

METHOD FOR THE PRODUCTION OF CONDUCTIVE POLYMER NANOFIBERS AND NANOFIBER COMPOSITES

G. A. Gaddy,^{1†*} Matthew S. Bratcher,^{1†} Joseph M. Deitzel,² C. Krauthauser,² Sean R. Stevens,³ Chris Ziegler,^{1†} Frederick L. Beyer,^{1†} Max D. Alexander,⁴ Brandon Black⁴ and Hilmar Koerner⁴

¹United States Army Research Laboratory, [†]Sensors and Electron Devices Directorate, Adelphi, MD 20783

[†]Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005

²Center for Composite Materials, University of Delaware, Newark, DE 19716

³University of Delaware, Department of Chemical Engineering, Newark, DE 19716

⁴United States Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio 45433

ABSTRACT

Palladium ion-containing polyamic acid nanofibers have been made using an electrospinning process. The fibers are ~ 500 nm in size and have high aspect ratios.

1. INTRODUCTION

The need for new conducting materials technologies is ever growing with the consumer push to make electronics faster, lighter and less expensive. The Army also strives for improved electronic capabilities in communication, vehicle and other platforms.

Carbon nanotubes (CNTs) have been of interest for electronic applications for nearly 10 years. There have been billions of dollars allocated for this research. The predictions of the electrical properties of CNTs suggest that these materials can provide enormous advances in the field. Although, the applications of CNTs have been highly billed, to date, there remains a disappointing lack of useful CNT applications as electronic device materials. The manufacture of CNTs is expensive, and the techniques used to generate CNTs have seen few improvements over the years.

This research investigates an electrospinning technique to produce nanofibers as the host for metallization chemistries that will afford usable conductive nanofibers. The proposed technique is inexpensive and makes efficient use of starting materials.

Electrospinning is a process which uses an electrostatically driven jet of polymer fluid (solution or melt) to generate submicron - nanometer scale diameter polymer fibers. Typically, a voltage is applied to the fluid which is pumped through a spinnerette. The spinnerette can be a glass pipette, a syringe needle, or simply a hole in a conductive plate. Typical flow rates are very slow, and range from 0.5

to a few tens of mL/hour. Prior to application of the voltage, a drop of fluid will form at the end of the spinnerette. Once the voltage is applied, the drop deforms into the shape of a cone in the presence of the resulting electric field. When the electric field strength at the tip of this cone exceeds a critical value, a jet of fluid will erupt from the apex of the cone and proceed to the nearest target that is at a lower electrical potential, usually a collection plate or drum that is electrically grounded. Initially, the solution jet follows a linear trajectory, but at some critical distance from the spinnerette, the jet begins to whip about in a chaotic fashion. This is commonly referred to in the literature as a bending instability. At the onset of this instability, the jet follows a diverging helical path. As the jet spirals toward the collection mechanism, higher order instabilities manifest themselves resulting in a completely chaotic trajectory. For this reason, electrospun materials are usually collected in quantity in the form of a randomly oriented non-woven mat. However, recent work has demonstrated the dampening of the instability through a variety of methods, and that the electrospun fiber can be collected in ordered patterns.

Although the phenomena of electrospinning has been observed and studied for more than a century, it is only in the last five years that interest in the technology has reached a critical mass in the research community, spurred on by the on going interest in biotechnology and materials engineering at the nanoscale. The recognition that electrospun fibers can be assembled into structures that mimic morphologies in biology, and that the surface area associated with electrospun textiles can be a platform from which nanoscale chemical and biological processes can operate, has driven the explosion of scholarly interest and publications. The goal of the proposed effort will be to use the electrospinning process to fabricate submicron - nanoscale diameter polyimide fibers doped with palladium ions, then to thermally imidize the fibers to produce structures

Report Documentation Page				Form Approved OMB No. 0704-0188		
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1. REPORT DATE 00 DEC 2004		2. REPORT TYPE N/A		3. DATES COVERED -		
4. TITLE AND SUBTITLE Method For The Production Of Conductive Polymer Nanofibers And Nanofiber Composites				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) United States Army Research Laboratory, Sensors and Electron Devices Directorate, Adelphi, MD 20783; Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited						
13. SUPPLEMENTARY NOTES See also ADM001736, Proceedings for the Army Science Conference (24th) Held on 29 November - 2 December 2005 in Orlando, Florida. , The original document contains color images.						
14. ABSTRACT						
15. SUBJECT TERMS						
16. SECURITY CLASSIFICATION OF:				17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 2	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified				

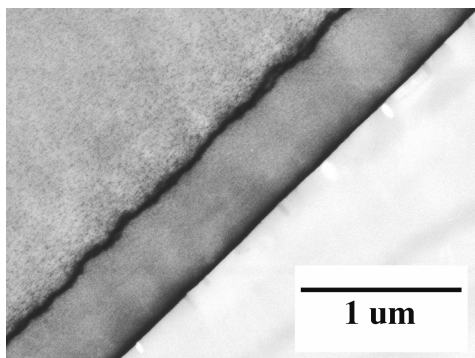


Figure 1: TEM of interlayer formation of Pd in BTDA - ODA polyimide film.

similar to that seen in the film form of the doped resin, Figure 1. These films have unique mechanical properties that are currently being optimized. The films show possible uses as micro optical mechanical systems (MOMs), Figure 2.

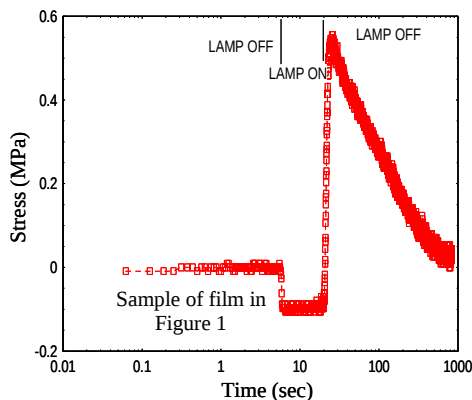


Figure 2: Force measured as a function of illumination and illumination duration. Illuminated with a white light source of 151.5 mW/cm² intensity.

2. EXPERIMENTAL

The process for generating the polymer resin and Pd additive are described in detail elsewhere.¹ Briefly, polyamic acid is synthesized from BTDA and ODA precursors. The precursors are dissolved in DMAC and stirred under nitrogen for ~24 hours. The Pd(S(CH₃)₂)₂Cl₂ was added to the resin and stirred. The end product is a solution of Pd²⁺ doped polyamic acid in DMAC. To produce the fibers, several milliliters of the solution are drawn into a syringe which is placed into syringe pump with a feed rate set at ~1mL/hour. An electrode from a high voltage power supply is attached to the metal syringe needle and a voltage of 7-8 kV is applied. The polyamic acid fibers are collected on a metal screen set at a distance of 10 cm from the tip of the syringe.

3. RESULTS

The method proposed was utilized to generate fibers of polyamic acid both with and without the addition of the Pd metal precursor. The micrographs in Figure 3 show the electrospun fibers. The fibers obtained using the undoped resin yielded fibers with

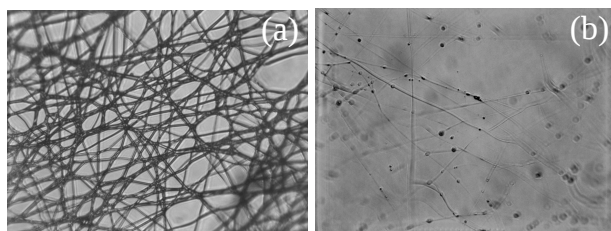


Figure 3: Micrographs of electrospun polyamic acid (a) and Pd²⁺ doped polyamic acid (b). Magnification is 500x.

diameters 1-6 μm. The fibers obtained using the Pd doped resin produced fibers with diameters ~ 500 nm. The fiber mats that are generated from these resins are white in color due to the scattering effect of the small fibers. From the micrographs in Figure 3, the utility of this method becomes evident, in that much longer nano-fibers can be achieved with high aspect ratios.

4. DISCUSSION

Electrospinning Pd²⁺ doped polyamic acid has been demonstrated. The electrospun mats are currently being prepared for thermal imidization to determine whether the surfaces will become conductive and if the unique interlayer structures formed in films of the same resin are produced in the fibers.

REFERENCES

1. Gaddy, G. A., Miner, G. A., Stoakley, D. M., Locke, Edward P., Moore, Rick L., Schultz, John, Creyts, Don, Knotts, Michael. *MRS Proceedings*, **2003**, 797, 255.
2. Gaddy, G. A., Locke, Edward P., Mills, G. Broughton, R. Albrecht-Schmitt, T. E., Miller, M. E. Submitted to *J. Phys. Chem B*, May **2004**.