Final Report for Award Number DE-FG02-06ER46349

Recipient (Institution): Rensselaer Polytechnic Institute

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Project Title: Advancing Renewable Materials by Integrated Light and X-ray Scattering

Accomplishments

With the ultimate goal to design PHA polymer nanocomposites with tailored properties, we have completed systematic study of the influence of cooling rate [Xie et al, *J. Appl. Poly. Sci.,* 2008] and nanofiller [Xie et al, *Polymer* 2009] characteristics on model bionanocomposites. Structure-property relationships for a model bionanocomposites system were investigated. These results yielded new fundamental knowledge that supports the discovery of cost-effective manufacturing technologies for a family of promising polyhydroxyalkanoates (PHAs) polyesters, with the potential to replace polyethylene and polypropylene (see **Noda** letter). Our results show that simple two-phase composite models do not account for the data. 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. Instead, improvement depends on the molecular weight of the polymer matrix and unknown filler-matrix interactions.

Nodax$^{\text{TM}}$ PHA copolymers originally developed by Procter & Gamble (P&G) are designed to achieve mechanical properties and processing characteristics comparable to those of thermoplastic polyolefins such as polyethylene and polypropylene. Nodax$^{\text{TM}}$ copolymers (**Figure 1**) consist predominantly of 3-hydroxybutryate (3HB) and 3-hydroxyalkanoate (3HA) co-monomer units. The secondary 3HA comonomer units must have side groups consisting of at least three carbon atoms.

Examples of PHAs with medium-chain-length (mcl) side groups include poly (3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx, n=2), poly (3-hydroxybutyrate-*co*-3- hydroxyoctanoate) (PHBO, n=4), poly (3-hydroxybutyrate-*co*-3-hydroxydecanoate)(PHBD, n = 6), and poly (3-hydroxybutyrate-*co* 3-hydroxyoctadecanoate) (PHBOd, n = 14).

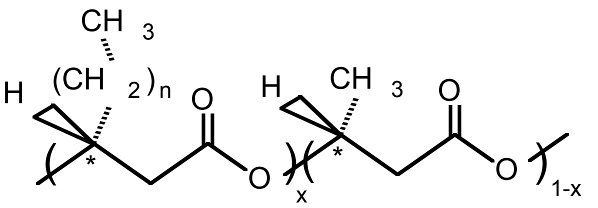

Figure 1: Molecular structure of Nodax$^{\text{TM}}$ class PHA copolymer. The value of x (mcl-3HA units) is between 2 to 50 %. Chemical structures of more familiar linear PHAs: PHB is poly(3-hydroxybutyrate) (x=0) and PHBV is poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (n = 1).

Our key results are summarized below:

Influence of polymer backbone structure

To facilitate a molecular-level understanding of structure-property relationships of PHAs, we have studied the influence of cooling rates on the thermal behavior and solid-state morphologies of PHB, PHBV and PHBHx. We also initiated molecular modeling studies to predict the influence of molecular structures and cooling rate on the morphologies of PHB. The thermal behavior was studied by differential scanning calorimetry (DSC). The crystal structures (~nm), lamellar (~10 nm), fibrillar (~ 100 nm) and spherulitic (~μm) morphologies of PHB, PHBV and PHBHx crystallized under different cooling rates (1, 10 and 50 $^{\circ}$C/min) were studied using small-angle x-ray scattering (SAXS), wide-angle x-ray scattering (WAXS), ultra small angle x-ray scattering (USAXS) and polarized optical microscopy (POM), respectively. The results of this work are detailed in a recent paper [Xie et al, *J. Appl. Polym. Sci.,* 2008]. The thermal behavior and morphologies of PHAs studied were observed to strongly depend on cooling rate. If impurities are present, multiple melting peaks of PHAs can be due to both melting, recrystallization and remelting process and impurities. The long period (L) and average lamellar thickness (l_c) increased with decreasing cooling rate for PHB, PHB8V and PHBHx. The lamellar morphology reflects the exclusion of the Hx comonomer and the inclusion of the HV comonomer from the HB crystal lattice. The size of the spherulites of PHAs studied decreased when the cooling rate increased. The WAXS pattern of the PHB, PHB8V and PHBHx studied at room temperature showed that they all have an orthorhombic structure, $P2_12_12_1$ (D_2^4) ($\alpha = \beta = \gamma = 90^o$), with a = 5.76 Å, b = 13.20 Å, c = 5.96 Å (fiber repeat), which is identical to that of the PHB crystal system. There was little influence of cooling rate on the crystal structures. USAXS results (**Figure 2**) suggested that impurities were localized on the surfaces and interfaces of the fibrils.

Influence of nanofillers

To understand the influence of nanofillers on the morphology and properties of PHAs, structure-property relationships for a model system – silica/poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx) nanocomposites were investigated. Two molecular weights of PHBHx (PHBHx072, M_w=903,000 g/mol, 7.2 mol % Hx and PHBHx069 M_w=633,000 g/mol, 6.9 mol %) and two types of silica nanoparticles, spheres (10 – 15 nm in diameter, surface area=200-300 m^2/g) and fibers (9 – 15 nm in diameter, length of 40 – 100 nm, surface area=200-300 m^2/g, aspect ratio = 3 - 11) according to the manufacturer, were used to prepare the nanocomposites [Xie et al, *Polymer* 2009].

The mechanical properties were measured using tensile tests in accordance with ASTM 882-02 (for thin films less than 1.0 mm in thickness) at room temperature on an Instron (Model 5843) load frame with a 1-kN load cell and an Instron video-extensometer. The speed of testing was 1 mm/min. The Young's modulus was determined from the slope in the elastic region (0-0.4% strain) of the stress-strain curve. The toughness was calculated as the area under the stress-strain curve. The ultimate strength was obtained from the maximum stress on the stress-strain curve. At least five replicates averaged. All samples were tested after two days of conditioning at 23 ± 2 °C and 50 ± 5 % relative humidity (RH).

In order to understand the mechanical properties observed, the thermal behavior, spherulitic morphology and the deformation mechanism of the nanocomposites as well as the dispersion state of the nanofillers were studied. Filler dispersion was characterized by ultra-small-angle x-ray (USAXS) scattering and field emission scanning electron microscope (FESEM). Some key results are described below.

Small-angle x-ray scattering (**Figure 2**) shows that the sphere and fiber nanoparticles had similar surface areas and primary particle size, but differed in degree of aggregation of the primary particles. For the spheres, primary particles (average size = 58 Å) are aggregated as a mass fractal cluster of dimension 2.8 and radius-of-gyration of 662 ± 80 Å. Aggregation number (N_{agg}=11) is at least 1000 times smaller than the nominal fiber-type filler. For the fibers, primary particles (average size = 56 Å) are aggregated as a mass fractal of dimension 2.1. The size of the aggregate exceeds 0.5 μm and the persistence length is 70 Å a from fractal rod model. The average size of the clusters obtained from USAXS is consistent with the average sizes from the SEM micrographs.

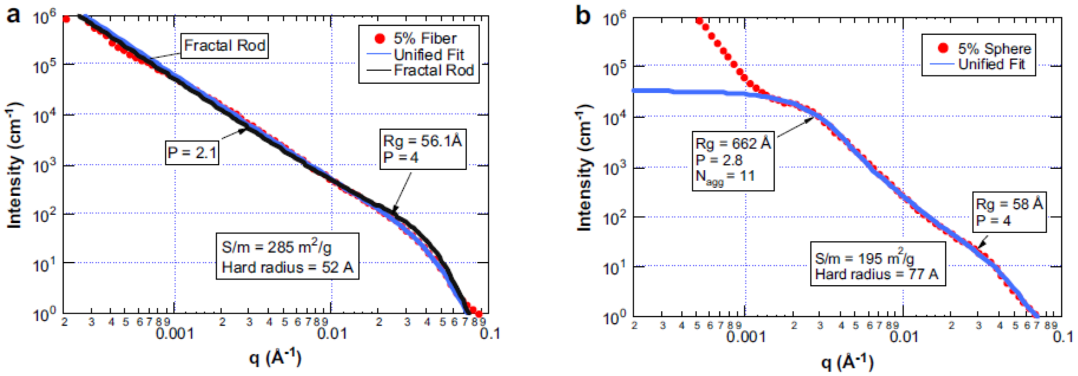

Figure 2. Analysis of USAXS data for (a) the 5-wt% SiO_2 fiber/PHBHx072 at 170 °C and for (b) the the 5-wt% SiO_2 sphere/PHBHx072 at 170 °C.

The thermal stability of the PHBHx matrix was slightly improved by the addition of nanofillers. Simultaneous improvement of both stiffness and toughness was observed at 1-wt% loading for the higher molecular weight matrix. The more highly aggregated SiO_2 fibers had a greater toughening effect than the less-aggregated SiO_2 spheres. Compared to the unfilled polymer matrix, a 30 % increase in Young's modulus and 34 % increase in toughness were obtained for the 1-wt% SiO_2 fiber/PHBHx072 nanocomposite. The addition of the less-aggregated SiO_2 spheres to PHBHx072 resulted in the same increase in Young's modulus (30 %) but a smaller increase (11%) in toughness. When the loading was 3 wt% and above, the Young's modulus continued to increase, but the strain at break and toughness decreased. The ultimate strength did not change compared with the unfilled polymer.

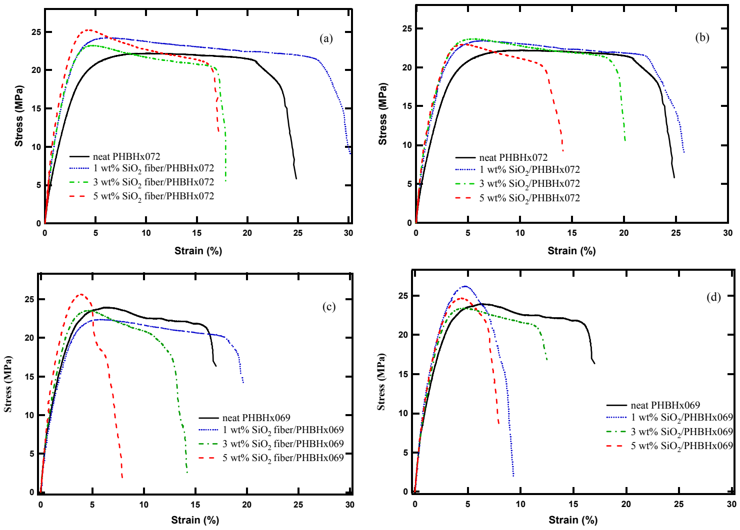

Figure 3: Typical stress-strain curves of (a) SiO_2 fiber/PHBHx072, (b) SiO_2/PHBHx072, (c) SiO_2 fiber/PHBHx069, and (d) SiO_2/PHBHx069 nanocomposites with different filler content.

What influences the mechanical properties of PHA?

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, dispersion state of the particles in the polymer matrix, etc.

Matrix characteristics do not change significantly in the nanocomposites. From the DSC data, the transition temperature (T_g= 8 ± 1^{o}C) for all the samples did not change, indicating that there are no strong attractive or repulsive interactions between the nanoparticles and the polymers. Therefore, the interfacial adhesion between them must be weak. In addition, changes in degree of crystallinity and spherulitic morphology caused by the addition of filler are minimal at 1-^{o}C/min cooling rate. From the tensile testing results, the neat PHBHx069 is stiffer but less ductile than the neat PHBHx072.

The major difference between the neat PHBHx072 and the neat PHBHx069 is their molecular weights. In general, decreasing the molecular weight results in a faster crystallization, which is to be expected on the basis of mobility considerations and has been observed for many polymers. Although we do observe higher crystallinity in the lower molecular weight sample (PHBHx069), the difference is only 2%.

Stress whitening is seen in all samples. Plastic tensile deformation of crystalline polymers can cause cavitation, producing sudden polymer whitening near the yield point. If the interfacial adhesion is not high, debonding at the particle-polymer interface can occur, leading to crazing and/or shear yielding. In our case, this mechanism may have been active in the 1-wt% SiO_2/PHBHx072 and 1-wt% SiO_2 fiber/PHBHx072 nanocomposites, which fractured with a slight necking that led to a more ductile behavior.

Although void formation is a secondary factor contributing to toughness (in other words, only a small part of energy dissipation may contribute to toughness), it plays an important role for the activation of further plastic deformation. When filler loading is low (1 wt%) the formation of voids during deformation releases strain constraints and induces local shear deformation in polymer ligaments between nanoparticles. As loading increases, however, the aggregates act as flaws that trigger brittle response and premature material failure before the shear yielding begins.

In principle modulus should be less sensitive to defects and therefore easier to interpret. In our case, however, the modulus is strongly dependent on the matrix, which, based on the above results, is nearly the same for the two polymers. **Figure 4** shows the experimental values of the relative modulus $E_r = E_c/E_m$ and the predictions based on the simplified Halpin-Tsai model (5) for randomly distributed rigid fibers at low volume fraction

$$\mathrm{E}_r = 1 + 2\left(\frac{L}{D}\right)\mathrm{C_a}\varphi \tag{1}$$

where the angular factor, C_a, is approximately 0.2 (45). Equation (**1**) is relevant to the systems studied here since it shows that large aspect ratio, L/D (length/diameter), is essential to fiber reinforcement. Equation (**1**) assumes L/D >> 1. In the limit L/D → 1, the Smallwood limiting law for independent spherical particles obtains, which is independent of filler size:

$$\mathrm{E}_r = 1 + 2.5\varphi \tag{2}$$

Based on the USAXS results, the primary particles are nearly symmetric for both the nominally spherical and nominally fiberous fillers. **Eq. (2)**, therefore, should be applicable. Even if the value of the aspect ratio from Nissan is assumed (L/D = 11) the prediction changes little. Both predictions agree with the 069 data, but fall outside the error bars for the 072 data.

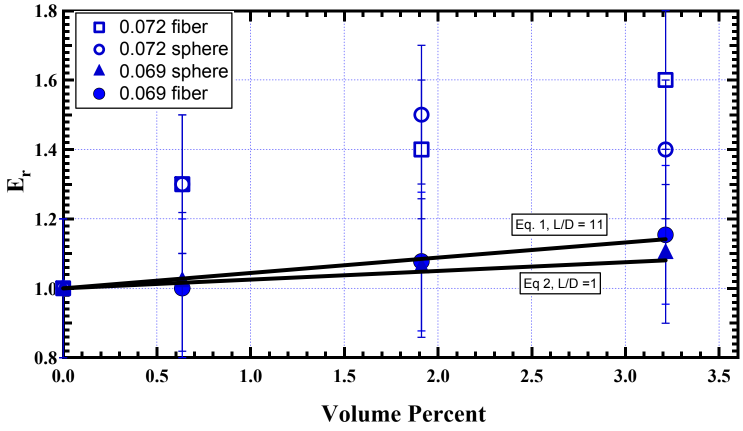

Figure 4: Measured relative modulus compared to the prediction for reinforcement with symmetric and asymmetric particles. The 072 matrix seems to give anonymously large reinforcement.

Eqs. (1) and (2) assume independent, rigid particles so that the elastic energy is stored in the strain field around the particles. In principle these equations could be altered for aggregated particles. Interactions between the strain fields of the primary particles would also alter these simple predictions. **Eq. (2)** represents the minimum expected reinforcement because it neglects energy stored in the filler itself (5). At least in the case of the HBHx069 matrix, it seems that these compromising factors are not relevant.

Some insight into the anomalous modulus enhancement for the PHBHx072 material comes from the observation that the enhancement would be "normal" if the modulus of the unfilled materials were under estimated by 30%. That is if the modulus of the filled samples is extrapolated to zero loading, the intercept is too high by about 30%. This observation leads us to believe that the enhancement is due the impact of the filler particles on the matrix. The stiffness of semicrystalline PHA is controlled not only by the overall crystallinity but also by the mechanical properties of the amorphous region of material. Given that a semicrystalline polymer is itself a composite consisting of a stiff crystalline regions and more elastic amorphous regions, the particles could enhance the modulus of the amorphous regions more than the crystalline regions. Being less crystalline, the PHBHx072 sample is therefore more susceptible to enhancement. These observations indicate that modulus enhancement in PHAs depends in a yet unknown way on the intrinsic properties of matrix and filler as well as interactions between matrix and filler.

Publications to date:

Books (1 total)

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

Journal Articles (6 total)

- Akpalu, Y. A. "Scattering from Polymers", Polymer Reviews, **2010**, 50:1, 1-13.
- Ian Tolle[1], Xinqun Huang[1], Yvonne A. Akpalu*, Lealon L. Martin*, "A modified Network Component Analysis (NCA) methodology for the decomposition of x-ray scattering signatures from polymers", *Industrial & Engineering Chemical Research*, **2009**, 48(13), 6137-6144.
- 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.
- Z. Xiao, Y. Li & Y. A. Akpalu, "Enabling Controlled Dispersion in Polyethylene Nanocomposites Using Small-Angle Scattering", Polymer Composites, **2009**, 30(5), 559-568.
- Yuping Xie, Isao Noda, Y. A. Akpalu*, "*A *s*tudy 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.
- Akpalu & Peng, "Probing the melt miscibility of a commercial polyethylene blend by small-angle light scattering", Materials Manufacturing, **2008**, 23:3, 269-276.

Conference papers (3 total) (Presenter underlined)

- Akpalu YA, Noda I, Schaefer DW: Polyhydroxyalkanoate Nanocomposites with Optimal Mechanical Properties. *Materials Research Society Symposium Proceedings(Reewable Biomaterials and Bioenergy-Current Developments and Challenges).* **2010**, *1219E.*
- 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**.
- Y. Xie1 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**.

Presentations (11 total)

- **Nov. 2009** Department of Chemical & Materials Engineering, University of Cincinnati,"Structure Property Relationships in Polyhydroxyalkanoate Nanocomposites"
- **Oct. 2008** Department of Materials Science & Engineering, Rutgers University, "Renewable Polymer Nanocomposites with Optimal Mechanical Properties"
- **Sept. 2008** Department of Chemistry, Polymer Science Seminar, University of Massachusetts, Lowell,"Designing Polymer Nanocomposites with Optimal Strength and Toughness"

- **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".

- **March 2008** Department of Chemistry, College of Staten Island City University of New York, "Knowledge Based Design of Polyhydroxyalkanoates with Controlled Properties".

- **Jan 2008**, Gordon Research Conference, Polymer Nanocomposites, "Controlled Dispersion in Polymer Nanocomposites Using Small-Angle Scattering" Coauthors: Zhicheng Xiao and Yuping Xie.

- **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.

- **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.

- **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.

- **May 2007**, NSTI Nanotech 2007: "Elucidating the Effect of Processing Conditions on the Morphologies of Polyhydroxyalkanoates", Yuping Xie and Yvonne A. Akpalu.

- **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

Y. A. Akpalu (Principal Investigator)	Senior/Faculty	Summer Salary
Lealon. L Martin (co Principal Investigator)	Senior/Faculty	Summer Salary
Yuping Xie	Graduate Student	Full

Current and Pending Support

	Amount($)	*Title*	*Dates*	*Status*
NSF DMI 0600317	411,821	Advancing the Engineering Design of Bionanocomposites with Controlled Properties (**Akpalu (PI)** and Martin (co-PI)) *Relationship to DE –FG02-06ER46349* Structure-process relationships being developed under this DOE grant are being used to build structure-property relationships under this NSF grant. The focus here is on tensile properties.	05/2006-04/2009	Awarded
NSF DRL 0754948	$ 75,000	Easing the "Quiet Crisis" (**Akpalu (PI)**, Bennett (co-PI) and Lister (co-PI)) Duration: 1 year *Relationship to DE –FG02-06ER46349* NONE	04/2008 – 03/2009	Awarded

December 22, 2009

Materials Sciences and Engineering Division
Office of Basic Energy Sciences
SC-22.2/Germantown Building, Room F-421
U.S. Department of Energy
1000 Independence Avenue, SW
Washington, D.C. 20585-1290

Dear Yvonne,

This is a letter of support for proposed DOE BES project on Nodax^{TM} biopolymers. We have been happy to support your work in the past by providing well-characterized samples of various NODAX^{TM} copolymers. Your work to date has provided knowledge and understanding that supports technological advances that could lead to significant increases in the usage of biodegradable polymers.

We are pleased to continue our working relationship on the nanoparticles reinforcement of Nodax^{TM}. I will certainly supply more samples as they are needed for your studies. Moreover we can help out with access to polymer processing, mechanical and rheological measurement facilities at our Westchester R&D site.

P&G has licensed the majority intellectual properties of Nodax^{TM} technology to Meridian Inc., Bainbridge, GA. Meridian is scheduled to produce multi million lbs of PHA biopolymers by the end of 2009 and further expand the commercial production to a larger scale within several years.

I am pleased to offer my support for your work.

Sincerely yours,

Isao Noda, Ph. D.,

Research Fellow