

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 19-07-2017		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-May-2013 - 30-Apr-2017	
4. TITLE AND SUBTITLE Final Report: Towards Ultra-light Weight Hybrids, Foams and Green Bodies: Structure-Property Relationships in novel Polymer grafted nanoparticles			5a. CONTRACT NUMBER W911NF-13-1-0132		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 206022		
6. AUTHORS Subramanian Ramakrishnan			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Florida A&M University 1700 Lee Hall Drive 400 FHAC Tallahassee, FL 32307 -3200			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 62885-MS-REP.6		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Nanoparticles and their mixtures have emerged as critical technology enablers for a wide range of aerospace and commercial applications, including pulsed power capacitors, body armor, multifunctional composites, active layers for energy harvesting devices, and inks for printed flexible electronics and displays. In these applications, control of nanoparticle arrangement and distribution in a polymer matrix is the most critical factor determining the final processing and property suite. Work in the final year resulted in one journal publication in collaboration with Dr. Vaia. Three manuscripts have been developed but not published yet (1 is submitted). Graduate student Esham					
15. SUBJECT TERMS composites, X ray scattering					
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT		15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		Subramanian Ramakrishnan
				19b. TELEPHONE NUMBER 850-410-6159	

RPPR
as of 01-Sep-2017

Agency Code:

Proposal Number:

Agreement Number:

Organization:

Address: , ,

Country:

DUNS Number:

Report Date:

for Period Beginning and Ending

Title:

Begin Performance Period:

Report Term: -

Submitted By:

EIN:

Date Received:

End Performance Period:

Email:

Phone:

Distribution Statement: -

STEM Degrees:

STEM Participants:

Major Goals:

Accomplishments:

Training Opportunities:

Results Dissemination:

Plans Next Period:

Honors and Awards:

Protocol Activity Status:

Technology Transfer:

Scientific Progress

AMSRD-ARL-RO-SI Proposal Number: 62885-MS-REP

PI: Subramanian Ramakrishnan

1) I am happy to say a paper has been published in ACS Macro Letters: (abstract attached below)

Che, J., Jawaid, A., Grabowski, C., Chakkalakal, G., Ramakrishnan, S., & Vaia, R. (2016). Stability of Polymer Grafted Nanoparticle Monolayers: Impact of Architecture and Polymer–Substrate Interactions on Dewetting. *ACS Macro Letters*, 5(12), 1369-1374.

Abstract: The stability of polymer thin films is crucial to a broad range of technologies, including sensors, energy storage, filtration, and lithography. Recently, the demonstration of rapid deposition on solid substrates of ordered monolayers of nanoparticles (PGN) has increased potential for inks to additively manufacture such components. Herein, enhanced stability against dewetting of these self-assembled PGN films (gold nanoparticle functionalized with polystyrene (AuNP-PS)) is discussed in context to linear polystyrene (PS) analogues using high throughput surface gradients: surface energy (20–45 mN/m) and temperature (90–160 °C). PGNs exhibit a lower surface (γ_p) and interfacial (γ_{sp}) energy relative to linear polymers, which results in increased thermal and energetic stability by 10–25 °C and 5–15 mN/m, respectively. This enhanced wetting–dewetting transition is qualitatively consistent with the behavior of star macromolecules and depends on the architecture of the polymer canopy. Increased film stability through canopy architecture expands the manufacturability of thin film hybrids and refines post processing conditions to maximize local PGN order.

2) The following paper has also been published

Frketic, J., Ramakrishnan, S., & Dickens, T. (2017). Automated Manufacturing and Processing of FRP Composites: An Additive Review of Contemporary and Modern Techniques for Advanced Materials Manufacturing. *Additive Manufacturing*, 14, 69-86.

Abstract: High throughput automated techniques are nowadays playing a key role in polymer composite manufacturing in a number of industries such as automotive and aerospace. There is a need to produce high volume parts efficiently. Automated manufacturing methods such as automated tape layup and automated fiber placement can produce composite parts efficiently, and with the advent of additive manufacturing the complexity of these components are increasing. This paper will review contemporary composite manufacturing methods filament winding, automated tape layup, and automated fiber placement, and the newer automation techniques of robotic pick-and-place and continuous tow shearing. It also addresses recent advances in composite additive manufacturing using vat photopolymerization, binder jetting, material extrusion, sheet lamination and powder bed fusion. Methods, materials and testing results of the manufactured components will be discussed.

3) In the area of polymer grafted nanoparticles – we expect this paper to be published soon (I apologize for the delay).

Structure, Rheology and Thermal Properties of Polymer Grafted Nanoparticles Diluted with Free Polymer Chains

Polymer tethered nanoparticles are set of hybrid materials has achieved much research attention nowadays because of the synergistic effect and fine tuning of polymer corona and core nanoparticles to develop composite materials of desired properties. Contrary to the reported studies of dispersing low volume fraction (ϕ) of surface tethered nanoparticles in compatible polymer matrix, here we investigate the structure and the influence of conformation towards the thermal and shear rheology of bulk polystyrene (PS) tethered silica nanoparticles (NPs) diluted with low ϕ_{PS} of free polystyrene chains. Most of the published studies are based on composites and their properties with tethered nanoparticles of high graft densities (σ). In order to study the influence of conformation, we have synthesized two sets of PS grafted silica NPs in two grafting limits: low ($\sigma = 0.06$ chains/nm², $M_{n, D1} = 55$ kDa) and high ($\sigma = 0.33$ chains/nm², $M_{n, A1} = 28$ kDa) graft densities. Either sets of PS grafted nanoparticles were blended with $\phi_{PS} \sim 0.05$ of free PS chains having molecular weights below (10 kDa) and above (100 kDa) entangled molecular weight (M_e) respectively for dilution studies. Thin and bulk film morphology of particles and blends their blends were characterized by microscopy (TEM) and x-ray scattering experiments (GISAXS and SAXS). Studies shows the influence of glass transition T_g (obtained from systematic DSC experiments) on total volume fraction (V_F) of pristine randomly packed low graft *D1* particles and closely packed HCP like structure of densely grafted *A1* and the influence of low ϕ_{PS} free polymer chains in respective blends. It is found that as the total volume fraction increases the resultant T_g values decreases. Master curves constructed from oscillatory shear rheology measurements shows the influence of conformation, graft density (σ) and graft molecular weight ($M_{n, g}$) of pristine tethered nanoparticles and the added free polymer on storage moduli G' .

4) 3D printable low-k nanocomposite materials: Dielectric and magnetic properties of nickel and iron oxide loaded polystyrene

We are about to submit the paper for publication. The work was carried out by graduate student Faheem Muhammed who was a recent recipient of the DOD SMART fellowship.

The development and miniaturization of electronics has increased the need for high-density, high-speed, and high-frequency microelectronic packaging. In order to reduce electromagnetic interference, a low-k approach is necessary. The incorporation of magnetic particles into highly insulative mediums offers the benefits of attenuating electromagnetic incident waves, while featuring low dielectric constants and minimum dielectric losses. Soft-magnetic nanoparticles have been shown to enhance EMI insulation by converting AC fields to thermal energy and by reflection due to the free electrons in their valence shell. The inclusion of sufficiently small particles (<80 nm) further enhances this effect due to a larger surface-to-volume ratio, single magnetic domain, minimal magnetic hysteresis, and a greater impact on the dielectric/magnetic loss in comparison to bulk material. Polystyrene was chosen based upon future printability, filler compatibility, and high dielectric breakdown voltage. The efficacy of the fillers enhancement to the nanocomposite system was determined through dielectric spectroscopy and magnetic measurements.

5) Research Carried out at Army Research Labs, Aberdeen Maryland.

Graduate student Faheem Muhammed spent 9 months at Army Research Labs working on research projects with Larry Holmes. Following is a summary of the research projects. We are about to sign a CRADA with ARL and will carry forward the work and publish it. We are grateful to DOD for giving us the opportunity to send the student to ARL. *This has resulted in the student receiving the DOD SMART fellowship – first at FAMU and the first SMART fellowship in the Department of Chemical and Biomedical Engineering.* Given below is a summary by Faheem himself of the different projects he had worked on at ARL.

5a) Additive manufacturing of reclaimed materials

Importance: On bases/military site there is an excess of waste materials that can be repurposed to address quality of living concerns of the soldier. There is a wide array of thermoplastics utilized in shipping and food packaging that can be used as additive manufacturing feed material. The combination of readily available filler materials (sieved sand, metallic scraps) and reclaimed thermoplastics could provide the means for immediate repair of common equipment failures. Currently, replacement parts must be shipped into combat areas. This causes delays in critical need repairs.

Key Questions that need to be addressed for this technology: (1) Can the use of inhomogeneous filler material provide the necessary rigidity for replacement parts? (2) Is particle orientation a concern - filler materials may be a combination of spheroids and rod-like particles. (3) Reproducibility- Would there be variations in the printed parts due to the filler/thermoplastic material caused by inhomogeneous filler orientation? (4) What effects would thermal expansion/retraction of thermoplastics during/post printing cause? Environmental resistance - Can the composite material perform in strenuous conditions?

Approach: Identify the key plastics that are used on site and analyze the material properties. Simulate the conditions faced by the soldiers, by utilizing filler materials that would be available to them. Demonstrate reproducibility in printing and material properties. Produce CAD files and example structures that would address common equipment failures

What Was Done: Viability of Meal-Ready-to-Eat (MRE) food packaging as thermoplastic materials was tested. Dog bone structures were made for mechanical testing, Elongation studies were carried out to test tensile strength and rigidity.

Key Findings/Results: Print Reproducibility was found to be problematic due to the polymer retracting when cooled. The printer head clogged consistently at the print conditions and higher temperature prints caused the thermoplastic to start decomposing. Slower print speeds caused the printed structure to delaminate from the surface.

Future Plans: (1) Simulate sieved sand fillers with fumed silica microparticles. (2) Test material properties as function of particle loading/size and ensure mechanical properties are suitable for replacement parts. (3) Use a Heated Chamber for printing - by printing at isothermal conditions (ambient air $T = \text{Bed } T$) the reproducibility of printed parts should increase. (4) Utilization of flexible dual printer head should reduce print clogging due to the design of the head.

5b) Materials Design for frequency-dependent applications

Importance: The ability to tune signaling/shielding structures facilitates the rapid deployment of counter measures to enemy attack. Composite structures can be dielectrically modified to

attenuate specific frequencies which would provide an effective deterrent to signal interception. Composite materials can also act as waveguides that would enhance certain frequencies with minimal energy loss. Strategically placed structures could direct mission-critical signals over large distances while (1) reducing energy requirements (2) limiting signal attenuation due to outside forces (3) prevent disturbances due to electromagnetic pulse (EMP) device. Electromagnetic interference shielding can be achieved through the inclusion of metallic/ceramic particles in polymer matrices. Shielding would prevent EMP attacks by effectively reflecting/absorbing the pulse wave before electronic failure

Key Questions: Electrical Properties - Can the dielectric properties be tuned to reflect/absorb specific frequencies? Can the breakdown voltage of materials be increased by the addition of magnetic/ceramic/carbon filler? Can the dielectric properties be predicted by theoretical/experimental models? Accurate predictions would aid in the rapid deployment of countermeasures

Approach: (1) Develop composite materials that effectively shield/enhance specific frequencies. (2) Demonstrate tunability that would allow broadband approaches. (3) Simulate attenuation/enhancement of signals in modeling software to anticipate properties and rapid development.

What was Done: (1) Constructed nanocomposite of different loading and particle type. (2) Utilized magnetic/non-magnetic particles - Magnetic nanoparticles have been shown to enhance electrical insulation by converting AC fields to thermal energy. Metallic nanoparticles have been shown to enhance the dielectric constant due to particle size and dispersion. (3) Used theoretical models to characterize composites.

Key Findings: (1) The dielectric properties exhibited a size-dependence at the nanoscale. (2) Particle dispersion had a large effect on the dielectric constant - Particles with incompatible surface coatings were suspected to be aggregated and aggregation caused the dielectric constant to be greatly increased at low volume percentages. (3) At lower frequencies, surface polarizability, and particle interactions affects the dielectric properties to a high degree which in turn affects the ability to model the system.

Future Plans: (1) Use different polymer matrices depending on the application a) Insulating polymers - polymers of a lower dielectric constant would provide enhanced shielding. b) Conducting polymers c) Thermoplastic/Thermosets - thermoplastic-based composites could be recycled and repurposed to reduce waste and high particle loadings can be achieved in thermoset polymers which would allow for more conductive composites. (2) Utilization of composite materials in additive processes.

5c) Development of composite materials for optical applications

Importance: Gold nanorods have demonstrated tunable plasmonic behavior based on the morphology of the particles. Future development of optically-based applications (i.e. optical computing, high-k dielectric material, negative index materials) requires a two-fold approach – (1) Intelligent chemistry and particle synthesis of monodispersed systems and (2) Materials engineering to address application-specific design requirements - composite materials that utilize clear materials (SiO₂, acrylic polymers) with plasmonic filler material could effectively transform incident light to shorter wavelengths that are not visible to the naked eye. This type of material could offer camouflage and aid in soldier safety

Key Questions: (1) What is the effect of shear-orientation on printed composite optical properties? (2) Does the thermal processing of the materials effect the final plasmonic properties?

Approach: (1) Demonstrate the ability to reproduce gold/silver particles with tight size/morphological distributions. (2) Produce structures that uniformly incorporates plasmonic materials in acrylic polymers. (3) Utilize modeling to predict the required material properties for visible light attenuation.

What Was Done: (1) 3D printed structures utilizing gold nanorods of different surface chemistries and particle anisotropy - Particles of various surface coating (to provide compatibility/dispersibility in solvent) were combined with clear acrylics to study the UV-absorption properties.

Key Findings: (1) The effects of thermal degradation were not seen in printed composites. (2) Due to the nature of voids in printing, there were inconsistent optical properties in the UV-samples. (3) To prevent particle build-up in the printer head, a 125 micron tip was used.

Future Plans: (1) Synthesis of gold nanorods with tunable length/diameter ratio. (2) Adjust surface characteristics of rods to prevent aggregation during processing. (3) Use of smaller tip sizes to create higher quality prints - smaller tip sizes would reduce the size of the air voids in the system.

6) Key Outcomes/Accomplishments

The project has played a key role in procurement of a NSF Center Grant.

6a) Ramakrishnan, S. (PI), Dickens, T., Sachdeva, M., Mateeva, N., & Dev, S. (Feb 2017). *CREST: Center for Complex Materials Design (CoManD) for Multidimensional Additive Processing*. Submitted to NSF (**\$4,999,389**).

The DOD project and the subsequent DURIP laid the foundation for the Center proposal and it would not have been possible without the help and support of Dr David Stepp. The collaborations with ARL and Larry Holmes and possibilities of state of the art education for minority students due to this collaboration was a key criterion that helped us procure this center grant. This is huge for FAMU.

6b) Course on Colloidal Science and Engineering:

This course was offered by S. Ramakrishnan during Spring 2017 – This was the first course in the department that combined both theoretical lectures with lab demonstrations and experiments. Students learnt about basics of polymer and particle characterizations and went into the lab and saw demos of the experiments in action. Examples of the current nanocomposite research in the DOD grant was presented in class.

6c) “Polymer and Polymer Materials Science and Engineering Division ACS”:

This chapter was established for the first time at the FAMU-FSU College of Engineering. The first General Body Meeting was held on April 14, 2017.

<https://fsu.collegiatelink.net/organization/PMSE>

In addition, as a group we attended the ACS Poly FAME meeting in Tampa, FL during May 2017 – 2 talks and 2 poster presentations. We hope to organize a session next year at the ACS meeting and are in touch with the organizers.

Florida A&M– Florida State
Chapter



Polymer and Polymer Material
Science and Engineering
Division ACS

Contacts

Advisor: Dr. Ramakrishnan
s.ramakrishnan@famj.edu

President: Roneisha Blakeney
roneisha1.blakeney@famj.edu



7) Presentations

Muhammed, F., Ramakrishnan, S., Vakil, P., Strouse, G., & Holmes, L. (poster presented 2017, May). *Additive Manufacturing of Low-k Dielectric Materials*. Poster presentation at American Chemical Society, Florida Annual Meeting and Exposition (FAME) 2017, ACS, Tampa, FL.

Muhammed, F., Ramakrishnan, S., Vakil, P., Strouse, G., & Holmes, L. (oral presentation 2017, September) *Additive Manufacturing of Low-K Dielectric Nanocomposites*. Materials Science & Technology, Additive Manufacturing of Composites and Complex Materials II 2017, Pittsburgh, Pennsylvania

Roy, M., Frketic, J., Strouse, G., Ramakrishnan, S., Holmes, L., and Dickens, T. *Tunability via Field-Assisted Printing of Magnetic-Mechanoluminescent Nanofibers*. Conference paper and presentation at Materials Science & Technology, Additive Manufacturing of Composites and Complex Materials II Symposium, 2017, Pittsburgh, PA.