the 60s and 70s and now dominate high-performance fibers manufacturing and research. They yield highly crystalline fibers and it is commonly believed that high chain orientation and resulting high modulus and strength are impossible without high crystallinity (and outside of these two processes and a limited number of polymers they cover). We show that not only is it possible, but it also brings additional benefit of ultrahigh toughness. While we demonstrate this on ultrafine electrospun nanofibers, we think this phenomenon is more general as other processes can be envisioned. This is a major finding for polymer science. Also, this goes beyond the size effects and nanotechnology.

In contrast to most synthetic nanomaterials such as carbon nanotubes, electrospun nanofibers are continuous (infinite in length). Also, unlike most mechanical studies of nanomaterials in the literature that were conducted on micron-long specimens using AFM or MEMS devices, our study was performed on the specimens that were three orders of magnitude longer. This makes our results macroscopically relevant. Nanofiber continuity provides an easy way to bridge scales. Nanofiber manufacturing is much easier and cheaper than synthesis and processing of carbon nanotubes; issues with stress transfer and imperfect structure of CNT fibers and yarns continue to hinder their properties and applications. Our demonstrated ultrahigh mechanical performance and continuous nature of electrospun nanofibers make them immediately useable in macroscopic applications. The latter has been recognized by several recent journal covers and numerous highlights of our research in the magazines and science news outlets, including Nature, ACS Nano, Adv Funct Materials, NanoToday, Materials Today, Materials 360, Science 360, NSF and others.

LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Principal Investigators:
  Y. Dzenis
  S.Z.D. Cheng
  F. Harris

Graduate Students:
  D. Papkov (Ph.D., 2014)
  J. Wang (Ph.D., 2014)
  K. Yue (Ph.D., 2013)
  R. Cheng (MS, 2013)
  M. Kartashov (Ph.D., 2013)
A. Desyatova (Ph.D., 2012)
T. Stockdale (Ph.D., curr)
N.M. Andalib (Ph.D., curr)
Y. Liu (Ph.D., curr)
Y. Zou (Ph.D., curr)
J. Jiang (Ph.D., curr)
K. Maleckis (Ph.D., curr)

Undergraduate Student:
A. Paolini

Post-docs:
Dr. M. Kartashov, Dr. A. Desyatova, Dr. J. Wang

LIST OF PUBLICATIONS AND OTHER OUTCOMES

Graduated Students

Dr. Dimitry Papkov, Size Effects in Continuous Polymer, Composite and Carbon Nanofibers, Ph.D. Dissertation, Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, 2014 (Advisor: Y. Dzenis)

Dr. Jing Wang, Crystal structure analysis of a series of semiconducting small molecules based on sulfur-hetero benzo[k]fluoranthene, University of Akron, 2014 (Advisor: S.Z.D. Cheng)

Ms. Ren Cheng, PAN Nanofibers and Nanofiber Reinforced Composites, MS Thesis, Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, 2014 (Advisor: Y. Dzenis)

Dr. Mikhail Kartashov, Dynamic Fracture of Advanced Composites with Nanoreinforced Interfaces, Ph.D. Dissertation, Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, 2013(Advisor: Y. Dzenis)
Dr. Kan Yue, Design, synthesis and self-assembly of giant surfactants based on polyhedral oligomeric sellesquioxane-polymer conjugates, University of Akron, 2013 (Advisor: S.Z.D. Cheng)

Dr. Anastasia Desyatova, Engineered Interfaces for Toughening of Advanced Structural Materials, Ph.D. Dissertation, Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, 2012 (Advisor: Y. Dzenis)

Journal Papers

11. Seven additional papers are in preparation

Covers, Highlights

Paper [6] (primary support - AFOSR/LDM) was featured in:
- Highlight in *Nature*, 2013, Vol. 495, 284
- Numerous (hundreds) articles in science news outlets worldwide following UNL press release in April 2013

Paper [10] (primary support – MURI/ARO; AFOSR/LDM co-support acknowledged) was featured in:
- Frontispiece (Internal Cover) *Adv Funct Mater*, Vol. 23, Iss. 46 (December 2013)
- Several articles in science news outlets following UNL press release in Dec 2013 (still appearing)

Honors / Awards

Yuris Dzenis

- Associated Editor of Frontiers In Materials: Composite Materials (Nature Publishing Group, 2014-pres)

Invited Keynote and Plenary Lectures:
- Plasticity ‘14, Freeport, Bahamas, Jan 2014 (invited keynote lecture)
- Invited plenary lecture at APMAS 2014, Apr 2014
- Invited keynote lecture at HTPM-VII, Beijing, 2014
- Invited plenary lecture at the ICCPC 2014 (Kerala, India)
• Invited keynote lecture at the Seventh Jordan International Chemical Engineering Conference, Amman, 2014
• US-Korean Workshop on Manufacturing and Advanced Materials, Korea, May 2013 (part of US Government delegation; invited)
• American Society for Composites 28th Technical Conference, September 9–11, 2013, State College, Pennsylvania, USA (invited plenary lecture)
• IV ECCOMAS Conference 2013, September 25-27, 2013, S. Miguel, Azores, Portugal (invited plenary lecture)
• 12th International Conference on Fracture and Damage Mechanics (FDM 2013), September 17-19, 2013, Sardinia, Italy (invited plenary lecture)
• International conference MCM-2012, Riga, Latvia (invited plenary lecture)
• SICOMP ’12, SWEREA, Lulea, Sweden (invited keynote lecture)
• ECCM-15, Venice, Italy, 2012 (invited keynote lecture)
• 7th Asia-Pacific Congress of Applied Mechanics, Adelaide, Australia, 2012 (invited plenary lecture)
• NANOSMAT ’12, Prague, 2012 (invited plenary lecture)
• X Russia Congress of Theoretical and Applied Mechanics, N. Novgorod, 2011 (invited plenary lecture)
• ICCE-19, Shanghai (invited keynote lecture)
• Invited lecture at FDM 2011, Dubrovnik

Stephen Z. D. Cheng

• Polymer Physics Prize, American Physical Society (2013)

Plenary Lectures (from more than 60 invited talks in the reporting period):

• Stephen Z. D. Cheng, Giant molecules based on “nano-atoms”: a new platform for engineering structures at nanometer feature size, Polymer Physics Prize Award Lecture, American Physical Society, Baltimore, March 2013.
• Stephen Z. D. Cheng, Molecular nanoparticles are unique elements for macromolecular science. Plenary Lecture at Pacific Polymer Conference, Kaohusing, Taiwan, November 2013.
• Stephen Z. D. Cheng, Giant polyhedra and giant surfactants based on nano-atoms: Tuning from crystals, to quasicrystals, to Frank-Kasper phases: An interconnection between soft and hard matters. Plenary Lecture at 13th Conference for Supramolecules and Liquid Crystalline Polymers, Changchun, Jilin, China, August 2014.
• Stephen Z. D. Cheng, Giant polyhedra and giant surfactants based on nano-atoms: Tuning from crystals, to quasicrystals, to Frank-Kasper phases: An interconnection between soft and hard matters. Plenary Lecture at North American Thermal analysis Society Annual Meeting, Santa Fe, New Mexico, September 2014.
• Stephen Z. D. Cheng, Precisely Functionalized molecular nanoparticles are unit elements for macromolecular science: Giant molecules based on nanoatoms. Plenary Lecture at The Adhesion Society, Savannah, Georgia, February 2015.
Frank W. Harris

• Fellow, National Academy of Inventor

Dimitry Papkov

• Finalist in the UNL Outstanding PhD Dissertation Award Competition

INTERACTIONS/TRANSITIONS

Conference Presentations

The total of over 90 presentations, including numerous keynote and plenary lectures by the team members listed above.

Interactions with AFRL and other DoD Labs

The PI (Dzenis) conducted three separate invited day-long workshops on simultaneously strong and tough nanofibers at AFRL, ARL, and NRL (2013-2014)

Other Interaction / Dissemination Activities

• Invited visit/lecture and discussions at AFRL (OMC M&P RT, RXCC)
• Invited visit and discussions at ARL (Multifunctional Materials and Materials for Soldier Protection, Composite and Hybrid Materials Branch)
• Interaction on polyimides with NASA (LARC-D307)
• Recruitment of domestic PhD students and planned summer research at AFRL/NASA
• Small business research activities at UNL funded by US Army, DoE
• Continuing development of UNL Advanced Nanomaterials and Nanomanufacturing Laboratories (Director – Y. Dzenis): among other things obtained external funding (DURIP/AFOSR and NSF) for acquisition of the state-of-the-art Raman Microscopy System as well as High-Rate System for Nanofiber Manufacturing and Coating. The laboratories were extensively used in this project.

• We have developed electrospun PI NFs for the application of separation membranes in Li batteries. The quality of the membranes are better than any commercialized ones yet the temperature resistance is 100 degree C higher than the commercialized ones. We are collaborating with a few industries and hopefully, they can be commercialized in the near future.
Continuous Polyimide Nanofibers for Next Generation Lightweight Aerospace Composites

Yuris Dzenis (PI)
Department of Mechanical and Materials Engineering
Nebraska Center for Materials and Nanoscience
University of Nebraska-Lincoln

Stephen Cheng (co-PI), Frank Harris
College of Polymer Science and Polymer Engineering
University of Akron

FA9550-11-1-0204
LDM Program Director: Joycelyn Harrison

Motivation

• Advanced reinforcing fibers possess excellent strength, but they are brittle
• Nanomaterials may help overcome brittleness
• Nanoparticles, such as carbon nanotubes, are difficult to process into a high-performance composite
• Continuous nanofibers can theoretically possess both high strength and toughness

Objectives

• Demonstrate feasibility of fabrication of continuous nanofibers from a range of specially synthesized soluble polyimides
• Characterize and study their mechanical behavior and properties
• Fabricate and characterize polyimide nanofiber-reinforced composites

Electrospinning Process

• Top-down nanomanufacturing process: Spinning polymer liquids in high electric fields
• Continuous polymer, carbon, and ceramic nanofibers with diameters in the range from 1.5-5000 nanometers
• Mechanical properties of electrospun nanofibers were considered to be poor

Solution bath
Capillary tube
Steady state jet
Collector
5kV to 20kV
Jet instabilities

Comparison with Conventional Advanced Materials and Fibers

Why Polyimides?

• Aromatic polyimides (PI) are products of polycondensation of diamines and dianhydrides
• They possess high chemical and thermal stability and good mechanical properties for lightweight aerospace applications

Dianhydrides

BTPDA
3,3',4,4'-Benzophenone tetracarboxylic dianhydride

BPDA
biphenyl dianhydride

Diamines

4,4'-DDS
4,4'-diaminodiphenylsulfone

4,4'-Oxydianiline
p-PDA
para-phenylene diamine

Benzene-1,3-diyl bis(4-aminophenoxy)ether
TPE-R
1,3-Bis (4-hydroxyphenyl) benzene

PMDA
Pyromellitic dianhydride

PDA
p-phenylene dianhydride

BPA
bisphenol A

Why Polyimides?

• Aromatic polyimides (PI) are products of polycondensation of diamines and dianhydrides
• They possess high chemical and thermal stability and good mechanical properties for lightweight aerospace applications

Dianhydrides

BTPDA
3,3',4,4'-Benzophenone tetracarboxylic dianhydride

BPDA
biphenyl dianhydride

Diamines

4,4'-DDS
4,4'-diaminodiphenylsulfone

4,4'-Oxydianiline
p-PDA
para-phenylene diamine

Benzene-1,3-diyl bis(4-aminophenoxy)ether
TPE-R
1,3-Bis (4-hydroxyphenyl) benzene

PMDA
Pyromellitic dianhydride

PDA
p-phenylene dianhydride

BPA
bisphenol A
Two-Step Processing of Aromatic PIs

- Step one (polymerization):
  - Polyamic acid
  - Easily soluble
  - Processable

- Step two (curing):
  - Polyimide
  - Thermal and chemical stability

Examples

<table>
<thead>
<tr>
<th>Property</th>
<th>Evonic P84</th>
<th>Arimide</th>
<th>UBE Ind.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>120</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>113</td>
<td>171</td>
<td>171</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>114</td>
<td>171</td>
<td>171</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>440</td>
<td>90</td>
<td>n/a</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.2±0.2</td>
<td>1.6±0.4</td>
<td>n/a</td>
</tr>
<tr>
<td>CarbonContent</td>
<td>60.0±0.1</td>
<td>45.0±0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>60±5</td>
<td>60±5</td>
<td>60±5</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>3.2±0.2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>116±5</td>
<td>116±5</td>
<td>116±5</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>116±5</td>
<td>116±5</td>
<td>116±5</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>90±5</td>
<td>45±5</td>
<td>n/a</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.2±0.2</td>
<td>1.6±0.4</td>
<td>n/a</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>113±5</td>
<td>171</td>
<td>n/a</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.2±0.2</td>
<td>1.6±0.4</td>
<td>n/a</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>60±5</td>
<td>60±5</td>
<td>60±5</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>3.2±0.2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>116±5</td>
<td>116±5</td>
<td>116±5</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>116±5</td>
<td>116±5</td>
<td>116±5</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>90±5</td>
<td>45±5</td>
<td>n/a</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.2±0.2</td>
<td>1.6±0.4</td>
<td>n/a</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>113±5</td>
<td>171</td>
<td>n/a</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.2±0.2</td>
<td>1.6±0.4</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Exploratory Work: Nanofibers by Two-Step Imidization (BPDA-ODA)

- Step one:
  - Polymerization - polyamic acid
  - Soluble
  - Forming (electrospinning)

- Step two:
  - Imidization by thermal curing - polyimide

Poly(p-phenylene biphenyltetracarboximide) (BPDA/PDA) Nanofibers

Mechanical Testing of BPDA/PDA Nanofibers

- Decent mechanical properties:
  - σ = 1.7 ± 0.12 GPa
  - E = 78 ± 12 GPa

- Problem encountered:
  - Nanofiber fusion during imidization of NF assemblies

Efforts to Reduce Fusion: Drying in Vacuum

- Residual solvent was removed
  - Slight reduction of fusion
Efforts to Reduce Fusion: Washing

- Worse than drying

![Graph showing differences between washed and unwashed samples.]

Efforts to Reduce Fusion: Additives

- Dodecylethyldimethylammonium chloride
  - Fusion was reduced but still present
  - Fused NFs are unlikely candidates for high-performance nanocomposites

![Graph showing the effectiveness of additives.]

Alternative Approach to Combat Fusion: Organo-Soluble Polyimides

**One-step Polyimide Chemistry**

- **Pros:**
  - Avoid problems with the second step (conditions of chemical or thermal imidization affect the properties of final products)
  - Avoid problems with instability of polyamic acids
  - Completely soluble
  - Better control of structures and morphologies; avoidance of NF fusion
- **Cons:**
  - Requiring monomers with specific modification to break the conjugation length, yet to keep chemical rigidity.

![Diagram showing the synthesis of one-step polyimide.]

Organo-Soluble Polyimide: How?

- Introducing fluorine-containing groups
  - Bulky pendant groups to disrupt the chain package, twist the chain backbones, and break the conjugation lengths
  - Flexible or non-symmetrical linkages to reduce rigidity
  - Copolymerization to interrupt the periodicity along the chain direction and retain structural rigidity

![Diagram showing the mechanisms of Organo-Soluble Polyimides.]

Conventional Fibers from Soluble Polyimides

- BPDA/DMB fibers developed by F. Harris, S. Cheng & collaborators at Akron in the 90s
  - Strength (3.3 GPa) rivaled the strength of Kevlar 49 and PBZO
  - Modulus (130 GPa) was higher than modulus of Kevlar 49
  - However, elongation at break was only 2.5%

![Graph showing properties of conventional fibers.]

Initial Polyimides Studied

<table>
<thead>
<tr>
<th>Polyimides</th>
<th>Tg (°C)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS-C2</td>
<td>242</td>
<td></td>
</tr>
<tr>
<td>6FDA/6FBDA/6FOBDA 80/20/100</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>B15ADA/PFMB/C6BP 100/80/20</td>
<td>155</td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing properties of initial polyimides.]

PI Nanofiber Manufacturing

- Single-step nanomanufacturing with no post-processing
- No fiber fusion!

Control of Polyimide Nanofiber Diameters

Mechanical Testing Protocol for Individual PI Nanofilaments

- NanoUTM nanomechanics testing system
  - Large deformation testing through failure
- Specimen fabrication and mounting protocols
  - Long 5-10 mm specimens
  - Results relevant to macro applications
- Evaluation of diameter by SEM
  - Sections adjacent to the tested one to avoid radiation damage effects
  - Non-uniform nanofibers discarded

X-Ray Diffraction vs Diameter

XRD Peak Parameters

Nanomanufacturing and Mechanical Behavior: AJ-E-010-1
Nanomanufacturing and Mechanical Behavior: 1-BisADA-ODA

Nanomanufacturing and Mechanical Behavior: 2-6FDA-PFMB

Nanomanufacturing and Mechanical Behavior: 3-ODPA-PFMB

Size Effects on Mechanical Properties
Nanomanufacturing and Mechanical Behavior: 4-BisADA-OTOL

Nanomanufacturing and Mechanical Behavior: 5-6FDA-PFMB-6FOBDA

Nanomanufacturing and Mechanical Behavior: 7-6FDA-BPDA-PFMB
Comparative Analysis of New Polyimide Nanofibers

Comparative Analysis of All Tested Polyimide Nanofibers (9 Families)

Nanofiber Composites
- Oriented and random PAN-epoxy
- Two-step and soluble PI-epoxy
- Two-step and soluble PI-PEI
  - Matrix solution infiltration
  - Dry matrix pressing

Property Correlations

Nanofabrication of Oriented NFs
Nanofabrication of Oriented NFs

NF Sheet Testing

Aligned

Random

Comparison

<table>
<thead>
<tr>
<th></th>
<th>Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Toughness (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aligned – 1 hour</td>
<td>20.82</td>
<td>541.40</td>
<td>64.44</td>
</tr>
<tr>
<td>Aligned – 2 hours</td>
<td>17.86</td>
<td>329.07</td>
<td>73.16</td>
</tr>
<tr>
<td>Random</td>
<td>9.89</td>
<td>150.07</td>
<td>73.99</td>
</tr>
</tbody>
</table>

Nanocomposite Testing: Method, Specimen, and Data Reduction

- **Fracture Testing**: Double Edge Notch Test
  - Stress Intensity Factor $K_I$ can be estimated as $K_I = \sigma \sqrt{\pi b a}$
  - $\sigma$ is the applied stress
  - $b$ is the thickness of the specimen
  - $a$ is the crack length

- **Specimen Preparation**
  - In the specimen, $a=2mm$, $b=4mm$
  - $F_{app} = \frac{P}{4b}$
  - $F_{net} = \frac{P}{4b}$

Fracture Testing

Aligned [0]

Random

Aligned [90]
Comparison

<table>
<thead>
<tr>
<th>Nanorheinforcement</th>
<th>Absolute Improvement</th>
<th>Volume Fraction</th>
<th>Improvement per 1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two Step PI NFs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>12.2%</td>
<td>2.8%</td>
<td>4.33%</td>
</tr>
<tr>
<td>P2</td>
<td>16.3%</td>
<td>0.6%</td>
<td>2.23%</td>
</tr>
<tr>
<td>P3</td>
<td>4.10%</td>
<td>3.00%</td>
<td>1.10%</td>
</tr>
<tr>
<td>Soluble PI NFs</td>
<td>35.1%</td>
<td>0.07%</td>
<td>40.4%</td>
</tr>
</tbody>
</table>

Mechanical Testing

Typical Stress – Strain Curves

Fracture Surface

Soluble PI Nanofibers – Epoxy

Typical Stress – Strain Curves

Fracture Surface

Optical Transparency

Two Step PI NFs

Soluble PI NFs
Polyetheramide (PEI) Matrix for PI NFs

- Motivation:
  - Non-crystalline
  - Easy to process
  - Heat resistant yet with relatively low $T_g = 216^\circ C$
  - Inexpensive

Two Step Polymide NFs – PEI Composites

Manufacturing

Mechanical evaluation

Soluble Polymide NFs – PEI Composites

- Matrix: PEI wt. 5-14%
- Solvents tried:
  1. DMAc/THF (1:1)
  2. DMAc/THF (4:6)
  3. DMAc/THF/DMSO (4:4:2)
  4. THF/DMSO (1:1)
  5. Chloroform

Comparison: PI – PEI Nanocomposites

- Soluble vs Two-Step PI NF Composites:
  - 4-7 times higher fracture toughness at 4-9 times lower Vf
**Alternative Nanomanufacturing: Dry Film Pressing**
- PEI film preparation
  - Using drawdown machine for high-quality uniform films
  - Spin-coating
- Drying conditions affect residual solvent amount
  - Atmosphere: < 10 % residue
  - Vacuum: no residue detected
- Nanocomposites: by film melting in press clave

**Nanocomposite Manufacturing by Hot Film Pressing**
- Nanofibers
  - APS-C2
  - 3-ODPA-PFMB (higher Tg)
- PEI matrix from solution in:
  - Chloroform
  - DMAc
  - No residual solvent

Example
Press clave conditions:
120-180 psi
Temperatures covered:
- 215 °C
- 230 °C
- 250 °C
- 260 °C
- 270 °C

---

**Initial Nanocomposite Manufacturing: Poor Impregnation**

**Improved Manufacturing: Nanofiber Survival**

**New Manufacturing Breakthrough: Good Impregnation and Nanofiber Survival in PI/PI Nanocomposite**

**Highly Aligned Dense Sheets of Polyimide Nanofibers by Modeling-Based Optimal Nanomanufacturing**
Bulk Production of Ultrafine PI Nanofibers via Process Optimization

Other Relevant Work
- Ballistic potential of continuous PI nanofibers
- Dynamic impact toughening of advanced composites
- Further improvement of properties in nanofiber yarns
- Polyimide-derived carbon nanofibers
- Polyimide NF separators for Li-ion batteries

Extraordinary Ballistic (Omega) Parameter of PI Nanofibers

Spec Strain Energy vs. Strain Wave Velocity for PI Nanofibers

Impact Behavior of Advanced Composites with Nanoreinforced Interfaces

First Continuous Carbon Nanofibers from PI Precursors
Poor Graphitic Structure

Comparison with PAN-Based CNFs

PI Nanofiber Membranes Used as High-T Li-Battery Separator

Crosslinked PI Nonwoven: Porosity and Electrolyte Uptake
Cross-linked PI Nonwoven: Thermal Dimensional Stability

Treated at 150 °C for 2 hours

TMA measurement

Cross-linked PI Nonwoven: Ionic Conductivity

EIS Test:

Stainless-steel

Pl separator

Stainless-steel

Ionic conductivity:

δ = d/(R S)

TEAM : PI-uncrosslinked: 3.41 × 10⁻³ S/cm

PI-crosslinked : 1.32 × 10⁻³ S/cm

Celgard : 0.38 × 10⁻³ S/cm

Summary

- Novel soluble polyimides were synthesized and successfully electrospun into continuous nanofibers in a single step process (first)
- Nanofibers were mechanically evaluated in a range of diameters
- Strong size effects were recorded with simultaneous increases in strength, stiffness, AND toughness
- Best nanofibers exhibited ultrahigh strength and toughness up to 20 times the toughness of commercial high-performance fibers
- PI nanofibers have been used in composites, batteries, and as precursors for carbon nanofibers
- Simultaneously strong, tough, and T-resistant continuous PI nanofibers will be beneficial for lightweight aerospace structures

Control of PI Nanofiber Properties via Chemistry (UA) and Processing (UNL)

Circumvention of the Classical Strength-Toughness Trade-Off (Major Outcome)

Simultaneously Strong and Tough Continuous Nanofibers

1. Report Type
   Final Report

Primary Contact E-mail
Contact email if there is a problem with the report.
ydzenis@unl.edu

Primary Contact Phone Number
Contact phone number if there is a problem with the report
4024720713

Organization / Institution name
University of Nebraska-Lincoln

Grant/Contract Title
The full title of the funded effort.
ADVANCED SINGLE-POLYMER NANOFIBER-REINFORCED COMPOSITE - TOWARDS NEXT GENERATION ULTRALIGHT SUPERSTRONG/TOUGH STRUCTURAL MATERIAL

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".
FA9550-11-1-0204

Principal Investigator Name
The full name of the principal investigator on the grant or contract.
Yuris Dzenis

Program Manager
The AFOSR Program Manager currently assigned to the award
Joycelyn Harrison

Reporting Period Start Date
08/15/2011

Reporting Period End Date
04/15/2015

Abstract
The goals of this research were to establish feasibility of manufacturing and to evaluate performance of novel continuous polyimide nanofibers and their nanocomposites. The specific objectives were: (1) demonstrate feasibility of fabrication of continuous nanofibers from a range of specially synthesized soluble polyimides; (2) characterize their mechanical behavior and properties; and (3) fabricate and characterize polyimide nanofiber-reinforced composites. Continuous nanofibers were successfully manufactured from several specially designed polyimides and tested in the broad range of diameters. Significant simultaneous improvements in strength and toughness with the reduction of diameter were observed and analyzed. The best nanofibers were as strong as advanced conventional fibers while maintaining higher toughness. It was shown that chemical structure and processing control nanofiber properties and toughness. Polyimide nanofibers were also successfully incorporated into nanocomposites. It was demonstrated that continuous nanofibers may provide unique advantages for future structural nanocomposites.
Distribution Statement
This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

Explanation for Distribution Statement
If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

SF298 Form
Please attach your SF298 form. A blank SF298 can be found here. Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

Form Page FA9550-11-1-0204 Final Report Full Fin.pdf

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.

FA9550-11-1-0204 Final Report Full Fin.pdf

Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

Archival Publications (published) during reporting period:

Changes in research objectives (if any):

Change in AFOSR Program Manager, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

<table>
<thead>
<tr>
<th></th>
<th>Starting FY</th>
<th>FY+1</th>
<th>FY+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salary</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equipment/Facilities</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Supplies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

Apr 17, 2015 13:39:46 Success: Email Sent to: ydzenis@unl.edu