

2009-2010 Annual Report

**Center for Environmentally Benign Functional
Materials (CEBFM)**

by

G. Caneba, Director

CEBFM Overview for 2009-2010

The Center for Environmentally Benign Functional Materials became operational in 2006 with the purpose to increase and then sustain research activities into synthesis, characterization, and analysis of materials that are capable of performing multiple functions in a wide variety of applications. CEBFM brings together researchers and creates a knowledge-base to develop technologies for challenging applications critical to the growing technological needs of the US and the world. The Center promotes and fosters an environment that crosses the traditional departmental and disciplinary boundaries to advance knowledge and support the overall mission of the University. Central to the mission of the CEBFM is that all materials developed through the center must be environmentally benign, meaning that they are more environmentally responsible compared to current equivalent materials and their production methods.

In September 2009, Dr. Rajesh Tiwari arrived from Boston University, in order to assist the center in projects related to the studies of the use of FRRPP-based polymeric surfactants for oil spill mitigation, cleanup and dispersion from surface and under water regions.

A number of proposals were submitted, and several journal publications were produced. A book was already published contract with Springer-Verlag (Heidelberg), and the second volume is being written, with submission date of December 31, 2010. It is the hope that these book publications will provide a boost to the reputation of the center for future funding, collaborations, and continued growth.

Current faculty membership of the center is:

1. Gerard Caneba (Chemical Engineering) – Director
2. Gordon Parker (Mechanical Engineering-Engineering Mechanics) – Associate Director
3. David Shonnard (Chemical Engineering) – Member
4. Gregory Odegard (Mechanical Engineering-Engineering Mechanics) – Member
5. Spandan Maiti (Mechanical Engineering-Engineering Mechanics) – Member
6. Patricia Heiden (Chemistry) – Provisional Member
7. Jim Hwang (Materials Science and Engineering) – Provisional Member
8. Wenzhen Li (Chemical Engineering) – Provisional Member
9. Mohan Rao (Mechanical Engineering-Engineering Mechanics) – Provisional Member

CURRENT PROJECTS

Title: CO₂ Sequestration in Polymer Formulations
Sponsor/Collaboration: Cascade Engineering Inc.

Period: October 2007 – ongoing

Faculty Participants: Gerard Caneba, Jim Hwang, Munir Tasdemir

Industry Participant: Dr. Bo Wang of Cascade Engineering, Inc.

Graduate Student Participant: Brian Ott

Project Description: The project involves the incorporation of CO₂ into polymer formulations. The purpose is carbon sequestration while at the same time imparting flame retardancy, dimensional stability, and some mechanical property improvement in the polymer formulations. The sabbatical fellowship of Dr. Munir Tasdemir of the Chemical Engineering Dept., Marmara Univ. (Istanbul) is instrumental in the initial implementation of this project. Polymer test samples were generated at MTU, which contain absorbed CO₂, and mechanical tests are being done at Marmara University.

Title: Chaos in Ultrasonic Dispersion of Nanoscale Materials

Sponsor/Collaboration: NASA-Johnson Space Center, Coatings Research Institute of Eastern Michigan University

Period: September 2008 – ongoing

Faculty Participants: Gerard Caneba, Mohan Rao

Graduate Student Participant: Colina Dutta, Mathkar Alharthi

Project Description: This project involves theoretical and experimental studies of a novel ultrasonic method for the efficient dispersion of various nanomaterials in a fluid. The procedure was implemented at NASA-Johnson Space Center and applied to the dispersion of single-walled carbon nanotubes. Efficiency increases are in the order of 10-20 times compared to current ultrasonic dispersion practices. Such a procedure is also applicable to the dispersion of cellulosic materials before fermentation to produce cellulosic ethanol.

Title: Mathematical Modeling and Computer Simulation of the FRRPP Process

Sponsors: King Abdullah Scholarship Program, Government of Saudi Arabia

Period: October 2009 – January 2011

External Funding: MS Fellowship for Mr. Mathkar Alharthi

Faculty Participant: Gerard Caneba

Graduate Student Participant: Mr. Mathkar Alharthi

Project Description: The project involves the quantitative mechanistic investigation of the FRRPP process, through the use of thermodynamic, kinetic, phase separation, and transport concepts. An initial approach was made with mathematical modeling/computer simulation efforts of kinetics of phase separation and thermodynamic-kinetic-heat transport aspects of the FRRPP process. Results were published in the first FRRPP monograph (Caneba, 2010) and in an MS thesis (Alharthi, 2010). Future efforts will include differential overall and component mass balances in steady and unsteady modes of the FRRPP behavior.

Title: FRRPP-based Halogenated Block Copolymer Membranes

Period: September 2009 – ongoing

Faculty Participants: Gerard Caneba, Prof. Jim Hwang

Potential Sponsors: ARPA-E, EPA, NSF-UIRC with CBERD

Project Description:

This project involves the use of the FRRPP process to generate halogenated block copolymers for CO₂ separation and bioseparation membranes. This project involves the generation of hollow fiber asymmetric membranes for CO₂ separation from exhaust gases of power plants and vehicles, which is a finalist of the 2010 ARPA-E solicitation on the IMPACCT program. The membranes are also being developed for separation of components from pyrolysis of biomass.

Title: VA-AA-based Surfactants from the FRRPP Process as oil spill control/dispersant/cleanup materials

Period: September 2010 – ongoing

Faculty Participant: Gerard Caneba and Prof. Tony Rogers

Research Fellow: Dr. Rajesh Tiwari

Student Participants: Mr. Zach Abrams-Tangetti, Chemical Engineering Senior Plant Design group

Potential Sponsors/Collaborators: University of Alabama-Birmingham, University of Louisiana-Lafayette

Project Description:

This project involves the use of the FRRPP process generate VA-AA-based foaming surfactants as oil spill control agent. Also, the surfactants have been modified to improve their efficacy as oil dispersants and oil cleanup agents.

In section 5.2 of the first FRRPP monograph, a particular type of vinyl acetate-acrylic (VA-AA) salt tapered block copolymer (called B6-1) was shown to exhibit excellent performance as a foaming surfactant for enhanced oil recovery. The underlying reason was cited as the capability of the polymeric surfactant to form a relatively stable displacement front between the aqueous phase and oil phase, while the aqueous phase is being pushed against the oil phase by a foaming gas. It should therefore be no surprise that the same mechanism could be used in the displacement of oil from the water surface laterally toward areas where it can be efficiently collected or disposed of. The same foam front can be used to raise an underwater oil plume to the surface of the water, where it can be collected. Finally, the foam can be used to separate and raise the oil that is stuck on the seafloor, where it can be further raised to the surface with the same foam system.

We are also developing crude oil dispersants based on VA/AA surfactants. Preliminary scaled-down Swirling-Flask test involving these surfactants and Louisiana light crude indicate that Oil Dispersion Effectiveness values are only in the 25% range without the use of volatile organic compounds (VOCs) in the formulation. To increase this value, VA/AA surfactants have been modified by reaction with stearic acid, in order to increase its affinity with hydrocarbon components in crude oil.

Title: Biodegradable VA-AA-based Polymeric Surfactants for fast neutralization and cleanup of the Red Mud Caustic Sludge from Bauxite Ore Tailings

Period: September 2010 – ongoing

Faculty Participant: Gerard Caneba

Potential Sponsors: European Union, NSF

Project Description:

The capability of the multifunctional surfactant for fast neutralization of the simulated red mud depends on its concentration in water. For a resulting pH of 7 from the pH of 9, there is a need for 0.36 wt % equivalent VA/AA copolymer surfactant in water. If one assumes a porosity of 50% for the red mud and the requirement to cover one pore volume of the red mud with the multifunctional surfactant solution to attain a pH of 7, the areas and contamination depths (5 cm depth of 400 hectares and 10 cm depth of 400 hectares) will require 7,334,000 kg of equivalent VA/AA copolymer solid surfactant. If this were produced in bulk scale as a commodity polymer (\$1.5-2/lb), it will cost in the order of 24-32 million \$ to manufacture the copolymer. Other minor material costs include: neutralizing KOH (to neutralize 6 wt % of surfactant solid made up of acrylic acid segments), water, initiator, and polymerization solvent (first batch and subsequent make-up amounts). As for the speed of manufacture, if there are no major scale-up problems, it will take around 50 days to produce the entire amount using a 20,000 gallon reactor (3 batches per day). If a 5,000 gallon reactor is to be used, it will take around 200 days to produce the entire amount. It should be noted that the reaction can be done in an atmospheric reactor; thus, it is possible to find large-scale atmospheric autoclave units from a chemical or polymer manufacturer company.

Title: Artifacts Preservation Materials/Systems

Period: September 2009 – ongoing

Faculty Participants: Gerard Caneba, Prof Tim Scarlett

Project Description:

This project pertains to the use of supercritical CO₂ to remove liquid contaminants from iron-based and other historical artifacts. Then, controlled *in situ* polymerization is to be carried out in order to produce protective coatings onto porous surfaces of the artifacts.

CEBFM Education and Outreach

The following students/fellows obtained research experiences in the laboratory under CEBFM Provisional and Full Members:

Dr. Rajesh Tiwari – CM Research Fellow

Brian Ott – CM PhD student

Hwi Yeung Lee – CM PhD student

Mathkar Alharthi – CM MS student

Shubham Borole – CM MS student

Colina Dutta – CM MS student

Le Xin – CM MS student

International outreach is also a center activity, which includes contacts with the following universities/companies/nationals labs:

1. Marmara University, Turkey

2. Truman College, a minority serving institution in Chicago
3. University of Alabama – Birmingham
4. University of Louisiana – Lafayette
5. University of Wisconsin – Madison
6. Akzo-Nobel, N.V., Bridgewater, New Jersey
7. Center for Nanoscale Materials - Argonne National Lab
8. NASA – Johnson Space Center
9. Cascade Engineering, Grand Rapids, MI
10. Coatings Research Institute, Eastern Michigan University
11. Grace Performance Chemicals, Cambridge, MA
12. Battelle Pacific Northwest National Laboratory
13. Hungary Academy of Sciences

Center Financial Information

Opening Balance - July 1, 2009

\$ 43366.5

Total Indirect Return Revenues

None

Total Expenses*

\$10754.78

Ending Balance - June 31, 2010

\$32611.72

*Breakdown of major expenditures

Post-doc Stipend (Dr. R. Tiwari) - \$6489.54

Rental of Storage Space - \$799.88

CEBFM Lab Maintenance/Supplies - \$1082.08

Travel/Conference Fee - \$2394.74

Publications

Journal Articles

- Tasdemir, M., Biltekin, H., and Caneba, G.T., "Investigation of Properties of PE & PP /Wood Flour Polymer Composites", *Journal of Applied Polymer Science*, 112, 3095-3102 (2009).
- G.T. Caneba, "Nanoporous Structure and Enhanced Thermal Properties of a Carbon Nanotube/Polyimide Composite", *Journal of Minerals and Materials Characterization and Engineering*, 8, 15-24 (2009).
- G.T. Caneba, C. Dutta, V. Agarwal, and M. Rao, "Novel Ultrasonic Dispersion of Carbon Nanotubes", *Journal of Minerals and Materials Characterization and Engineering*, 9, 165-181 (2010).
- B. Ott and G.T. Caneba, "Solubility of Supercritical CO₂ in Polystyrene during Foam Formation via Statistical Associated Fluid Theory (SAFT) Equation of State", *Journal of Minerals and Materials Characterization and Engineering*, 9, 411-426 (2010).
- Taşdemir, M., Caneba, G.T., Tiwari, R., and Wang, B., "Characterization of PP/Clay/ Mg (OH)₂ Polymer Composites with Supercritical Carbon Dioxide (scCO₂)", accepted and under revision, *The Journal Polymer-Plastics Technology and Engineering*, (2010).
- Taşdemir, M., Caneba, G.T., "Extrusion and characterization of ABS/Clay/ Mg (OH)₂ Polymer Composites with Supercritical Carbon Dioxide (scCO₂)", submitted to, *International Journal of Polymeric Materials*, (2010).

Book

- G.T. Caneba, "Free-Radical Retrograde-Precipitation Polymerization (FRRPP): Novel Concept, Processes, Materials, and Energy Aspects", Springer-Verlag, Heidelberg, ISBN 978-3-642-03024-6, 2010.

PhD Dissertation

- "Fluid Phase Equilibrium as Modeled by the Statistical Associated Fluid Theory (SAFT) Equation of State", Brian Ott, PhD Dissertation, Michigan Technological University, 2009.

Proposals

- "Thermally-Resistant Membranes from Halogenated Radicalized Polymer Particulates for CO₂ Separation", G. Caneba (PI), D. Shonnard, J.-Y. Hwang, ARPA-E, \$584,912, 7/15/2010-1/14/2012, 18 months, finalist but eventually declined.
- "Sustainability Emulsion-Based Polymer Experiences", G. Caneba (PI), NSF-TUES Program, \$199,864, 12/01/2010-11/13/2012, 24 months, declined.

“Chemical Mediator-free Controlled Chain Polymerization onto Surfaces”, NSF-MSN Program, G. Caneba (PI), \$239,627, 1/15/2011-1/14/2013, 24 months, declined.

“Chemically-Mediated and Advanced Generation II FRRPP Materials/Systems for WMD Protection”, G. Caneba (PI), DOD-DTRA, \$993,302, 6/1/2010-5/31/2015, 60 months, declined.