Final Report for Award Number DE-SC0002253

Recipient (Institution): University of Cincinnati
Principal Investigator: Akpalu, Yvonne A.
Project Title: Advancing Renewable Materials by Integrated Light and X-ray Scattering
Final Report for Period: 07/01/2009 - 06/30/2010
Submitted on: 06/30/2010

Accomplishments

Polyhydroxyalkanotes (PHAs), a group of newly developed, commercially available biopolymers, and their composites have the potential to replace petroleum-based amorphous and semicrystalline polymers currently in use for consumer packaging, adhesives, and coating applications and to have significant advantages in medical applications such as tissue engineering. While the potential of PHAs is recognized in the literature and has even been realized in some cases, knowledge of these systems is decades behind that of synthetic polymers. Composites based on PHAs, furthermore, are just emerging in the research community. We argue that widespread adoption of nano-enhanced PHA materials can only be achieved through a proper **characterization of the nanofiller morphology and its impact on the polymer matrix**. Our goal is to build a robust understanding of the structure-processing relationships of PHAs to make it possible to achieve fundamental control over the final properties of these biopolymers and their bionanocomposites and to develop cost-effective manufacturing technologies for them.

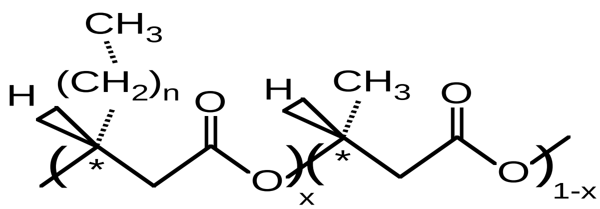

Figure 1: Chemical structure of polyhydroxyalkanoates (PHAs) investigated. PHB is poly (3-hydroxybutyric acid) (x=0), PHBV is poly (3-hydroxybutyric acid-*co*-3-hydroxyvaleric acid) (n=1) and PHBHx is poly (3-hydroxybutyric acid-*co*-3- hydroxyhexanoic acid) (n=2). HB, HV and HHx have methyl, ethyl and propyl side chains respectively. The value of x (mcl-3HA units) is between 2 to 50 %.

With the ultimate goal to design PHA polymer nanocomposites with tailored properties, we have performed a systematic study of the influence of cooling rate on the thermal properties and morphology of linear PHAs (PHB M_w = 690,000 g/mol; PHBV M_w = 407,000 g/mol, 8 mol % HV) and branched (PHBHx, M_w = 903, 000 g/mol, 7.2 mol % Hx) copolymers. Structure-property relations for silica/PHBHx nanocomposites were also investigated. Our studies show that simple two-phase composite models do not account for the molecular weight dependent enhancement in the modulus. Although improvement of the mechanical properties (stiffness/modulus and toughness) must be due to alteration of the matrix by the nanoparticle filler, the observed improvement was not caused by the change of crystallinity or spherulitic morphology. Since the mechanical properties of polymer nanocomposites can be affected by many factors, such as the interaction between particles and a polymer matrix, crystallinity of the polymer, spherulitic morphology, molecular weight of the polymer matrix, the PHA system studied can serve as a model system for determining the unique influence of particle characteristics on the morphology and mechanical properties of renewable polymer matrices.

Motivated by our promising results, we have initiated a systematic morphology characterization studies on a series of branched PHA polymers to uncover conceptual models that predict reinforcement and toughening in renewable polymer nanocomposites as a function particle characteristics, molecular weight and polymer backbone structure. **Thus how enhancement in the mechanical properties occurs in PHAs is the focus of our work.** In March 2010, the PI discovered a process that will allow better control of particle dispersion in PHA matrices. A graduate student (Sandip Argekar) was added to the project to help test this discovery and the scale up potential for the low-cost manufacture of renewable polymer nanocomposite films. If successful, the PI and co-PI will submit an SBIR proposal to facilitate technology transfer of the discoveries under this award.

To date, our work has generated 8 peer-reviewed publications (1 book chapter, 5 journal articles, 2 conference papers), 15 presentations (7 invited, 8 contributed) and fruitful collaborations at DOE facilities (see letter from **Jan Ilavsky**) and with industrial scientists(see letter from **Isao Noda**). Invited presentations include presentations at the 2008 Gordon Research Conference on Polymer Nanocomposites and the 2009 MRS Symposium AA: Renewable Biomaterials and Bioenergy: Current Developments and Challenges.

Publications to date

Journal Articles (5 total)

1. Yuping Xie, Isao Noda, Y. A. Akpalu, "A study of the influence of cooling rate on the thermal behavior and solid-state morphologies of polyhydroxyalkanoates", *Journal of Applied Polymer Science*, 2008 109 (4), 2259-2268.
2. Yuping Xie, Doug Kohls, Isao Noda, Dale W. Schaefer, Yvonne A Akpalu, "Poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) Nanocomposites with Optimal Mechanical Properties" *Polymer*, 2009, 50 (19), 4656-4670.
3. Zhicheng Xiao, Ying Li, Y. A. Akpalu, "Enabling controlled dispersion in polyethylene nanocomposites using small-angle scattering", *Polymer Composites*, 2009, 30(5), 559-568.
4. Ian Tolle, Xinqun Huang, Yvonne A. Akpalu, Lealon Martin, "A modified Network Component Analysis (NCA) methodology for the decomposition of x-ray scattering signatures from polymers", *Industrial & Engineering Chemical Research*, 2009, 489(13), 6137-6144.
5. Akpalu YA, Noda I, Schaefer DW. Polyhydroxyalkanoate Nanocomposites with Optimal Mechanical Properties. *Materials Research Society Symposium Proceedings*, 2010, 1219E: in press

Conference papers (2 total)

6. Yuping Xie, Allyce Caines, Johanna Carroll, Sergei Shenogin, Isao Noda, Y. A. Akpalu **"**Advancing Multiscale Modeling Prediction of Mechanical Properties of Polyhydroxyalkanoates**",** *American Institute of Chemical Engineers Extended Abstract*, **2007**.

7. Y. Xie and Y. A. Akpalu **"**Elucidating the effect of cooling rate on the morphologies of polyhydroxyalkanoates**",** *PMSE Preprints, American Chemical Society, Division of Polymeric Materials: Science and Engineering*, **2007**.

Books (1 total)

8. Akpalu, Y. A., "Towards polyethylene nanocomposites with controlled properties", Polyolefin Composites Book", D. Nwabunma & T. Kyu (Eds.), Wiley, 2007, Chapter 13.

Presentations (15 total)

1. **Dec 2009** Materials Research Society Symposium on Renewable Biomaterials and Bioenergy-Current Developments and Challenges, "Polyhydroxyalkanoate Nanocomposites with Optimal Mechanical Properties"
2. **July 2009** Frontiers in Polymer Science, International Symposium Celebrating the 50th Anniversary of the Journal Polymer, Mainz Germany: "Renewable Polymer Nanocomposites with Optimal Mechanical Properties", Yuping Xie, Dale W. Schaefer, Doug Kohls, Isao Noda, Yvonne A. Akpalu.
3. **Nov. 2009** Department of Chemical & Materials Engineering, University of Cincinnati, "Structure-Property Relationships in Polyhydroxyalkanoate Nanocomposites
4. **Oct. 2008** Department of Materials Science & Engineering, Rutgers University, "Renewable Polymer Nanocomposites with Optimal Mechanical Properties"
5. **Oct. 2008** Department of Chemical & Biomedical Engineering, Florida State University, "Renewable Polymer Nanocomposites with Optimal Strength and Toughness".
6. **November 2008** American Institute of Chemical Engineers, Annual Meeting: "A Modified Network Component Analysis (NCA) Methodology for the decomposition of X-ray Scattering Signatures from Polymers", Ian Tolle, Yvonne A. Akpalu, Lealon Martin.
7. **Sept. 2008** Department of Chemistry, Polymer Science Seminar, University of Massachusetts, Lowell,"Designing Polymer Nanocomposites with Optimal Strength and Toughness"
8. **June 2008** 40th Central Regional Meeting of the American Chemical Society Symposium on Emerging Concepts in Polymer Science and Plastics Engineering: Synthesis, Modeling and Design, "Engineering Design of Polyhydroxyalkanoates with Controlled Properties".
9. **March 2008** Department of Chemistry, College of Staten Island City University of New York, "Knowledge Based Design of Polyhydroxyalkanoates with Controlled Properties".
10. **Jan 2008**, Gordon Research Conference, Polymer Nanocomposites, "Controlled Dispersion in Polymer Nanocomposites Using Small-Angle Scattering" Coauthors: Zhicheng Xiao and Yuping Xie.
11. **November 2007**, American American Institute of Chemical Engineers, Annual Meeting: "Topology-Based Parameter Identification for Decoupling Material Structure-Process-Property Relationships", Ian Tolle, Xinqun Huang, Yvonne A. Akpalu, Lealon Martin.
12. **November 2007**, American Institute of Chemical Engineers, Annual Meeting: "Advancing Multiscale Modeling Prediction of Mechanical Properties of Polyhydroxyalkanoates", Yuping Xie, Allyce Caines, Johanna Carroll, Sergei Shenogin, Isao Noda and Yvonne A. Akpalu.
13. **May 2007**, Argonne National Laboratory Users Week 2007: "Elucidating the Effect of Processing Conditions on the Morphologies of Polyhydroxyalkanoates", Yuping Xie and Yvonne A. Akpalu.
14. **May 2007**, NSTI Nanotech 2007: "Elucidating the Effect of Processing Conditions on the Morphologies of Polyhydroxyalkanoates", Yuping Xie and Yvonne A. Akpalu.
15. **March 2007**, American Physical Society Meeting: "An investigation of the effect of processing conditions on the lamellar and spherulitic morphology of polyhydroxyalkanoates (PHAs)", Yuping Xie and Yvonne A. Akpalu.

People Name	Type of Personnel	Type of Support
Y. A. Akpalu (Principal Investigator)	Senior/Visiting Scholar	3 Months
Dale Schaefer (co Principal Investigator)	Senior/Faculty	--------
Sandip Argekar	Graduate Student	2 months

Current and Pending Support (Excluding this award)

Pending Support:

Investigator: Yvonne Akpalu (PI), Dale W. Schaefer (coPI)
Project/Proposal Title: Advancing Renewable Polymers by Light & X-ray Scattering (Renewal Proposal)
Source of Support: Department of Energy, Basic Energy Sciences
Total Award Amount: $ 823,280
Total Award Period Covered: July 1, 2010 through June 30, 2013
Location of Project: University of Cincinnati
Person-Months per Year Committed to the Project: 9 Months (Akpalu) 1.0 Month (Schaefer)

Unexpended Funds

NONE