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ADVANCED SINGLE-POLYMER NANOFIBER-REINFORCED COMPOSITE

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Final Report

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

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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.

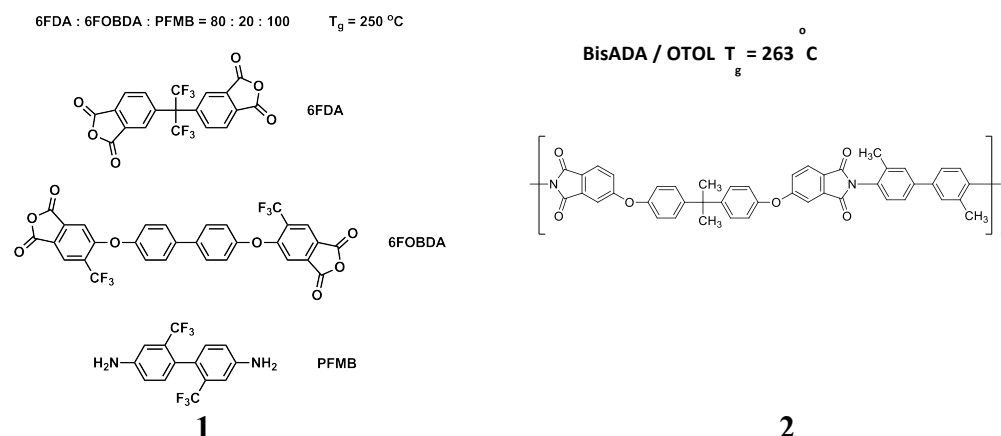
Novel Soluble Polyimides for High-Performance Nanofibers

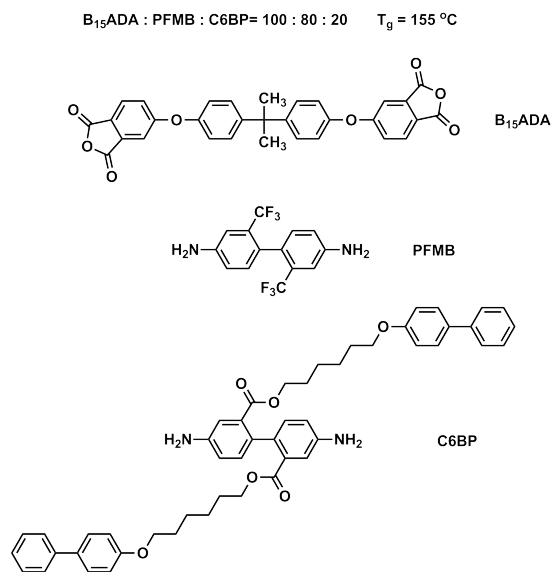
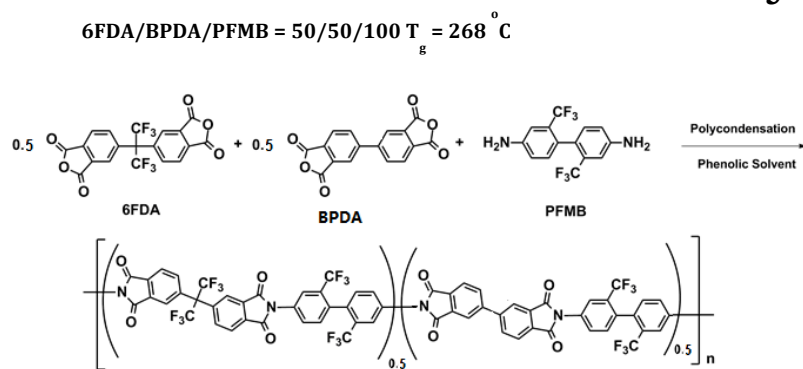
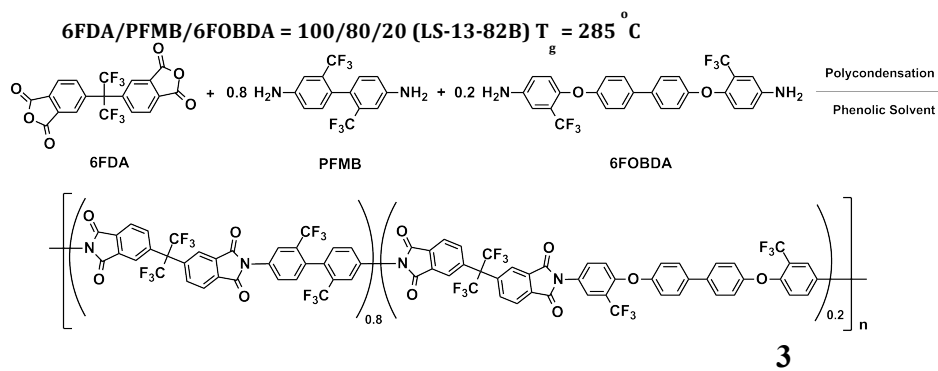
Several families of soluble polyimides suitable for electrospinning were produced. The focus was on chemical control of solubility that is essential for control of both polyimide synthesis and subsequent electrospinning of continuous nanofibers from solutions. Control of nanofiber structure formation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

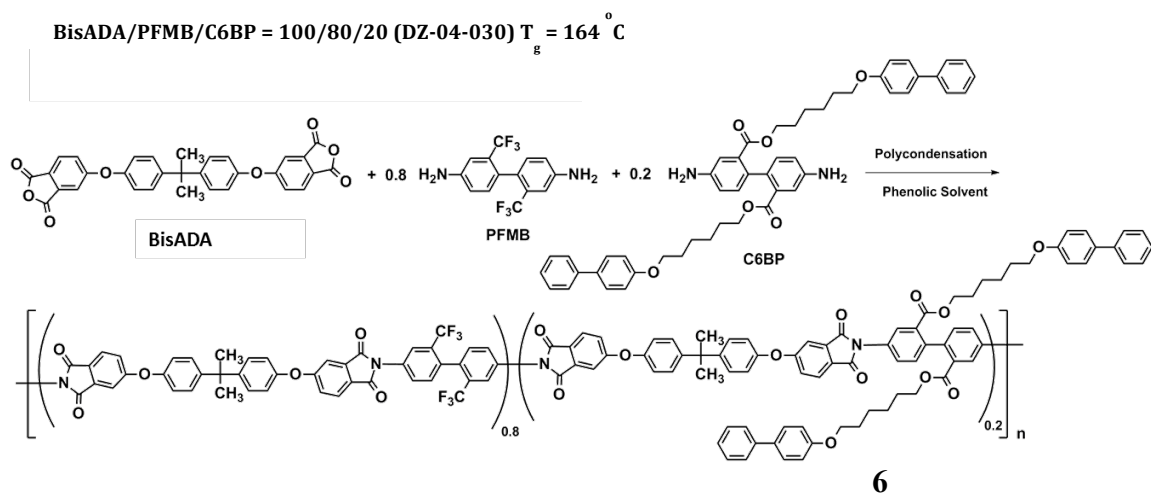
Aromatic polyimides have been classified as being insoluble or only soluble under extremely rigorous conditions. This chemical resistance is a useful feature for polyimide applications in harsh environmental conditions. There are several main factors influencing the solubility of polyimides. The insolubility 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:







Molecular characterizations of the resulting polymers have been performed including ^1H 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 (T_g), 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'-dimethyl-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 T_g 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 (Ω) 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.

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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 silsesquioxane-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

1. Wu, X., Salkovskiy, Y., and Dzenis, Y., "Modeling of Solvent Evaporation from Polymer Jets in Electrospinning", *Applied Physics Letters*, 2011, Vol. 98, 223108
2. Liu, L. and Dzenis, Y., "Simulation of Electrospun Nanofiber Deposition on Stationary and Moving Substrates", *Micro & Nano Letters*, 2011, Volume 6, Issue 6, pp. 408–411
3. Goponenko, A.V., Hou, H., and Dzenis, Y., "Avoiding Fusion of Electrospun 3,3',4,4'-Biphenyltetracarboxylic Dianhydride-4,4'-Oxydianiline Nanofibers during Conversion to Polyimide", *Polymer*, 2011, Volume 52, Issue 17, pp. 3776-3782
4. Li, Z.Y., Li, X.Z., Goponenko, A.V., Wang, C., Dzenis, Y., "Structural Characterization of Cu₂S Nanowires on Polyacrylonitrile Nanofibers by TEM", *Microsc. Microanal.*, 2012, 18, 1470-1471
5. Beese, A.M., Papkov, D., Li, S., Dzenis, Y., Espinosa, H.D., "In Situ Transmission Electron Microscope Tensile Testing Reveals Structure-Property Relationships in Carbon Nanofibers," *Carbon*, 2013, 10.1016/j.carbon.2013.04.018
6. Papkov, D., Zou, Y., Andalib, M.N., Goponenko, A., Cheng, S.Z.D., Dzenis, Y.A., "Simultaneously Strong and Tough Ultrafine Continuous Nanofibers," *ACS Nano*, 2013, 7(4), pg. 3324-3331 (Cover feature *ACS Nano*, April 23, 2013, Vol. 7, Iss. 4; highlighted in *Nature*, 2013, Vol. 495, 284)
7. Dorigato, A., Dzenis, Y., Pegoretti, A., "Filler Aggregation as a Reinforcement Mechanism in Polymer Nanocomposites," *Mechanics of Materials*, 2013, Vol. 61, pg. 79-90
8. Andalib, M.N., Lee, J.S., Ha, L., Dzenis, Y., and Lim, J.Y., "The Role of RhoA Kinase (ROCK) in Cell Alignment on Nanofibers," *Acta Biomaterialia*, 2013, 10.1016/j.actbio.2013.04.013
9. Papkov, D., Beese, A.M., Goponenko, A., Zou, Y., Naraghi, M., Espinosa, H.D., Saha, B., Schatz, G.C., Moravsky, A., Loutfy, R., Nguyen, S.T., Dzenis, Y.A., "Extraordinary Improvement of the Graphitic Structure of Continuous Carbon Nanofibers Templated with Double Wall Carbon Nanotubes," *ACS Nano*, 2013, 7 (1), pg. 126-142
10. Papkov, D., Goponenko, A., Compton, O.C., An, Z., Moravsky, A., Li, X-Z., Nguyen, S.T., and Dzenis, Y.A., "Improved Graphitic Structure of Continuous Carbon Nanofibers via Graphene Oxide Templating," *Advanced Functional*

Materials, 2013, 23, 5763–5770 (Frontispiece / Internal Cover Adv. Funct. Mater., 23, December 2013)

11. Seven additional papers are in preparation

Covers, Highlights

Paper [6] (primary support - AFOSR/LDM) was featured in:

- Cover of *ACS Nano*, 2013, Vol. 7, Iss. 4 (April 2013)
- Highlight in *Nature*, 2013, Vol. 495, 284
- Image of the Year in *Nature*, 2013, Vol. 504, 350-355
<http://www.nature.com/news/365-days-images-of-the-year-1.14303>
- Cover of *Nature* Special Issue: 2013 Review of the Year
<http://www.nature.com/news/specials/2013-1.14378>
- Feature/news articles in Materials Today, NanoToday, Materials 360, Science 360, NSF
- 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)
- *Materials Today* Top 10 Materials News from December 2013
<http://www.materialstoday.com/polymers-soft-materials/news/top-10-materials-news-from-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/TRANSITIONSConference 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 eletrospun 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.

APPENDIX: METHODS, PROCEDURES, AND DATA OUTCOMES




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



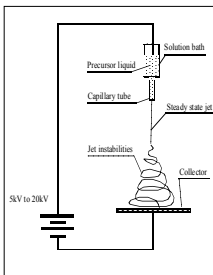
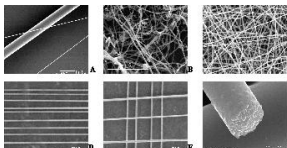

Motivation

- 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

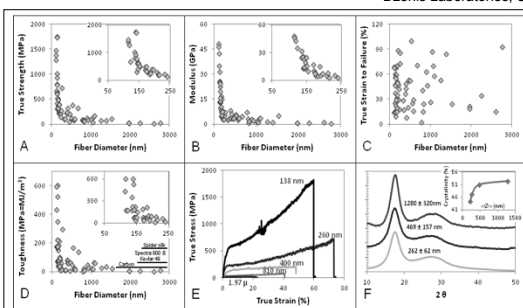



Y. Dzenis, Science, 2004, 1917-1919

- 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

Simultaneously Strong and Tough Continuous PAN Nanofibers

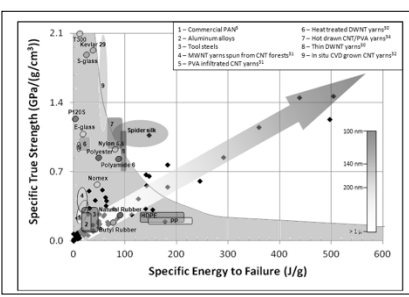
Dzenis Laboratories, UNL



ACS NANO 7 (2013) 3324-3331

Comparison with Conventional Advanced Materials and Fibers

Dzenis Laboratories, UNL



Legend for nanofiber samples:

- Commercial PAN
- Alumina nanofiber
- Tool steels
- MDMT nanofiber from CNT forests
- PVA infiltrated CNT yarns
- Heat treated DDMT yarns
- Hot drawn CNT/PVA yarns
- Thin DDMT yarns
- in situ CVD grown CNT yarns

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

Diamines

Nc1ccc(N)cc1
p-PDA
para-phenylene diamine

Nc1ccc(Oc2ccc(N)cc2)cc1
4,4'-ODA
4,4'-Oxydianiline

Nc1ccc(S(=O)(=O)c2ccc(N)cc2)cc1
4,4'-DDS
4,4'-diaminodiphenylsulfone

Nc1ccc(Oc2ccc(Oc3ccc(N)cc3)cc2)cc1
TPE-R
1,3-Bis(4-aminophenoxy) benzene

Dianhydrides

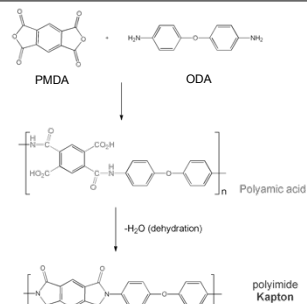
O=C1OC(=O)c2cc3C(=O)OC(=O)c3cc21
PMDA
Pyromellitic dianhydride

O=C1OC(=O)c2cc3C(=O)c4ccc(cc43)C(=O)c5ccccc251
BPDA
biphenyl dianhydride

O=C1OC(=O)c2cc3C(=O)c4ccc(cc43)C(=O)c5cc6C(=O)c7ccccc7c6cc51
BTDA
3,3',4,4'-Benzophenone tetracarboxylic dianhydride

Two-Step Processing of Aromatic PIs

- Step one (polymerization):
polyamic acid
 - Easily soluble
 - Processable
- Step two (curing):
polyimide
 - Thermal and chemical stability



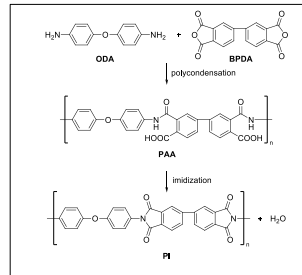
Examples

		PMR-15	Typical Epoxy Resin
Tensile Strength	MPa	55	28-100
Tensile Modulus	GPa	3.2	1-5
Compressive Yield Strength	MPa	110	104
Compressive Strength	MPa	186	173
Tg	°C	440	116-340
Density	g/cm ³	1.3	1.11-1.4
Coefficient of Thermal Expansion	10 ⁻⁴ °C ⁻¹	50.4	45 - 65

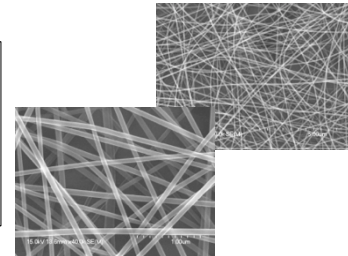
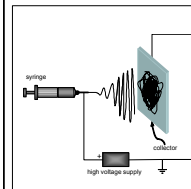
	Evonic P84	Arimide	UBE Ind.
Modulus	n/a	n/a	120 MPa
Tenacity	38 cN/tex (536 MPa)	60 cN/tex	230 cN/tex
Elongation at break	30%	13%	2.6%
Shrinkage	<3% (10 min @240°C)	<2% (@300°C)	n/a
Tg	315 °C	n/a	n/a
Density	1.41 g/cm ³	n/a	n/a

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

- Step one:
 - Polymerization – polyamic acid
 - soluble
 - Forming (electrospinning)
- Step two:
 - Imidization by thermal curing – polyimide

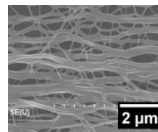
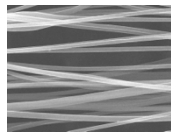


Poly(p-phenylene biphenyltetracarboximide) (BPDA/PDA) Nanofibers



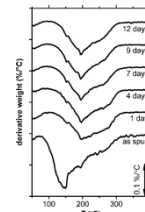
Mechanical Testing of BPDA/PDA Nanofibers

- Decent mechanical properties:
 - $\sigma = 1.7 \pm 0.12$ GPa
 - $E = 76 \pm 12$ GPa
- Problem encountered:
 - Nanofiber fusion during imidization of NF assemblies

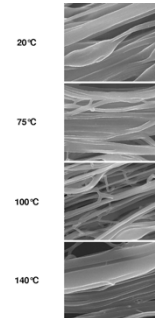


Efforts to Reduce Fusion: Drying in Vacuum

- Residual solvent was removed

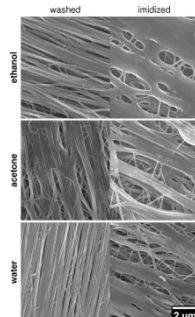
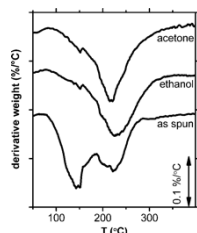


- Slight reduction of fusion



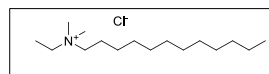
Efforts to Reduce Fusion: Washing

- Worse than drying

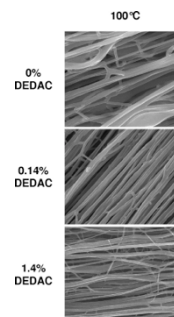


Efforts to Reduce Fusion: Additives

- Dodecylethylidimethyl-ammonium chloride

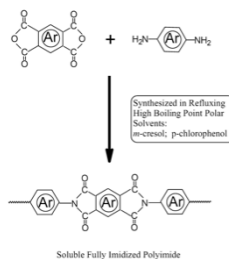


- Fusion was reduced but still present
- Fused NFs are unlikely candidates for high-performance nanocomposites



Alternative Approach to Combat Fusion: Organo-Soluble Polyimides

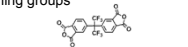
One-step Polyimide Chemistry



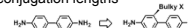
- Pros:
 - Avoid problems with the second step (conditions of chemical or thermal imidization affect the properties of final products)
 - Avoid problems with instability of polyamic acids
 - Completely soluble
 - Better control of structures and morphologies; avoidance of NF fusion
- Cons:
 - Requiring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

Organo-Soluble Polyimide: How?

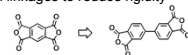
- Introducing fluorine-containing groups



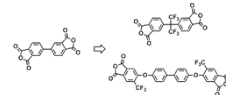
- Bulky pendant groups to disrupt the chain package, twist the chain backbones, and break the conjugation lengths



- Flexible or non-symmetrical linkages to reduce rigidity

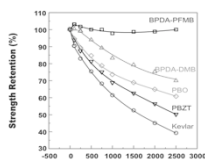


- Copolymerization to interrupt the periodicity along the chain direction and retain structural rigidity

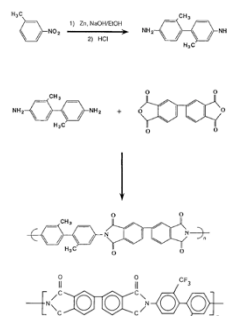


Conventional Fibers from Soluble Polyimides

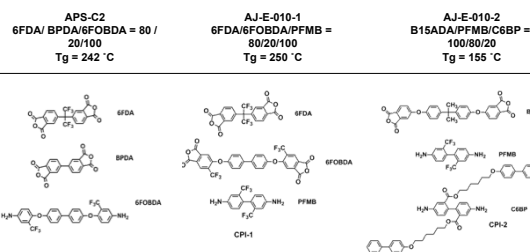
- BPDA/DMB fibers developed by F. Harris, S. Cheng & collaborators at Akron in the 90s
- Strength (3.3 GPa) rivaled the strength of Kevlar 49 and PBZO
- Modulus (130 GPa) was higher than modulus of Kevlar 49



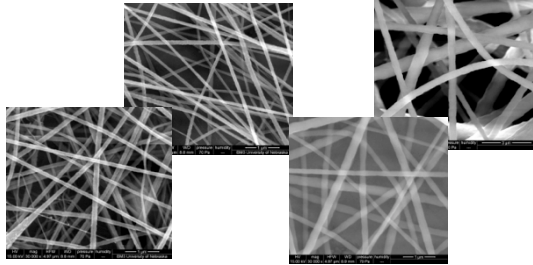
- However, elongation at break was only 2.5%



Initial Polyimides Studied

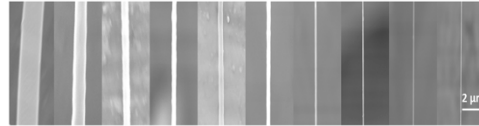


PI Nanofiber Manufacturing



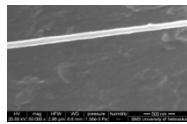
- Single-step nanomanufacturing with no post-processing
- No fiber fusion!

Control of Polyimide Nanofiber Diameters

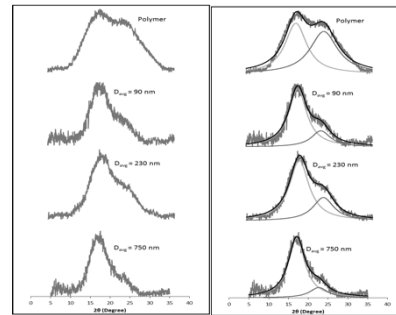


Mechanical Testing Protocol for Individual PI Nanofilaments

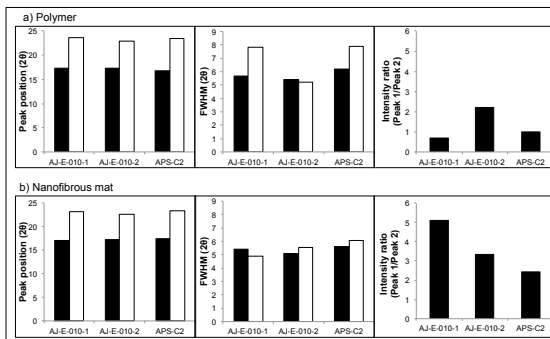
- NanoUTM nanomechanics testing system
 - Large deformation testing through failure
- Specimen fabrication and mounting protocols
 - Long 5-10 mm specimens
 - Results relevant to macro applications
- Evaluation of diameter by SEM
 - Sections adjacent to the tested one to avoid radiation damage effects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



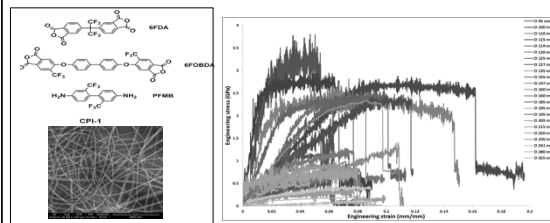
X-Ray Diffraction vs Diameter

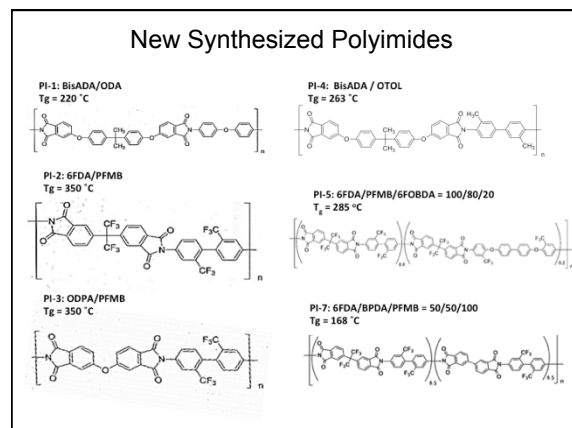
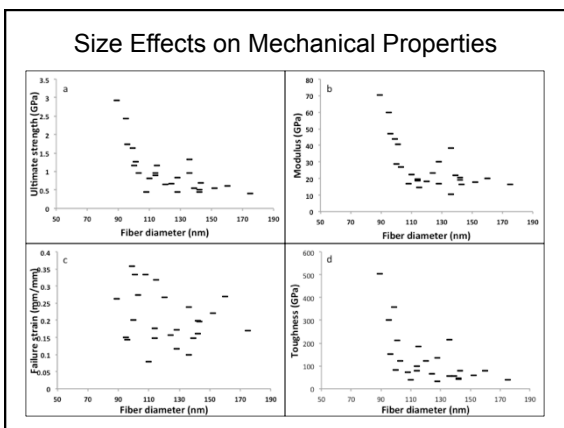
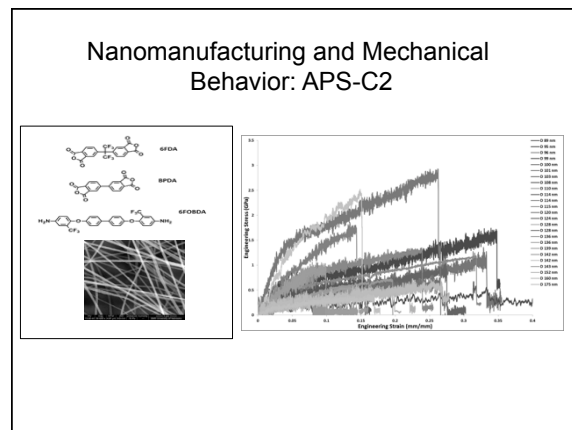
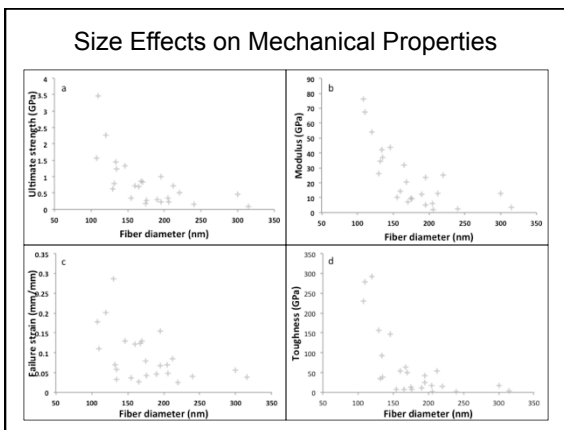
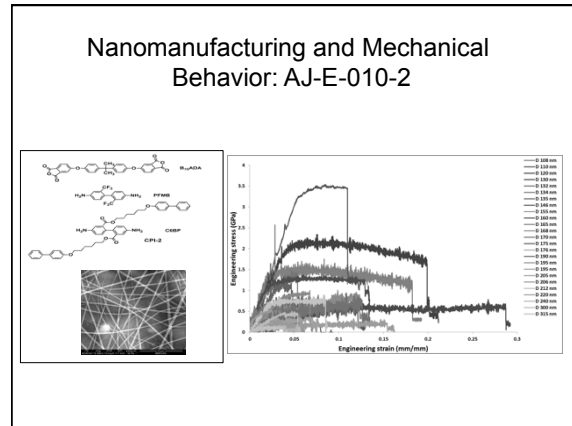
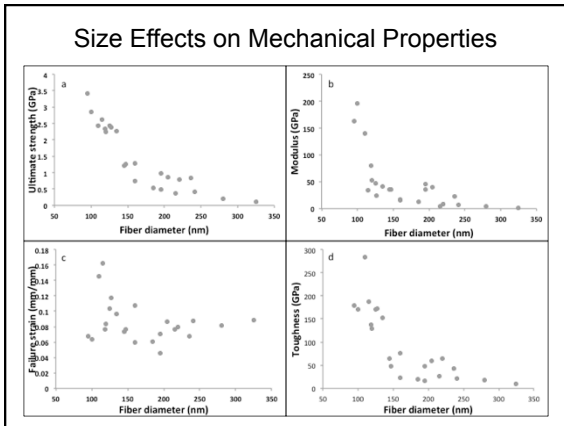


XRD Peak Parameters

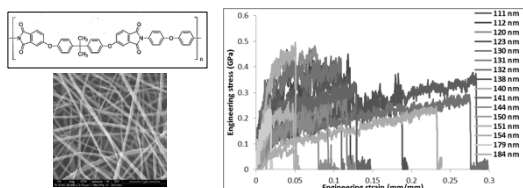


Nanomanufacturing and Mechanical Behavior: AJ-E-010-1

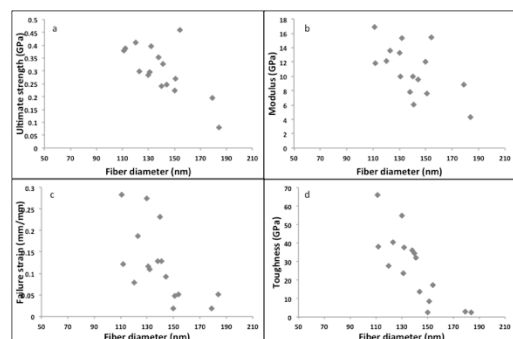




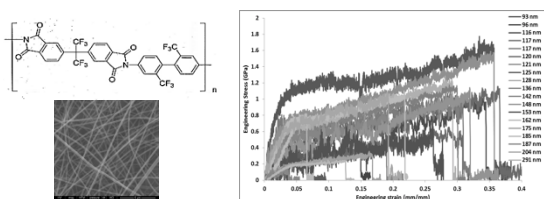
Nanomanufacturing and Mechanical Behavior: 1-BisADA-ODA



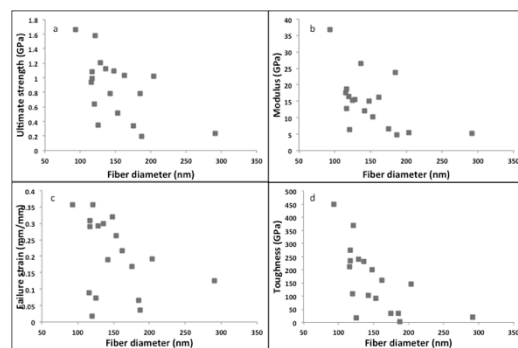
Size Effects on Mechanical Properties



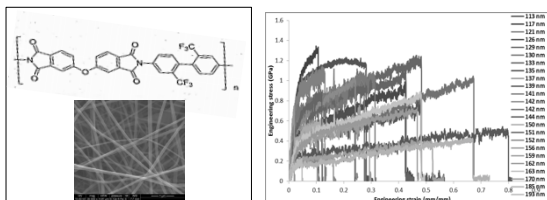
Nanomanufacturing and Mechanical Behavior: 2-6FDA-PFMB



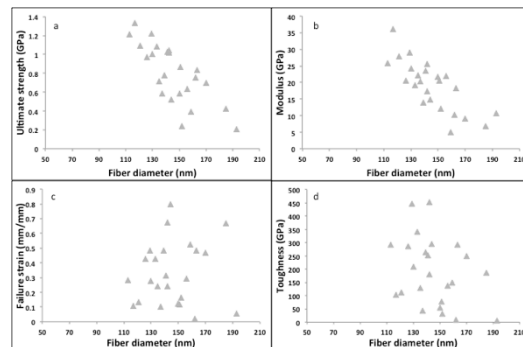
Size Effects on Mechanical Properties



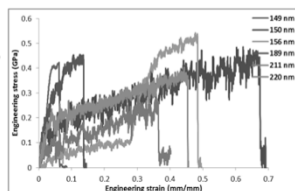
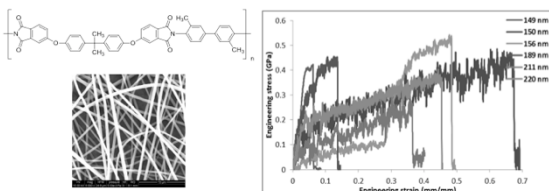
Nanomanufacturing and Mechanical Behavior: 3-ODPA-PFMB



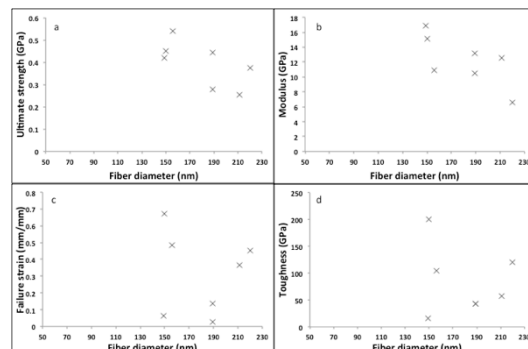
Size Effects on Mechanical Properties



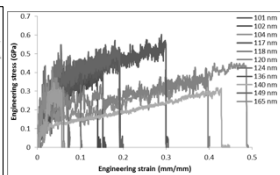
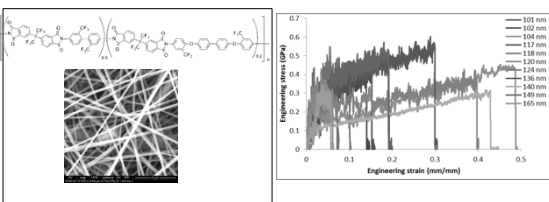
Nanomanufacturing and Mechanical Behavior: 4-BisADA-OTOL



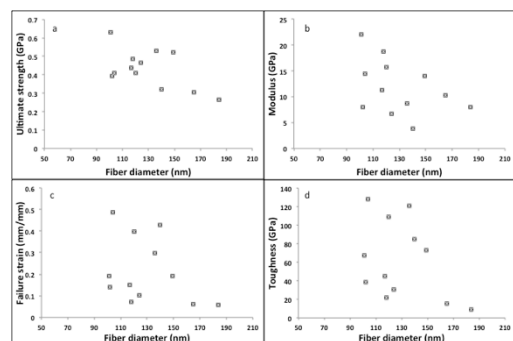
Size Effects on Mechanical Properties



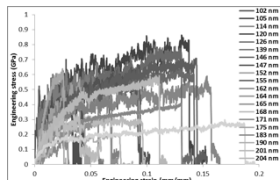
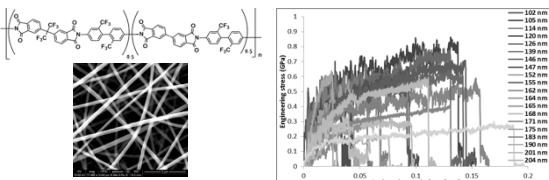
Nanomanufacturing and Mechanical Behavior: 5-6FDA-PFMB-6FOBDA



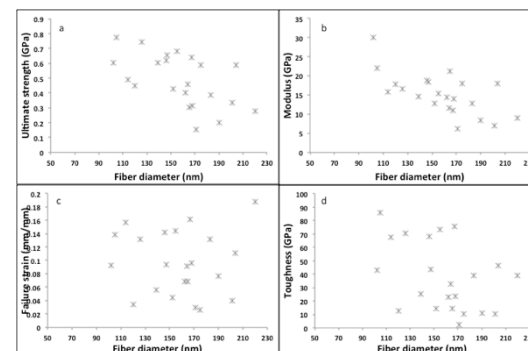
Size Effects on Mechanical Properties



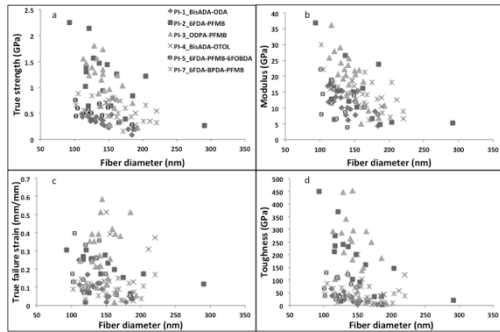
Nanomanufacturing and Mechanical Behavior: 7-6FDA-BPDA-PFMB



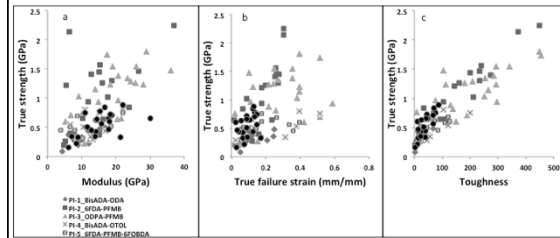
Size Effects on Mechanical Properties



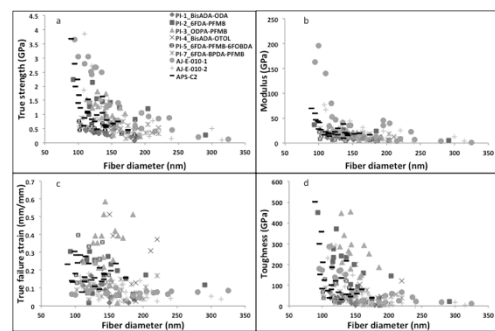
Comparative Analysis of New Polyimide Nanofibers



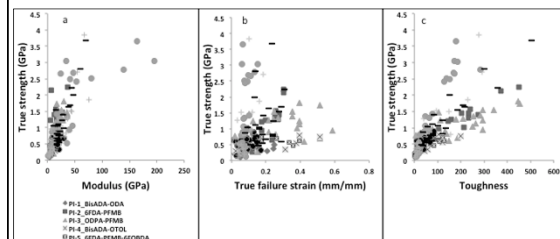
Property Correlations



Comparative Analysis of All Tested Polyimide Nanofibers (9 Families)



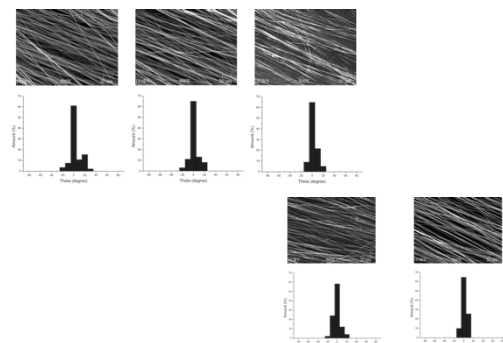
Property Correlations



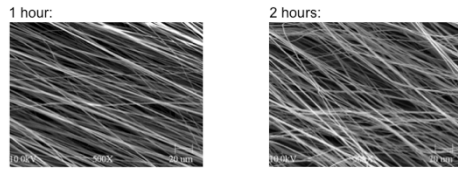
Nanofiber Composites

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

Nanofabrication of Oriented NFs



Nanofabrication of Oriented NFs

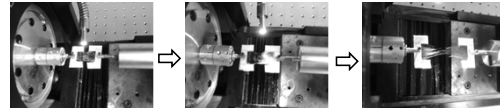


NF Sheet Testing

Aligned

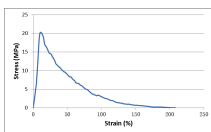


Random

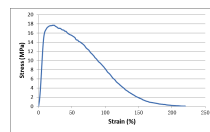


NF Sheet Testing

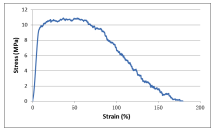
Aligned: 1 hour



2 hours

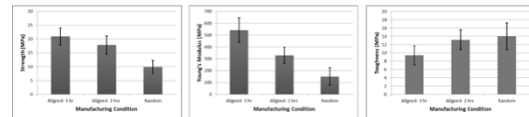


Random



Comparison

	Strength (MPa)	Young's Modulus (MPa)	Toughness (MPa)
Aligned - 1hour	20.92	541.40	9.44
Aligned - 2hours	17.86	329.57	13.16
Random	9.89	150.07	13.99



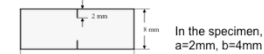
Nanocomposite Testing: Method, Specimen, and Data Reduction

- Fracture Testing: Double Edge Notch Test Stress Intensity Factor KI can be estimated as

$$K_I = \sigma \sqrt{\pi a} * F(a/b)$$

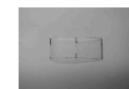
where $F(a/b) = \sqrt{\frac{2b}{\pi a} \tan \frac{\pi a}{2b}}$

- Specimen Preparation

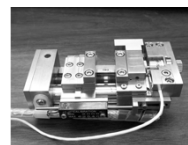


$$F(a/b) = \sqrt{\frac{2b}{\pi a} \tan \frac{\pi a}{2b}} = \sqrt{\frac{2(4)}{\pi(2)} \tan \frac{\pi(2)}{2(4)}} = \sqrt{\frac{4}{\pi} \tan \frac{\pi}{4}} = 1.128379$$

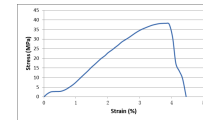
$$K_I = \sigma \sqrt{\pi a} * F(a/b) = \sigma \sqrt{\pi * (2 * 10^{-3})} * F(a/b) = 0.089443 \sigma$$



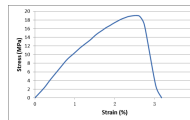
Fracture Testing



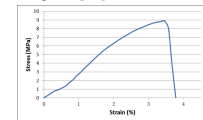
Aligned [0]



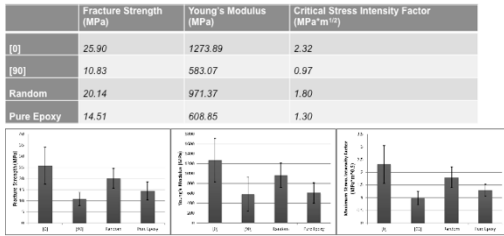
Random



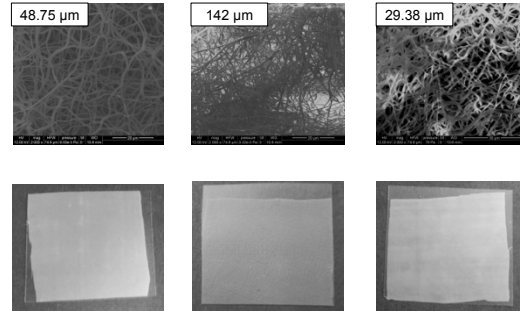
Aligned [90]



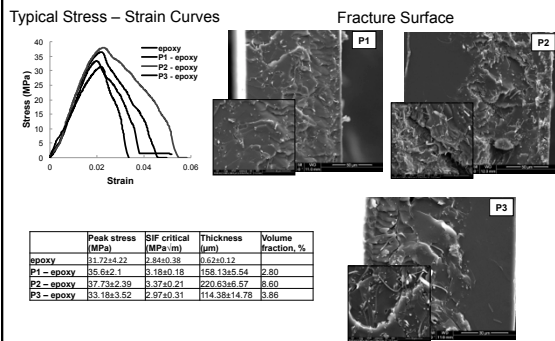
Comparison



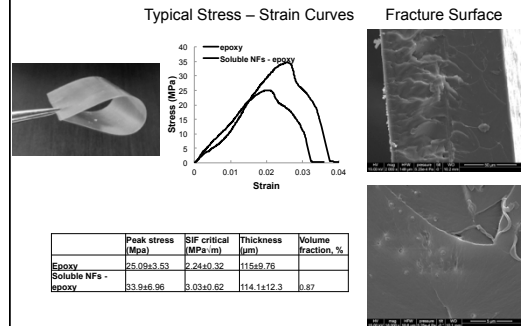
Two Step PI NFs – Epoxy



Mechanical Testing



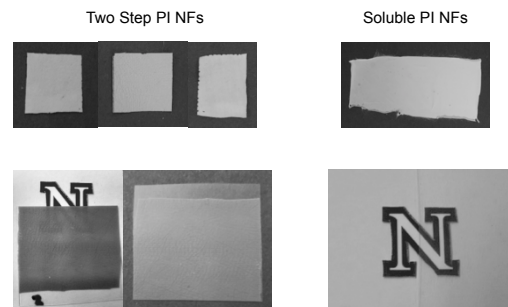
Soluble PI Nanofibers – Epoxy



Comparison: Effect of PI Nanoreinforcement on Fracture Toughness

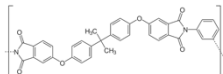
Nanoreinforcement		Absolute Improvement	Volume Fraction	Improvement per 1% V _f
2-step PI NFs	P1	12.2%	2.8%	4.35%
	P2	18.9%	8.6%	2.20%
	P3	4.58%	3.86%	1.19%
Soluble PI NFs		35.1 %	0.87%	40.4%

Optical Transparency



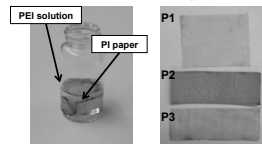
Polyetheramide (PEI) Matrix for PI NFs

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

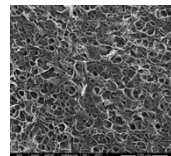
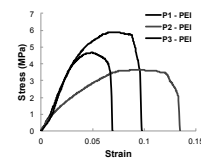


Two Step Polyimide NFs – PEI Composites

Manufacturing



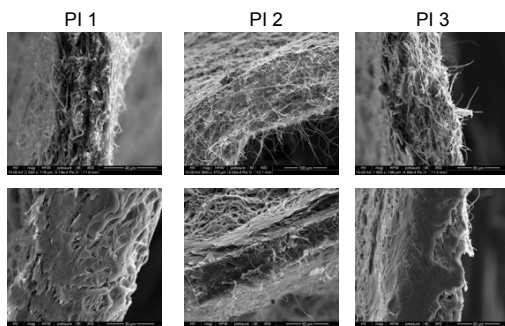
Mechanical evaluation



	Peak stress (MPa)	SIF critical (MPa·m)	ϵ_f (%)	Thickness (μm)	Volume fraction (%)
P1 – PEI	5.8±1.0	0.54±0.09	9.3±0.7	82.5±5.44	24.06
P2 – PEI	5.71±0.29	0.34±0.07	15.6±1.7	111.6±7.86	36.33
P3 – PEI	4.65±0.09	0.45±0.09	6.8±0.5	105±14.58	15.95

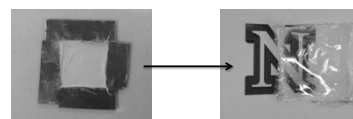
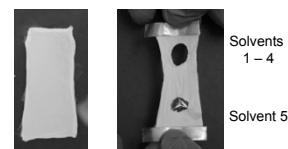
Matrix evaluation in progress

Fracture Surfaces

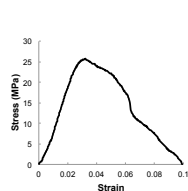


Soluble Polyimide NFs – PEI Composites

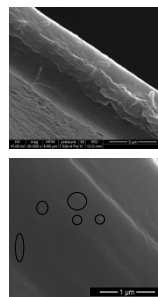
- Matrix: PEI wt. 5-14%
- Solvents tried:
 - DMAC/THF (1:1)
 - DMAC/THF (4:6)
 - DMAC/THF/DMSO (4:4:2)
 - THF/DMSO (1:1)
 - Chloroform



Mechanical Evaluation



Fracture surface



	Peak stress (MPa)	SIF critical (MPa·m)	ϵ_f (%)	Thickness (μm)	Volume fraction, %
Soluble PI NFs	23.03±5.88	2.13±0.05	9.6±0.3	17±5.1	4.4

Comparison: PI – PEI Nanocomposites

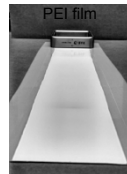
	Peak stress (MPa)	SIF critical (MPa·m)	ϵ_f (%)	Volume fraction, %
2-step PI NFs				
P1	5.8	0.54	9.3	24.06
P2	3.71	0.34	15.6	36.33
P3	4.65	0.45	6.8	15.95
Soluble PI NFs	23.03	2.13	9.6	4.4

- 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 pressclave

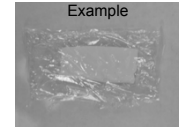


Spin-coater



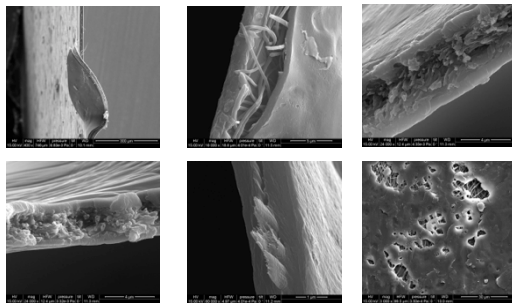
Nanocomposite Manufacturing by Hot Film Pressing

- Nanofibers
 - APS-C2
 - 3-ODPA-PFMB (higher Tg)
- PEI matrix from solution in:
 - Chloroform
 - DMAc
 - No residual solvent

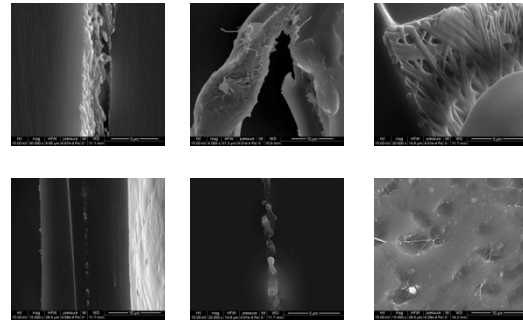


Pressclave conditions:
120-180 psi
Temperatures covered: .
.
.
.

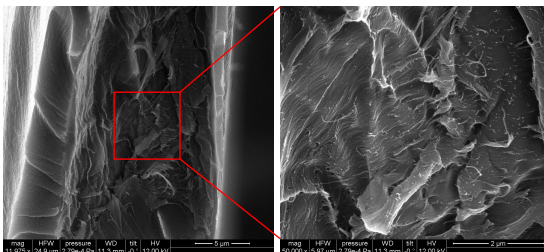
Initial Nanocomposite Manufacturing: Poor Impregnation



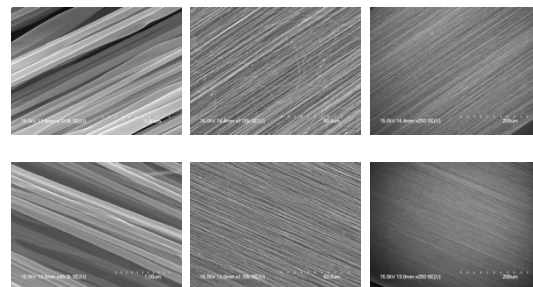
Improved Manufacturing: Nanofiber Survival



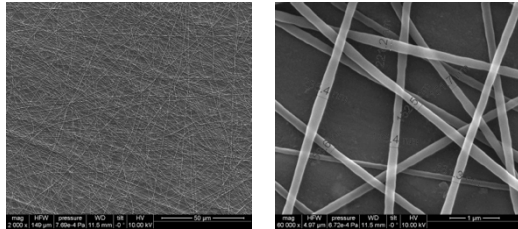
New Manufacturing Breakthrough: Good Impregnation and Nanofiber Survival in PI/PI Nanocomposite



Highly Aligned Dense Sheets of Polyimide Nanofibers by Modeling-Based Optimal Nanomanufacturing



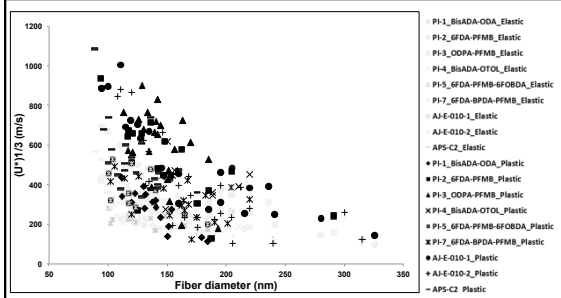
Bulk Production of Ultrafine PI Nanofibers via Process Optimization



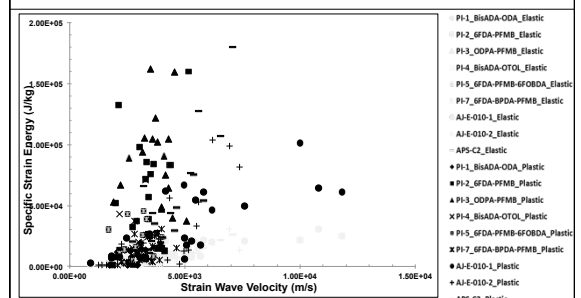
Other Relevant Work

- 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

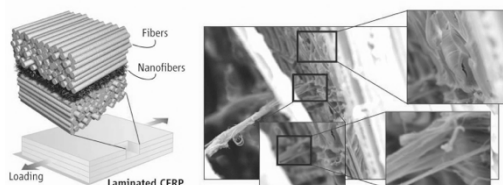
Extraordinary Ballistic (Omega) Parameter of PI Nanofibers



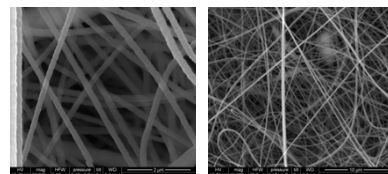
Spec Strain Energy vs. Strain Wave Velocity for PI Nanofibers



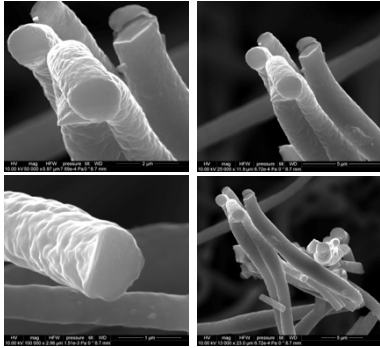
Impact Behavior of Advanced Composites with Nanoreinforced Interfaces



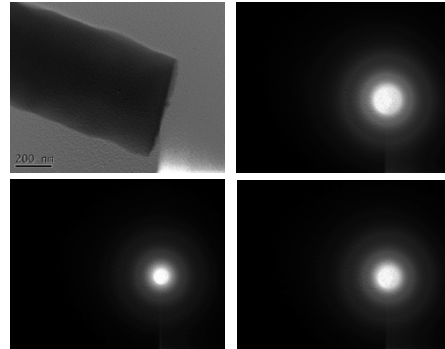
First Continuous Carbon Nanofibers from PI Precursors



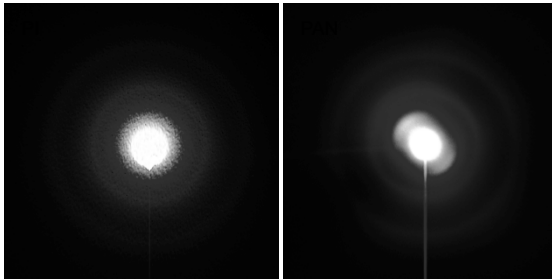
Carbonized PI Fibers



Poor Graphitic Structure



Comparison with PAN-Based CNFs



Poor graphitic structure and high carbon yield of CNFs from PI precursors can lead to inexpensive TOUGH carbon reinforcement

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

➤ Advantage:

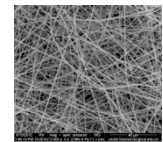
- high porosity (70-90%);
- good accessibility of electrolyte;
- processing simplicity (electrospinning);
- excellent properties of polyimides.

➤ Problems:

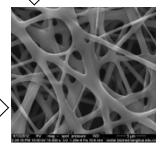
- undesirable pore structure: open pore structure and too large pore size;
- insufficient mechanical properties with thickness <25 μm , hard to produce excellent tensile strength.

<solution>

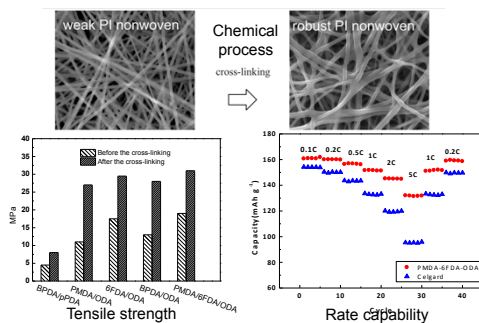
Nanofiber membranes with cross-linking morphologies



Introduce cross-linking structures



Crosslinked PI Nonwoven



Cross-linked PI Nonwoven: Porosity and Electrolyte Uptake

Polyimide	W1/mg	W2/mg	$\Delta W/\text{mg}$	Porosity
BPDA-ODA	19.41	63.70	44.29	79.9%
PMDA-ODA	12.23	41.50	29.27	80.6%
6FDA-ODA	16.03	65.28	49.25	84.2%
BPDA-PDA	11.03	56.92	45.89	87.9%
6FDA-PMDA-ODA	5.97	17.50	11.53	77.1%
Celgard 2400	26.27	45.60	19.33	45.0%

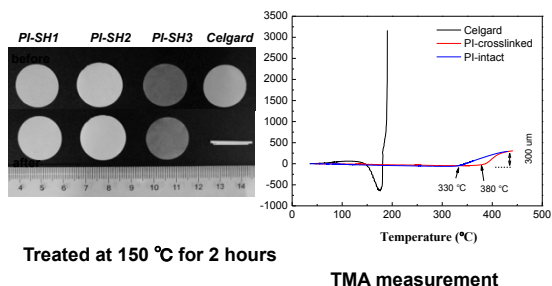
Increasing 77-88%

Celgard is the commercially available product.

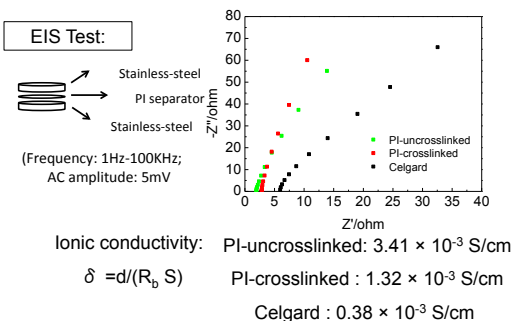
Polyimide	W1/mg	W2/mg	$\Delta W/\text{mg}$	Uptake
BPDA-ODA	18.52	50.38	31.86	172%
PMDA-ODA	11.17	38.75	27.58	247%
6FDA-ODA	17.10	62.00	44.90	263%
BPDA-PDA	12.53	54.00	41.47	331%
PMDA-6FDA-ODA	12.30	45.88	33.58	273%
Celgard 2400	26.27	45.60	19.33	71%

Increasing 170-330%

Cross-linked PI Nonwoven: Thermal Dimensional Stability



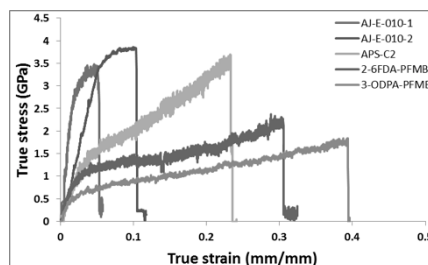
Cross-linked PI Nonwoven: Ionic Conductivity



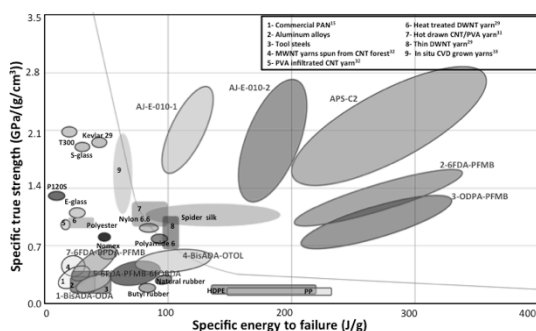
Summary

- 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



ACS NANO
Materials Today, NanoToday, NSF, Materials 360, Science 360, numerous sci outlets

1.

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.

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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)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

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