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14. ABSTRACT
The PIs used the funds from award number W911NF1510353 to purchase an Instron E-3000 ElectroPuls tensile tester. This instrument complements existing tensile analysis instrumentation by expanding our capabilities to include low loads. High performance lightweight composite materials address many of our nation's critical technological challenges including defense systems, sensors, personal protection and armor, vehicle components, and water security. This potential impact is attributed to the careful design, characterization, and modeling of

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Report Title

Final Report: Materials discovery: Characterization equipment to catalyze innovation in materials design

ABSTRACT

The PIs used the funds from award number W911NF1510353 to purchase an Instron E-3000 ElectroPuls tensile tester. This instrument complements existing tensile analysis instrumentation by expanding our capabilities to include low loads. High performance lightweight composite materials address many of our nation's critical technological challenges including defense systems, sensors, personal protection and armor, vehicle components, and water security. This potential impact is attributed to the careful design, characterization, and modeling of composite properties and performance. Our research efforts engineer novel composites that enable a nanoscale understanding of composite matrix failure modes, and thus, direct the assembly of enhanced high performance heterogeneous materials. Although the final composite materials have a high modulus and are resilient, analyzing a full range of crosslinking densities within the polymeric matrix further develops structure-property relationships and demands access to low modulus tensile testing. Moreover, analyzing the effects of environmental conditions, such as temperature, on stochastic model development requires experimental characterization tools that can perform thermomechanical testing on composites with varying moduli. Developing materials for damage detection in polymer matrix composites by using smart composite particles necessitates static and dynamic fatigue testing at low loads, and the information gathered has enabled next generation composite fabrication and implementation.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Green M. D. Integrating macromolecular design with controlled synthesis techniques to produce hierarchical and multifunctional materials. Spring 2017 Nanoscience Seminar Series, Arizona State University, Tempe, AZ, February 13, 2017.
2. Bridge, A. T.; Green, M. D. Solution Rheology: Scaling Theory and Membrane Applications. 2016 AIChE Annual Student Meeting, San Francisco, CA, November 13–14, 2016.
3. Lent, M.; Yang, Y.; Green, M.D. Electrospinning Stimuli-Responsive Fibers at the Nanoscale as Functional Drug Delivery Mats. 2016 AIChE Annual Student Meeting, San Francisco, CA, November 13–14, 2016.
4. Tronstad, Z.; Green, M. D. Tailoring the Hydrophilicity of Electrospun Membranes for Water Filtration. 2016 AIChE Annual Student Meeting, San Francisco, CA, November 13–14, 2016.
5. Green, M. D.; Yang, Y.; Hong, H.; Romero, F. N. Multiblock ionomers for membrane applications. 2016 AIChE Annual Meeting, San Francisco, CA, November 13–18, 2016.
6. Yang, Y.; Green, M. D. Multi-Block Copolymer Membranes for Water Purification and Desalination. National Graduate Research in Polymer Chemistry Conference, Akron, OH, USA, June 19-22, 2016.
7. Felmly, J. W.; Pathak, A.; Green, M. D. Tuning the Assembly of Polyelectrolyte-based Micelles. National Graduate Research in Polymer Chemistry Conference, Akron, OH, USA, June 19-22, 2016.
8. Wang, M.; Yang, Y.; Felmly, J. W.; Pathak, A.; Green, M. D. Poly(ethylene glycol) (PEG) Based Engineering Ion-containing Block Copolymers. National Graduate Research in Polymer Chemistry Conference, Akron, OH, USA, June 19-22, 2016.
9. Green, M. D. Engineering nanostructured ion-containing block polymers for membrane separation applications. 2016 NAMS Annual Meeting, Bellevue, WA, May 21–25, 2016. (Presentation delivered in Awards Session)
10. Green, M. D. Stimuli-responsive polymers as gene carriers. 2016 MCTB Symposium, Tempe, AZ, April 2, 2016.
11. Romero, F. N.; Hong, H.; Green, M. D. Engineering ion-containing block copolymers as next-generation water purification membranes. 251st ACS National Meeting, San Diego, CA March 12-17, 2016.
12. Green, M. D. Photoresponsive polymers for nucleic acid adhesion. 2016 Adhesion Society Meeting, San Antonio, TX, February 21–24, 2016.
13. Green, M. D.; Singh, P.; Yang, Y.; Hong, H.; Altraiki, M.; Romero, F.; Gaustad, J. Multiscale ionomeric block polymer assemblies for membrane applications. 2015 AIChE Annual Meeting, Salt Lake City, UT, November 8-13, 2015.
14. Green, M. D.; Singh, P.; Yang, Y. Ionomeric block polymer membranes for filtration applications. 250th ACS National Meeting, Boston, MA, August 16-20, 2015.

Number of Presentations: 14.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

PI Matthew Green: 2016 North American Membrane Society (NAMS) Young Membrane Scientist Award

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Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Most of the progress achieved during this reporting period included the successful purchase, delivery, and installation of the proposed instrument: the Instron E-3000 ElectroPuls tensile analyzer. The E-3000 came equipped with an environmental chamber and high temperature grips, which adds versatility to the suite of analytical instrumentation currently available for characterizing thermomechanical properties. This instrument offers a wide temperature range of operation from -100 to 350 °C and accurately determines the stress and strain of samples under tension. The unit offers a tremendous dynamic load capacity range from 30 to 3000 N and a static load capacity with an upper limit of 2100 N. The load accuracy is within +/- 0.5% of any reading. Additionally, frame speeds ranging from 0.05 mm/min to 102 m/min offer testing conditions for a wide range of materials. Finally, Instron's onsite training and online customer support is accessible and convenient, and the user-friendly WaveMatrix software ensures hassle-free operation of the instrument.

As described below, the Instron E-3000 captures the necessary features to support our current research efforts and enable new directions. The instrument accurately measures the tensile properties of polymer matrix composites, and the low load capacity (30 N) enables the analysis of softer composites, which were previously not suitable for fatigue analysis with the instrumentation available. Furthermore, the addition of an environmental chamber provides access to relevant testing conditions for materials employed in harsh environments such as excessive heat, high altitudes, and even submersed in saline solutions. Obtaining thermomechanical property behavior over the entire temperature range of the application window is now possible and allows for more accurate prediction of the performance through multiscale stochastic modeling.

The subsequent sections of the progress report are organized into two parts: compressive tests on soft hydrogels (work led by Prof. Lenore Dai) and the analysis of mechanoresponsive polymer matrix composites (work led by Prof. Matthew Green).

Compressive test of double network hydrogels using Instron E3000:

The Instron E3000 was able to perform the compressive tests on synthesized double network hydrogels in their wet state. All the samples were soaked in water at room temperature for 48 hours after they were synthesized to reach swelling equilibrium prior to the test. The tests were all carried out at the room temperature, and three different compression strain rates, 0.5 mm/min, 0.05 mm/min, and 0.005 mm/min, were explored in the studying the study the effect of ramp rate. Due to the toughness of the hydrogels based on the double network system, each sample was compressed to the inhibition position of the instrument to maximize the measureable range of the samples' stress-strain profile.
Two main goals were achieved by the above compressive tests via Instron E3000: 1) the overall stress-strain curves of the synthesized hydrogels were obtained; and 2) the effect of strain rate on the responding mechanical properties of the synthesized hydrogels. Figure 1 shows the enhanced mechanical property of PAAm-PAAc double network hydrogel (black) in comparison to pure PAAm (red) and PAAc (blue) single phase hydrogels as control samples. Next, Figure 2 shows the effect of strain rate in responding stress PAAm-PAAc double network hydrogels.
As noted above, the ability to control the temperature, environmental conditions (e.g., humidity), and potentially submerge the hydrogels are future studies of interest that will be explored using the acquired instrument.

Analysis of carbon nanotube-loaded mechanoresponsive polymer matrix composites:

The following summarizes experiments performed as a part of the work supported by the ARO through award number: W911NF-16-1-0271. Polymer matrix composites (PMCs) offer design solutions to produce smart sensing, conductive, or high performance (i.e., excellent thermomechanical properties) composites for a number of critical Defense applications, including: lightweight armor, machine components, electronic casings, antennae, and conduit. Nanoparticle additives, in particular, carbon nanotubes and/or metallic nanoparticles, have been investigated for their ability to improve the conductivity, thermal stability, and mechanical strength of traditional composites. However, a detailed understanding of nanoparticle dispersion, matrix-nanoparticle adhesion, and the composite morphology has not been developed fully; furthermore, the ability to predict composite failure mechanisms will improve PMC design and longevity. Thus, the following work seeks to tune the interactions between fluorescent quantum dots (QDs), fluorescently labeled carbon nanotubes (CNTs), and novel matrix chemistries to probe nanoparticle dispersion, composite morphology, and composite failure mechanisms. In particular, we will summarize our efforts to load fluorescently modified CNTs into polymer matrices as well as combinations of the QDs and the CNTs. The nanoparticles are selected such that they form a FRET pair, which enables observations of changes in fluorescence when the materials are placed under a mechanical stress or strain.

The composites investigated were comprised of a 2000 g/mol jeffamine crosslinker cured with bisphenol-A. These networks produce rubbery, elastomeric networks. Previous work in our lab investigated the dynamic mechanical behavior of these networks with varying amounts of CNTs added, showing that 0.5 wt% CNTs produced the optimal storage modulus and glass transition temperature. Figure 3 shows the stress-strain curve for a network to which 0.5 wt% fluorescently modified CNTs were added. The CNTs used were acid modified upon arrival, in other words modified with a carboxylic acid group. As observed, the networks exhibit a stress at break of approximately 0.24 MPa and a strain at break of 7000%. Also, the networks show a steady increase and constant slope at low strains, indicative of a material with high strength.

Next, networks containing both the fluorescent QDs and the dye-labeled CNTs were prepared. The equivalents of CNTs and QDs were kept constant during the formation. Figure 4 shows the stress-strain curve for the resulting composite, which, as expected, shows a slight decrease in the stress at break. The networks exhibited a stress at break of approximately 0.18 MPa and a strain at break of 7900%. Thus, the networks stretch to a greater extent, but to a lower stress. Also, the jagged curve indicates some potential slipping within the grips during the test, indicating further experiments are needed.

Now, through the tensile analyses presented herein and through previous dynamic mechanical tests, we can begin to utilize the dynamic capabilities of the E-3000 mentioned above. In this way, we can perform long term tests on the composites and observe changes in fluorescence associated to mechanical fatigue. In this way, a time-resolved and more accurate model of the nanoscale motion in composites under stress or strain can be developed. Additionally, testing conditions that mimic extreme environments such as high or low temperatures, arid or humid conditions, low or high pressures, underwater and saline conditions, etc., will be explored.

Summary:

Following the successful installation of the instrument, the research groups that contributed to the DURIP proposal (i.e., PI Matthew Green, and Co-PIs Aditi Chattopadhyay, Lenore Dai, and Mary Laura Lind) have begun to test the applicability of the instrument for samples developed within each lab. Student training and sample testing are well underway and the data shown herein provides an overview of recent efforts and exciting new data. User training and interest in the instrument have continued to expand, which will have a profound impact on DoD-supported research efforts at ASU.

Figures 1-4 are included in the attachments.

Technology Transfer

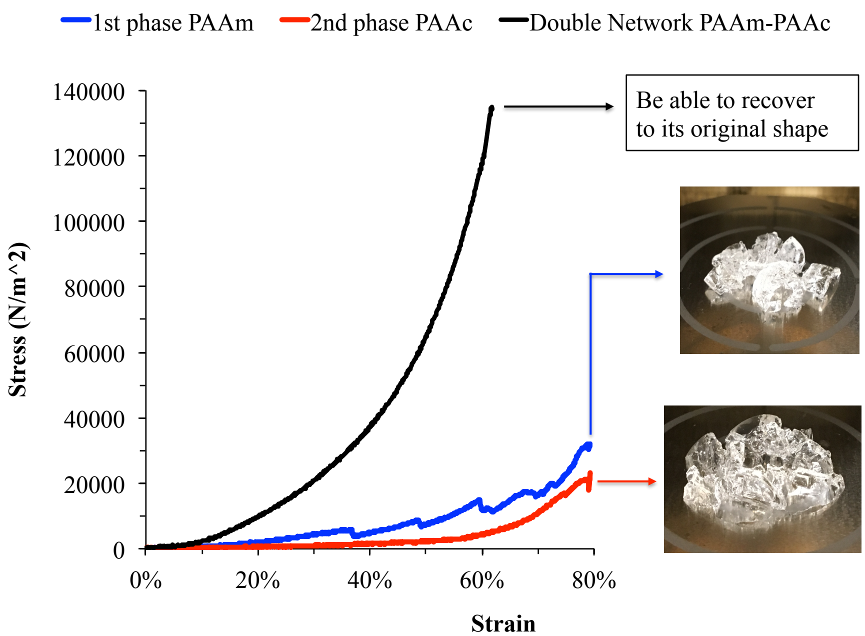

Figure 1 The stress-curve from compressive test using Instron E3000 shows the enhanced mechanical property of PAAm-PAAc double network hydrogel (black) in comparison to pure PAAm (red) and PAAc (blue) single phase hydrogels as control samples.

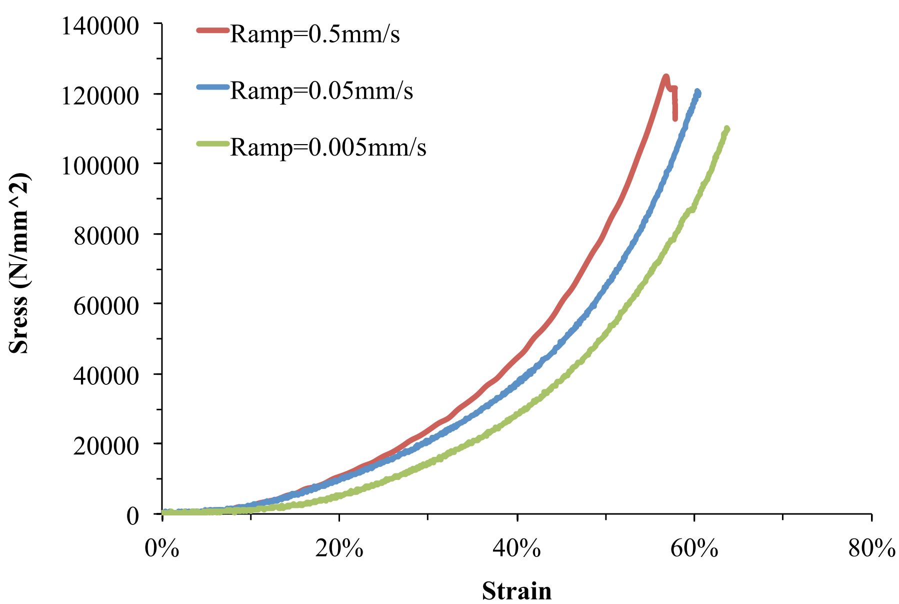

Figure 2. Effect of strain rate in responding stress PAAm-PAAc double network hydrogels.

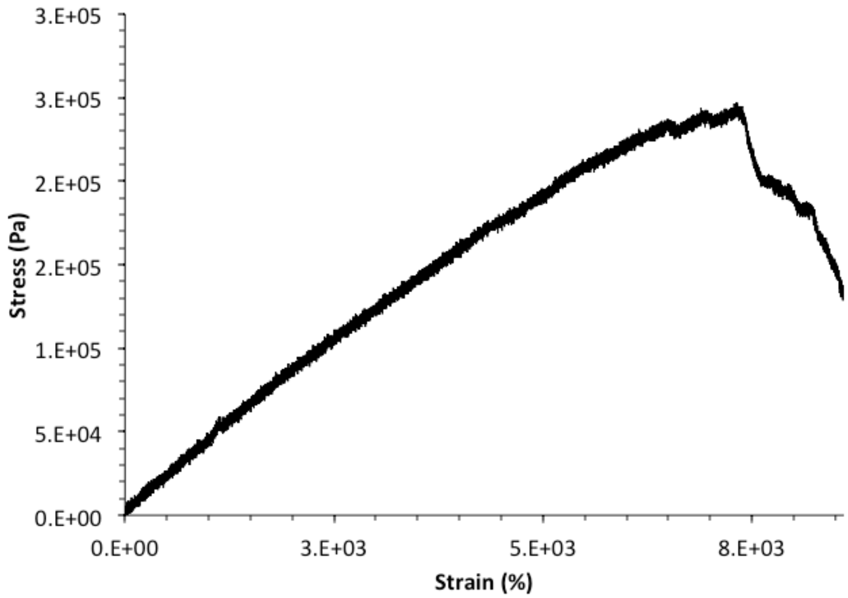

Figure 3. Strain-stress curve for a jeffamine2000-Bisphenol-A network modified with 0.5 wt% CNTs modified with a fluorescent dye.

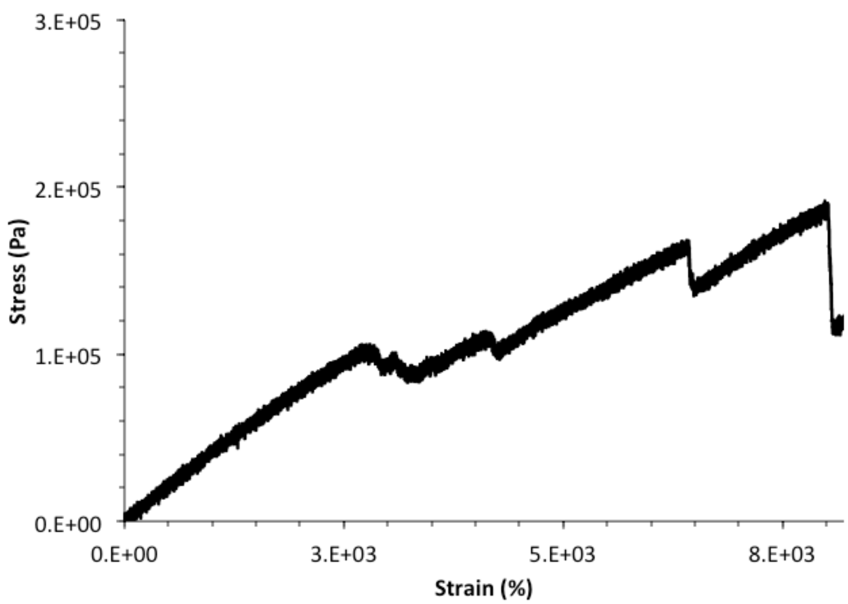

Figure 4. Stress-strain curve for a jeffamine2000-Bisphenol-A network modified with 1:1 CNTs:QDs, at 0.5 wt% of CNTs.