Center for Layered Polymeric Systems
http://clips.case.edu
NSF Science and Technology Center

# Annual Report for Year Five 2010-2011

## May 2011

**Lead Institution:**
Case Western Reserve University

**Partner Institutions:**
University of Texas at Austin
Fisk University
University of Southern Mississippi
Northwestern University
Cleveland Metropolitan School District
Kent State University

**Affiliate Schools:**
Ohio Northern University
Rose Hulman Institute of Technology
Youngstown State University

**National Laboratories:**
Naval Research Laboratory

**Center for**
**Layered Polymeric Systems**

**NSF Science and Technology Center**
**DMR-0423914**

**Annual Report for Fifth Year**

**Lead Institution:**
Case Western Reserve University

**Partner Institutions:**
University of Texas at Austin
Fisk University
University of Southern Mississippi
Northwestern University
Cleveland Metropolitan School District
Kent State University

**Affiliate Schools:**
Ohio Northern University
Rose Hulman Institute of Technology
Youngstown State University

**National Laboratories**
Naval Research Laboratory

**May, 2011**

# Remembering Anne Hiltner

***Director of CLiPS 2006-2010***

**Anne Hiltner**, Case Western Reserve's first female professor of engineering and an internationally recognized scientist and engineer, died in September, 2010, after a courageous battle with illness.

"Our campus has lost a remarkable academic leader," President **Barbara R. Snyder** said. "As a woman in the sciences and engineering, Professor Hiltner's entire career served as an inspiration to others. As a researcher of extraordinary ingenuity and accomplishment, she transformed her field. Her impact on the university, and on students and colleagues worldwide, cannot be overstated. We will miss her."

Professor Hiltner came to the university in 1967, after earning a doctorate in physical chemistry from Oregon State University. She served as a research associate for one year with chemistry professor Irvin M. Krieger, and then joined the laboratory of Professor Eric Baer, who was chairman of the Department of Macromolecular Science at the time. The connection with Professor Baer proved fortuitous, as the pair forged a powerful scientific collaboration that persisted to the present. They also discovered personal compatibility, marrying in 1999.

In 1974, Hiltner became the university's first female member of the engineering faculty when she became an assistant professor of macromolecular engineering. Seven years later she founded the Center for Applied Polymer Research (CAPRI), an organization that encouraged collaboration across disciplines and ultimately laid the groundwork for the program that she considered her greatest achievement, the awarding of a 10-year, $40 million National Science Foundation Science and Technology Center (STC), the Center for Layered Polymeric Systems (CLiPS).

"The STC made her feel she had reached to the top of Everest," Baer said. "She really reached the pinnacle of her career."

She was a Fellow of the American Chemical Society's Division of Polymeric Materials, the American Institute for Medical Biological Engineering, and the High Polymer Physics Division of the American Physical Society.

In 2001, Professor Hiltner was the recipient of the American Chemical Society's Cooperative Research Award in Polymer Science and Engineering. In 2004, Case Western Reserve named her the Herbert Henry Dow Professor of Science and Engineering. That same year, the Society of Plastics Engineers' Thermoplastic Materials and Foam Division presented Professor Hiltner its annual outstanding achievement award. In 2008, she received the American Chemical Society's Award in Applied Polymer Science. In announcing the honor, the society cited Professor Hiltner's "pioneering contributions in understanding the connections between hierarchical structure and properties of polymers, their blends and composites."

Even with all of the recognition, Baer said, "her greatest joy was her involvement with the graduate students. She loved the creative, productive side of her work."

**"The greatest tribute others can make to Hiltner," Professor Baer explained, "is to continue her creative mission through their academic work."**

## I.B. CONTEXT STATEMENT

### *CLiPS Vision and Goals*

The **Vision** of the Center for Layered Polymeric Systems (CLiPS) is to create an integrated program of research and education through the vehicle of a unique microlayering and nanolayering process technology at Case Western Reserve University (CWRU). CLiPS will be a powerful national model for distinguished research and for successful recruitment of American students from diverse backgrounds into the science and engineering workforce. CLIPS partner institutions include the University of Texas at Austin (UT), Fisk University, the University of Southern Mississippi, Northwestern University, the Naval Research Laboratory, Kent State University and the Cleveland Metropolitan School District. The Center Director is Professor Eric Baer. He is aided in the management of the Center by Associate Directors for Research, Education & Diversity, and External Affairs. The strategic plan for achieving the CLiPS vision is focused with the assistance of a diverse External Advisory Board.


**CLiPS Partner Institutions**

The Center:

- Integrates activities of research platforms with multi-level educational programs to train a diverse American workforce that can meet the challenges of new nanotechnologies.
- Focuses the impact of the integrated research and education activities on national priorities in defense, environment, energy, and health.
- Disseminates the knowledge developed through the integrated Center research and educational activities to the larger audience beyond the partner institutions.
- Serves as a compelling model for expanding relationships between minority-serving colleges and universities and with major research universities.

The CLiPS approach strategically integrates polymer science and engineering with research in nanotechnology, optics, laser physics, membranes, energy, device development and other scientific disciplines in a "**polymers-plus**" concept. The multidisciplinary nature of the research program flows naturally into graduate and undergraduate education. Integrated educational programs mirror the polymers-plus idea to introduce modular coursework in emerging cross-disciplinary areas. Students and faculty trained in this area are uniquely positioned to make major contributions to the fields of polymer science and technology, physics, chemical and polymer engineering, and nanotechnology. For example, the research and education partnership between CLiPS and Fisk University is broadening participation of African-American students in the science and technology programs at both universities. To attract undergraduate students to CLiPS REU and graduate programs, the Center is in the process of adding three new HBCUs to the Affiliates Program in addition to our regular recruiting efforts. The REU Program and Affiliate schools have been an important source of graduate students for CLiPS partner institutions. In addition, the Polymer Envoys Program engages high school students from the Cleveland Metropolitan School District in the exploration of polymer science and engineering as academic pursuits and eventual careers; this program is serving as a model for the partners to form linkages with local public high schools. CLiPS engaged large numbers of pre-high school students in STEM activities as part of our recruiting effort for the Polymer Envoys Program and to help fulfill CLiPS' educational mission.

Recognizing that personal contacts are an important influence in the career choice of college graduates, CLiPS has established affiliations with non-PhD-granting schools that offer strong undergraduate science and engineering programs to stimulate enrollment of American students in CLiPS graduate programs. As mentioned above, in addition to the three current CLiPS Affiliates, Ohio Northern University, Rose-Hulman Institute of Technology, and Youngstown State University, we are in the process of adding three HBCUs to the program.

Fundamentally new materials are obtained by forced-assembly of polymers into layers no thicker than the radius of gyration of an individual polymer molecule. CLiPS research activities are organized into four platforms to exploit the microlayer and nanolayer structures: (1) Rheology and New Processing focuses on integrating rheology into the multilayering process, and will explore combinations of rheologically dissimilar materials to create new polymer-based structures; (2) advanced Membranes and Transport Phenomena that exploit the layered hierarchy to achieve unique transport properties; (3) novel Optic and Electronic Systems based on the advanced layered materials, and (4) new Science and Technology Initiatives that probe a fundamental understanding and explore new opportunities for the layered structures.

The Center endeavors to become a unique global resource for the dissemination of knowledge in the area of layered polymeric systems and a national force for engaging audiences at all levels in polymer science and engineering. The Center fosters linkages between academia and industry in order to accelerate the development of new product initiatives.

### ***Highlights of 2010-2011***

- The management and operational structure was reorganized to set the stage for CLiPS legacy:
    - Three Associate Directors were appointed, Lei Zhu for Research, David Schiraldi for Education and Diversity, and Kenneth Singer for External Affairs
    - Two new platform leaders were named, João Maia for Platform I and LaShanda Korley for Platform IV
    - The enabling technology was centralized under the designation Facilities and Equipment operating out of the Office of the Director
    - Pamela Glover was appointed Executive Director for Education and Planning, supported by two Education Directors, Tryreno Sowell at CWRU and Pamela Cook at UT, and by Katherine Binder, Assistant for Operations.
- Platform I focused on rheology and new processing methods to enable multilayering of rheologically dissimilar materials. In the former case, a new extensional rheometer was developed, as was the capability to simulate computationally the flow inside feedblocks and the multiplier dies.
- Platform II continued fundamental understanding of transport phenomena in micro- and nano-layered systems by performing systematic experimental and modeling studies to identify the dominant controlling structural variables. Focus areas include solvent-free processing of membranes for gas separation and water purification, high performance barrier materials incorporating liquid crystalline polymers, multi-layered oxygen scavenging membranes, and layered systems with fouling resistance characteristics.
- Platform III's goal is to explore the science and application of micro- and nano-layered polymeric materials for photonics, optoelectronics, and energy technology. The platform added new investigators in the area of synthesis and optoelectronics. Bob Tweig (Kent State University) will be starting with synthesis of active molecules for the Laser and Optical Data storage project. Lei Zhu (CWRU) has joined the Active Materials project. Chris Ellison (UT) is contributing polymer

synthesis to the Laser project. The platform continues to develop optical data storage, all polymer lasers, active materials, and photovoltaics. Notably, an initial patent office action accepted the Bragg reflector claims; the distributed feedback laser claims are being incorporated in a second patent.

- Platform IV continued to focus on the nanoconfinement effect in micro- and nano-layered materials. The multilayered dielectric films have demonstrated high energy density, low dielectric and hysteresis losses, and can operate at high temperatures (~125 °C). These properties have way exceeded those for the current state-of-the-art biaxially oriented polypropylene (BOPP) films. Improvements in mechanical toughness have been demonstrated through a layer-thickness dependent shift in nanodeformation mechanics in multilayered films. Crystal growth and orientation within multilayered films has also been controlled via changes in layer thickness.
- CLiPS established connections with three new HBCUs in the affiliates program to increase efforts to attract students of diverse backgrounds to CLiPS graduate programs.
- CLiPS REU program at CWRU attracted the largest class to date with 27 undergraduate students joining CLiPS laboratories for this summer program.
- Stimulated by CLiPS support and led by Kenneth Singer (CLiPS Platform 3 Leader), the Materials for Opto/Electronics Research and Education (MORE) Center, a photovoltaic device facility, was established at CWRU.
- Initiated and supported by CLiPS, João Maia is establishing the Center for Advanced Polymer Processing (CAPP).
- CLiPS-developed technology was the foundation for a second new entrepreneurial venture, PolymerPlus LLC.
- Industrial funding in 2010 has exceeded the goal set for 2016.
- In 2010-2011, the amount of government funding almost doubled from the 2009-2010 level.
- The CLiPS 2$^{nd}$ Industrial Showcase attracted 44 attendees representing 29 companies and external organizations.
- CLiPS faculty members and students earned the following honors and awards:

  ***Faculty Members –***
  *Chris Ellison (UT)* – NSF Career Award
  *LaShanda Korley (CWRU)* – NSF Career Award, 2011 Diekhoff Graduate Mentoring Award, 3M Nontenured Faculty Award
  *João Maia (CWRU)* – 2010 Award of the British Society of Rheology, 2011 Morand Lambla Award of the Polymer Processing Society.
  *David Schiraldi (CWRU)* – 2011 Graduate Teaching Award

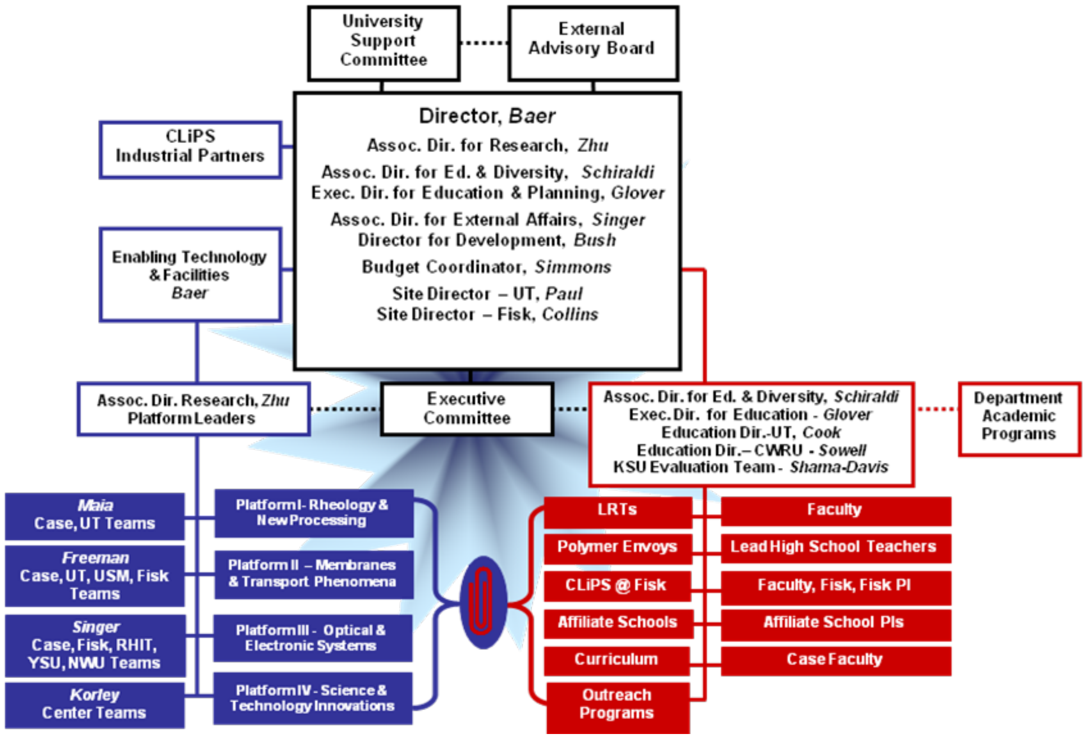
  ***Students -***
  *Ricardo Andrade (CWRU)* – 2010 FCT PhD Fellowship
  *Yaya Lai (CWRU)* – SPE ANTEC Award for Best Paper 2010
  *Ralm Ricarte (UT)* – 2011 NSF Graduate Fellowship.

***Leadership and Management***

The CLiPS organization and operation plan enables the Director and management team to:

- Provide leadership for realization of the Vision through the Strategic Plan
- Ensure integration of multidisciplinary research, education and knowledge transfer activities
- Promote broad participation of the various constituencies that make up CLiPS
- Establish team-based research programs with mechanisms for growth and renewal
- Create a national model for expanding relationships between minority-serving colleges and universities and research universities
- Enable recruitment and education of students with diverse cultural backgrounds into science-oriented careers
- Facilitate education of multi-disciplinary, team-oriented students within traditional university settings
- Maintain effective day-to-day management, fiscal responsibility and reporting functions

The management and operation plan was restructured during the past year as summarized in the Organizational Plan below (see also Appendix B). Due to the untimely death of Director Anne Hiltner, former Co-Director, Eric Baer, was appointed as the Director of CLiPS in the fall of 2010.




Professor Eric Baer is the Herbert Henry Dow Professor of Science and Engineering. He sets the Vision of CLiPS, leads the strategic planning process with involvement of the membership in an ongoing manner, acts as the intellectual leader in setting research priorities in collaboration with the Platform Leaders, verifies communication across participating groups, ensures integration of diversity throughout CLiPS programs, identifies and mentors new faculty into CLiPS, negotiates fiscal and policy issues with the university on behalf of CLiPS, and makes final decisions on key management positions and resource allocation. With the Associate Directors and the Executive Committee, the Director identifies measures for evaluating success in both research and education, and defines indicators of success of the program. He also leads the industrial outreach and spinoff activities of the Center.

The expanded management team includes the Associate Directors. Lei Zhu, Associate Director for Research, works with the Director to coordinate and develop research activities that extend across the CLiPS research platforms and identifies potential collaborative initiatives that cross platforms and/or institutions. David Schiraldi, Associate Director for Education and Diversity, with the Director oversees Education and Diversity programs, and provides technical leadership to the Center's educational vision and programming. Kenneth Singer, Associate Director for External Affairs, works with the Director to promote knowledge transfer and commercialization of CLiPS research and technologies, develops new sources of external funding, and enhances Center's outreach and external collaboration.

Pamela Glover serves as Executive Director for Education and Planning. She is a full-time staff member who leads in planning, implementation, assessment and innovation of the integrated research and education programs. She also assists the Director in day-to-day management of CLiPS. She is assisted in managing CLiPS education programs by Tryreno Sowell, Director for Education and Diversity, who is a full-time staff member at CWRU, and Pamela Cook, Director for Education and Diversity at the University of Texas where she is committed half-time to CLiPS education and outreach programs.

Patricia Simmons is the Budget Coordinator for CLiPS. She oversees all of the documentation and the fiscal reporting functions of the Center. She is assisted by Jeffrey German-Lortie, Accountant, who is also a full-time staff member.

Dr. Charles Bush serves as the Director of Development. He coordinates the intellectual property, industrial outreach and business development activities of the center. He comes from a 32-year career in management of industrial R&D and other technical functions at an executive level.

The committee structure facilitates effective and efficient operation of the research, education and diversity programs while maintaining close communication and interaction among the faculty and staff. The Executive Committee, chaired by the Director, meets monthly with faculty and staff members at the partner institutions via teleconference. The one-hour meetings cover management and organizational aspects of the center and include discussions of the research and education experience of the students and the integration of diversity into the programs.

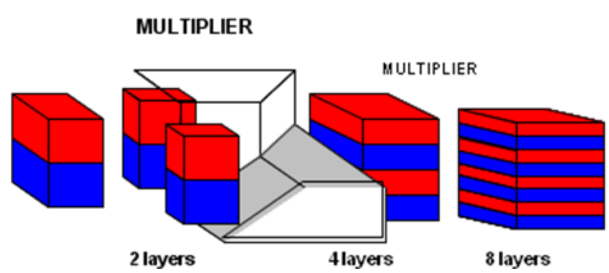
Technical topics are addressed in regular Platform meetings. The highly interactive research projects require regular meetings for planning and discussion. The platform committees are chaired by the platform leaders and consist of the platform faculty, students and research associates. Platform meetings are sometimes combined in order to facilitate interactions and coordination among the platforms. The flexibility of web-based meetings greatly facilitates inclusion of faculty and students at the partner and affiliate institutions.

The education and diversity programs are coordinated by the Education Program Committee, which meets twice a month to assist the Executive Director for Education & Planning with implementation, translation, and evaluation of the integrated education and outreach programs. The committee membership includes the Director, the Associate Director for Education & Diversity, the Executive Director for Education & Planning, the two Education and Diversity Directors (CWRU & UT), the KSU evaluation team, and the Education Program Coordinator at Fisk University.

The Director is assisted by a diverse External Advisory Board. Of the 12–member board, two of the members are African-American, two are women, and one has a disability. The EAB meets regularly to review the CLiPS Strategic and Implementation Plan (SIP), to review progress toward research and education goals, to assess the sufficiency of available resources for CLiPS to ensure achievement of the CLiPS integrated research and education mission, and to make a written assessment for the university administration.

***Intellectual Merit of the Center***

<u>Research Vision and Goals</u>




A broad range of new science and innovation is emerging from CLiPS unique technology. CLiPS is becoming a global resource for microlayered and nanolayered polymeric materials. The CLiPS research activities:

- Define and implement interdisciplinary research programs that exploit the large interfacial area and the unique nanoscale confinement made possible by reducing the dimensions and dimensionality of the layers.
- Use these architectures to create and explore new materials with unique transport behavior, dielectric behavior, and interactions with light.
- Focus the integrated research activities on national priorities of energy, environment, and security.

To achieve these goals, the research programs are organized into four research platforms:

- Rheology and New Processing (at CWRU and UT) enables fabrication of hierarchical microlayered and nanolayered complex polymer-based structures and systems using new feedblocks and multiplier dies, as well as the capability to accurately simulate multi-layered flows inside said equipment.
- Novel Membranes and Transport Phenomena exploit the layered hierarchy to achieve unique transport properties. Researchers from UT, CWRU, USM, and Fisk collaborate in this thrust area under the leadership of UT. We are focused on solvent-free processing of high-flux, high selectivity layered membranes for gas separation and water purification membranes; high performance barrier materials based on forced assembly of nano- and microlayered liquid crystalline polymers and nanocomposite systems; high barrier systems based on multilayered oxygen scavenging membranes; layered membranes with improved fouling resistance; and fundamentals of nanoconfinement on physical aging in layered systems.
- Innovative Optical and Electronic Systems are based on advanced layered materials. Teams from CWRU, Northwestern, Youngstown State, and Rose-Hulman collaborate in the development and testing of devices. The addition of new faculty members from Kent State University and the University of Texas will enhance our exploration of new materials. New work on active materials and polymer synthesis will strengthen the laser and optical data storage projects.
- The layer-multiplying process opens new opportunities for Science and Technology Initiatives. New knowledge and new properties from nanoconfinement effects of micro and nanolayered materials are being studied. Researchers from CWRU, UT, and Fisk are exploring how confined morphologies within multilayered films impact dielectric, mechanical, and crystallization phenomena. Multilayer dielectric films have demonstrated high energy density, high breakdown strength, and low dielectric and hysteresis losses. A new multilayer system also demonstrated high temperature operation up to 125 °C.

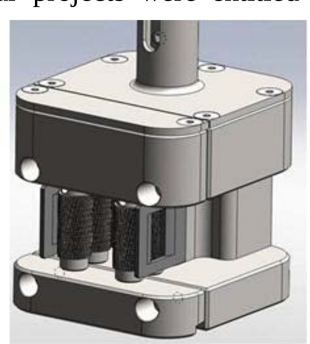
***Research Accomplishments and Highlights***

2010 was a pivotal year in the research activities of the Center as the focus shifted toward developing mid- and long-term legacy and planning for long-term sustainability. As part of the reorganization, Platform I was renamed and redefined. Formerly titled the "Enabling Technology," the multilayering technology that forms the foundation for CLiPS research, was taken out of the platform structure. It is now part of the Enabling Technology and Facilities Division that facilitates the needs of all of the platforms under the leadership of the Director.

**Platform I. Rheology and New Processing**

Under its new configuration, Platform I is led by Professor João Maia. The foci of the Platform I activities are: a) To fully integrate rheology into the layering process, be it from the angle of die and feedblock design or the matching of the pairs of materials for layering; b) To develop the technology to allow rheologically dissimilar and also multiphase polymeric systems to be layered, thus opening new areas of application of the technology.

In 2010 six projects were active in the Platform, four of which included researchers from both Case Western Reserve University and The University of Texas at Austin, with the remaining two being all-CWRU. Two of these projects, totaling $1,980,000 in direct industrial funding, are confidential in nature and won't be addressed in this overview. The remaining four projects were entitled "New microstructures", "Extended rheological characterization", "Computational flow modeling", and "Layering of rheologically dissimilar materials".



The new extensional rheometer

***New Microstructures***

The main goal of the "New microstructures" project, led by Eric Baer, is to develop fibers and/or fibrillar structures, to which purpose research is being performed in the production of checkered

2D structures and in post-extrusion layer delamination. Initial results are very encouraging, indicating that it is indeed possible to achieve delamination of nanometer-sized fibers *via* post-processing manipulation.

***Extended Rheological Characterization***

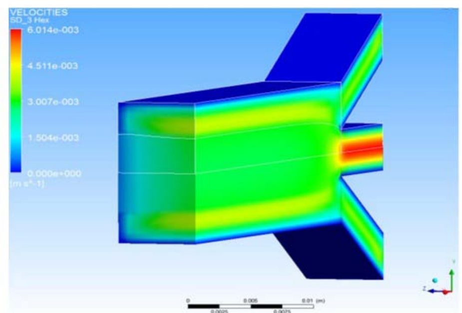
The "Extended rheological characterization" project, under the leadership of João Maia, is currently focused on the development of a new dual controlled stress/rate extensional rheometer for polymer melts that will allow CLiPS to perform the full spectrum of rheological characterization of the materials. This capability, which will be reached in Q1 2011, is vital to achieve the second goal, that of full viscoelastic modeling of the rheological behavior of these materials *via* the use of advanced multi-mode viscoelastic models such as the Phan-Tien-Tanner model.

***Computational Flow Modeling***

This ability to fully model the viscoelastic behavior of the polymers is absolutely instrumental to the success of the third project, entitled "Computational flow modeling", which is led by Roger Bonnecaze. In this, we are aiming at being capable of simulating the flow of co-extruded materials in different feedblocks and multiplying dies. At the end of 2010 the computational routines have already been developed and are being tested and validated for a variety of rheologically simple materials, such as Newtonian and weakly elastic fluids.

***Layering of Rheologically Dissimilar Materials***

Finally, the "Layering of rheologically dissimilar materials" project is devoted to the optimization of processing conditions and die flow geometry to allow the layering of materials of highly dissimilar rheological behavior, such as viscosity ratios up to order 10. In order to achieve this, it is first necessary to understand the kinetics of propagation of flow instabilities and with that in mind, a visualization die with the same channel geometry as the current multiplying die was developed. This die was manufactured at the end of 2010 and the visualization studies themselves are expected to begin in 2011.



Velocity profile (in Polyflow) for half cut of the Feedblock

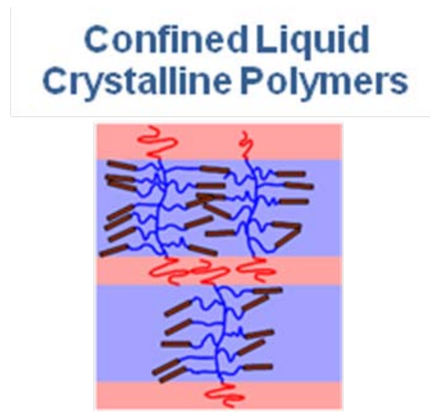
Overall, it can be stated that the activities of the renewed Platform I are progressing very well, and it is clearly on the way to achieving its main objectives. Although some publications have already resulted from the Platform's activities in 2010, as the projects mature and results are more forthcoming, it is expected that 2011 will see a big increase in publications, be they patents, scientific journals or conference presentations. 2011 will be a pivotal year in the Platform's activities that is hoped will launch it on a path towards long-term stability.

**Platform II – Membranes and Transport Phenomena**

Fundamental understanding of transport phenomena in micro- and nano-layered systems will be developed by performing systematic experimental and modeling studies to identify the dominant controlling structural variables. This understanding of fundamental transport phenomena will be used to design and optimize unique layered systems. Layered material systems will be optimized to exhibit transport-property profiles that may be otherwise inaccessible. For example, these layered systems may be used for modified atmosphere packaging for products such as meat and produce, and for high barrier applications such as packaging for electronic devices or pharmaceuticals. Further studies involve designing specialized membranes for separation applications such as desalination systems and the development of anti-fouling devices. The anti-fouling technology is being commercialized through the UT start-up company, Advanced Hydro, and research is continuing on additional filtration applications. It is important to note that the emphasis in the development of these new technologies is to be solvent-less and environmentally friendly.

***Development of High Barrier Layered Systems using Particulates***

The main goal of this proposal is to explore the potential of multilayer technology for the development of nanoparticulate filled structures with enhanced gas barrier properties. In particular the enhancement of oxygen and water barrier will be the target for applications in the area of electronic packaging. Three different nanoclays with aspect ratios (L/h) ranging from 27 to 1000 have been selected. Cloisite 20A, montmorillonite (MMT) (L/h = 200) and Laponite™ RD (L/h = 27) have been purchased from Southern Clay Products (USA). Synthetic Mica (Somasif ME-100, L/h = 1000) was modified with dimethyl dihydrogenated tallow ammonium chloride (the same surfactant used to make NaMMT into Cloisite 20A) in accordance with established literature procedures. To date a large number of nanoparticulates have been incorporated into the LLDPE matrices. They include montmorillonite, synthetic fluorinated mica, chrysotile nanotubes, and graphene nanoplatelets. With each system, upon optimization, significant increases in gas barrier properties were observed.




***Oxygen Scavengers for Packaging Applications***

Polymers containing unsaturated alkene bonds, such as polybutadiene, offer possibilities as oxygen scavenging materials. In this research, block copolymers, containing polybutadiene, which can be activated for oxygen scavenging, and polystyrene, which assists in blending and melt processing applications, were used as the basis for preparing novel oxygen scavenging systems. These materials were characterized with respect to their morphology and oxygen scavenging characteristics. A systematic modeling study was also undertaken as part of this effort, and two additional papers from the modeling study have been published. Additionally, we have identified conditions which should permit melt extrusion of scavenging compositions, and we are actively pursuing melt processing of oxygen scavenging layered systems.

***High Barrier Materials from LCPs***

Liquid crystalline polymers (LCPs) have among the highest barrier properties of all known families of polymers. However, they are typically expensive and can pose melt processing challenges (low melt viscosity with strong temperature dependence of viscosity). In this study, we seek to prepare multilayer films where one layer is a high barrier LCP and the other is a confining polymer. We will seek to understand whether the concepts discovered in confined crystallization can be extended to LCPs to reduce the amount of LCP needed to attain high barrier properties and enhance barrier properties via confined "liquid crystallization". During the beginning of this project, several materials synthesis approaches have been explored and new materials have been produced for further characterization.

***Multilayered Materials for Modified Atmosphere Packaging Materials***

The preservation of fresh produce as it passes through the supply chain is an important economic and safety issue. Although traditionally achieved through refrigeration, food preservation can also be addressed by controlling the gaseous atmosphere around the produce. This alternative, known as modified atmosphere packaging, or MAP, has recently been shown to be a useful strategy for use with or without refrigeration and has opened up significant opportunities for membrane technology. This project addresses deficiencies of current membranes for this application that ultimately may be solved using layering techniques. The immediate concern is to develop membranes with tunable $CO_2/O_2$ selectivity. Recent literature reports that poly(ethylene oxide), or PEO, materials have exceptionally high $CO_2/O_2$ selectivity; however, these materials are not directly suitable for this application, owing largely to their low gas permeability and high water solubility. A line of thermoplastic elastomers produced by Arkema Inc., known as PEBAX block copolymers, is an attractive option for packaging applications. Arkema Inc.

generously provided five different grades of PEBAX in pellet form for this investigation. PEBAX 2533 has been coextruded at CWRU, and initial membrane production and permeation measurements have been made. Films of PEBAX 2533 (80PTMEO-PA12) with thicknesses as little as 7 μm have been achieved, and composite films with selective layers in the tens of microns have been produced. However, thinner films are required to achieve the permeance necessary for packaging; a typical value used in existing packaging is ~ 35 GPU (1 GPU = 1 Barrer/μm) which corresponds to slightly more than 1 μm thickness in some PEBAX grades, and this will represent the processing challenge for the upcoming year on this project. Additionally, we are focusing this project more towards characterization of the porous layers that are required for membrane applications, and this focus is leading us to new applications of microlayering to produce porous membranes for filtration applications and potentially new materials for energy storage applications.

***Physical Aging of Glassy Polymers in Confined Environments***

Polymer glasses and other amorphous materials generally exist in a non-equilibrium state when they are below their glass transition temperature ($T_g$). In the glassy state, properties such as volume and enthalpy are in excess of their equilibrium values. Physical aging is a term that describes the spontaneous (but typically slow) evolution of these properties towards equilibrium values as the material undergoes structural relaxation. Aging in bulk polymer systems has been studied rather intensively for decades; however, recent observations suggest that the aging behavior of free-standing thin films (<1 μm) and other confined arrangements can differ markedly from that of bulk materials. In free-standing thin films, aging can be orders of magnitude more rapid than it is in the bulk state. This has tremendous practical consequences for polymeric gas separation membranes, many of which achieve separation by permeating gas through a dense glassy layer whose thickness is on the order of 100 nm. The practical importance of physical aging effects is not limited to separation membranes; rather, it extends to all applications that utilize glassy polymers in confined environments. Currently, the reasons for the thickness dependence of physical aging are not completely understood. Additionally, the role of interfaces during the aging process has not been well elucidated. Multilayered films with thin glassy layers can provide a novel means to study the role of interfaces during aging. Extruded multilayered films provide a large number of polymer-polymer interfaces, which will allow us to explore the role of interfacial interactions during aging and will provide new knowledge about the physical aging of polymers in confinement. The primary objective of this project is to explore the physical aging behavior of glassy polymers in layered arrangements via gas permeability measurement and DSC to better understand (a) the importance of interfaces during aging and (b) the reasons for the thickness-dependent aging rates that have been observed in some confined geometries. During the past year, DSC and permeation studies have been used to study physical aging in confined environments, and we are exploring the influence of hard vs. soft nanoconfining layer polymers on physical aging.

***Multilayer Desalination Membranes***

All desalination membranes currently in use are produced via solution processing of monomers that undergo an interfacial reaction at an oil/water interface to produce aromatic polyamide interfacial composite membranes. Large volumes of volatile, flammable hydrocarbon solvents are used in this process. Solution-based preparation is dangerous, and the costs associated with disposal of waste material are high. Thus, there is a great need for better methods for preparing desalination membranes. The goal of this research project is to develop solventless, melt-processible, coextruded membranes for desalination. A multilayer coextrusion process is envisioned to prepare disulfonated poly(arylene ether sulfone) (BPS) thin film composite membranes for desalination. By making membranes via coextrusion, it may be possible to achieve high quality BPS thin film composite membranes at lower cost with more efficient processing. One project, centered at UT, is aimed at developing melt processing protocols for desalination membranes and testing the water and salt transport properties of such materials. Another project, centered at Fisk, is aimed at synthesizing the next generation of materials for this application.

**Platform III - Optic and Electronic Systems**

Platform III continues to make excellent progress on its projects: 1) Light Emission and All-Polymer Lasers 2) GRIN Optics 3) Optical Data Storage 4) Electro-Optics 5) Active Materials 6) Photovoltaics and 7) Magneto-Optics. These are listed in order of initiation. We have recently added another synthetic chemist, Robert Twieg from Kent State University to enhance our exploration of new materials. He joins Tobin Marks from Northwestern, who was added last year, and Lei Zhu from CWRU and Chris Ellison from University of Texas who are all contributing new materials. Professor Twieg will be starting with synthesis of active molecules for the Laser and Optical Data Storage projects, Professor Marks is leading the Electro-Optics Projects, Lei Zhu (with Jie Shan) the Active Materials Project, and Chris Ellison is contributing polymer synthesis to the Laser Project.

***Light Emission and All-Polymer Lasers***

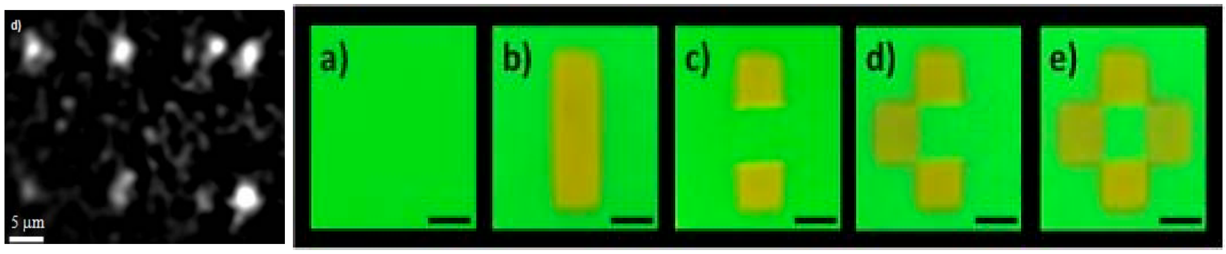
The Light Emission and All-Polymer Lasers Project is now being led by James Andrews at Youngstown State University along with Kenneth Singer. The project has completed the initial study of elastomeric lasers, demonstrating tunability over a wide range. A manuscript has recently been submitted for publication. The project focus is turning toward applications and lifetime issues. In the applications realm, medical applications for disposable laser sheets are being investigated and an intellectual property disclosure completed. Along these lines, the patent office has issued its initial office action on our pending patents on distributed Bragg reflector (DBR) and distributed feedback lasers (DFB). The action supported the claims on the DBR laser, and the DFB claims are being collected into a separate patent. Scientific attention now turns to lifetime issues with the initiation of mechanistic studies, as well as synthesis of new materials. Professor Twieg will contribute members of a class of highly stable fluorophores he has investigated for bioimaging purposes, and Chris Ellison will contribute dye-functionalized polymers also aimed at improving stability.

***Multilayer Gradient Refractive Index Optics***

Multilayer Gradient Refractive (GRIN) Optics will also continue to receive considerable attention. A winning DARPA grant moves much of the activity on GRIN lenses out of the center and into legacy. Thomas Oder at Youngstown State University is leading an effort to fabricate microlens arrays with CLiPS GRIN substrates. He is using photolithography techniques to define microlens arrays in multilayer films. Such films could have a number of important imaging and non-imaging applications including optical communication, solar energy, displays, and MEMs just to name a few. Good results with wet and dry etching and grey-scale masks for curved surfaces have been obtained. In the next year, activities will be focused on improving the processing using the current techniques as well as investigating the use of a new SEM/FIB tool. Characterization will also be carried out.

***Optical Data Storage***

The Optical Data Storage Project has moved forward with a manuscript having been submitted on our novel scheme for two-photon writing and a second being prepared describing the data resolution in our nonlinear writing scheme. Optical modeling has indicated that significant signal-to-noise improvements are possible with multilayering. We have demonstrated that data can be written deeply into a 64 layer multilayer film and will be preparing a manuscript on this soon. In the coming year, we hope to demonstrate CLiPS films as a revolutionary approach to optical data storage that can be integrated into current technology. We will also investigate new re-writable and permanent writing schemes and seek to understand the writing mechanisms more completely.




**Reversible Fluorescence Writing**

***Electro-Optics***

The Electro-optics project, led by Tobin Marks has made considerable progress this year. Three amphiphilic chromophores were designed and two were successfully synthesized. The third is currently being addressed. Initial alignment studies were carried out as well. The nonlinear optical characterization setup for second harmonic generation is nearly complete. Initial studies will be carried out soon. In the coming year, the third chromophore will be completed and second harmonic studies of alignment and angular distribution of the amphiphiles at the surfaces of monoliths and interfaces in biliths will be carried out. If all successful, then A-B-C films will be processed and studied.

***Active Materials***

The Active Materials project is focused on polymer coated nanoparticles, $BaTiO_3$ for dielectric application, and Ag for nonlinear optical/optical data storage. Polymer coatings will allow them to be blended in multilayer polymer films. Work on polystyrene polymer brush-coated particles in both cases was carried out. On $BaTiO_3$, adhesion issues are being addressed, while in Ag nanoparticles, aggregation has proved to be challenging. In the coming year, we hope to complete and scale up the graft-on coating of $BaTiO_3$, and to try a new route to PMMA brush-grafted Ag nanoparticles. We will also initiate rheological studies, nonlinear optical characterization, and processing studies.

***Photovoltaics***

The Photovoltaics project now mainly involves CWRU, YSU and Northwestern and is focused on polymer photovoltaics with an emphasis on optical design and properties for making very thin photovoltaic structures. We have completed a study of thickness dependence of polymer photovoltaic films relating optical and photoelectric properties indicating general agreement between our modeling and experimental results. In particular, we have demonstrated designs that capture a wider spectrum to increase efficiency. Manuscripts are being prepared. In the next year, we will examine longer wavelength, more efficient materials to demonstrate further efficiency increases by spectral broadening. We are also seeking to expand funding in this area.

***Magneto-Optics***

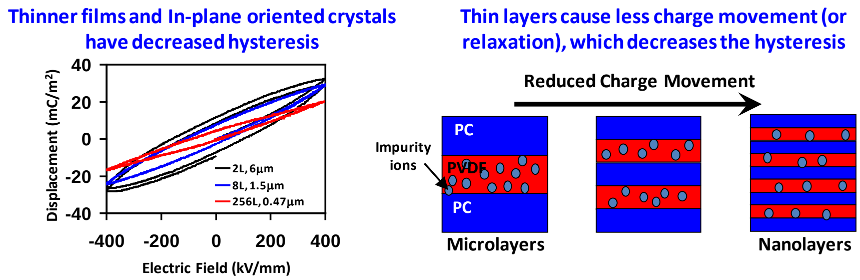
Magneto-optics in one-dimensional photonic crystal multilayer polymer films was studied this past year. The effects of slow-light on the magneto-optic effect were studied by modeling and by experiment. An ultrasensitive Faraday effect setup was developed. Results have been written up and will be submitted very soon. Because of the lack of appropriate materials with a large Faraday effect, this project will not be continued.

**Platform IV. New Science and Technology Initiatives**

Platform IV is the arena for exploring new science and technology initiatives. Current projects in this platform involve 1) understanding the dielectric properties of multilayer films in various configurations for electric energy storage applications; 2) manipulating block copolymers by combining forced with self-assembly to demonstrate different confinement effects for enhanced mechanical and barrier applications; 3) understanding the physics of crystalline behavior under nanoconfinement.

Platform IV involves teams from Case, UT, Fisk and NRL who explore new opportunities for the enabling technology under the new leadership of Professor LaShanda Korley.

***Dielectric Properties***




There is a need in power electronic systems and pulsed power applications for capacitors with high energy density and low losses. We have achieved a breakthrough by combining a high breakdown strength polymer with a high dielectric constant, PVDF, as multilayer films. The layered films exhibited significantly higher breakdown strength, lower dissipation factor, and low hysteresis. Their superiority was also demonstrated in prototype capacitors.

Currently, we have achieved understanding of the underlying mechanism of the better performance for these multilayer dielectric films. Fundamentally, the lossy dipolar switching is effectively prohibited in multilayer films, and only impurity ion polarization contributes to the hysteresis loss. In polycarbonate (PC)/PVDF multilayer films, ionic polarization can be further minimized with decreasing the layer thickness to nanometer scale, and hysteresis loss continues to decrease. Meanwhile, crystalline lamellar orientation can affect the ionic motion in multilayer films. A flat-on crystal orientation can further reduce the hysteresis loss, as compared to the edge-on crystal orientation.

In a poly(ethylene terephthalate) (PET)/PVDF-TFE system, biaxial orientation further enhanced film quality by increasing its mechanical property. As a result, the breakdown strength of biaxially oriented PET/PVDF-TFE multilayer films further increases. The energy density at breakdown has reached as high as 16 $J/cm^3$, which is about three times that of the state-of-the-art BOPP. Similar to the unstretched multilayer films, hysteresis loss decreases with decreasing the PVDF layer thickness. In addition, crystalline morphology also plays an important role in minimizing further the dielectric and hysteresis losses.

Recently, we have established the high temperature characterization capability in our laboratory. The PVDF/polysulfone (PSF) 30/70 multilayer film can operate at temperatures as high as 125 °C with a reasonably low hysteresis loss. This can be attributed to the blocking electrode effect from the 70 vol.% PSF layers. When the PSF layer thickness decreases, the "tunneling" effect starts to play an important role by increasing the charge carrier mobility at high temperatures. Future plans will study how to decrease charge carrier mobility at high temperatures.

***Forced and Self-Assembly***

The second focus area aims to combine forced assembly with self-assembly to influence specific properties, such as mechanical and barrier properties. Multilayer coextrusion is a unique platform to examine confinement effects of block copolymers. We have demonstrated a layer thickness-dependent change in deformation mechanics in multilayer films consisting of an elastomeric block copolymer confined between alternating layers of glassy polystyrene. Upon annealing, unprecedented BCP ordering is observed within the thinnest layers. Mechanical anisotropy is also a direct consequence of the BCP ordering and alignment within the multilayered films. We have explored the nanoscale deformation mechanisms of confined polyethylene oxide crystals with multilayer films, motivated by the discovery of nearly perfect polymer single crystals obtained by confined crystallization within nanolayers. These promising results motivate further studies using controlled block copolymer architectures with embedded functionality.

***Confined Crystallization***

The third focus area addresses the physics of polymers in ultrathin layers. One project explores the crystallization behavior of polymers when the conventional 3D crystal growth is frustrated. The continuous layers in coextruded films provide long-range, almost defect-free nanoscale confinement to study fundamental questions in confined crystallization. Initial work has focused on understanding and controlling the crystallization behavior of syndiotactic polypropylene in nanoconfinement. Future studies will emphasize crystallization kinetics and gas transport phenomena.

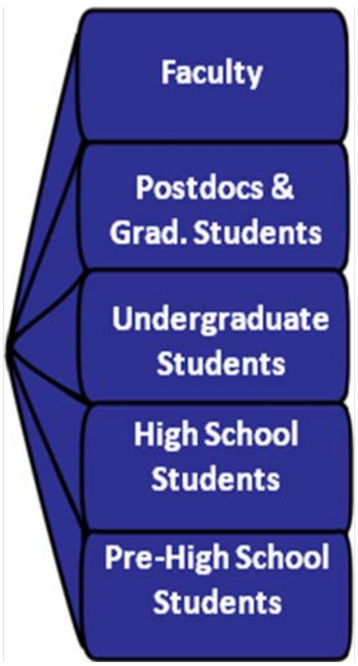
The research in Platform IV is leading to the discovery and understanding of new structures and new phenomena. These findings can be the basis for more complex hierarchical organizations and new materials systems.

***Integration of Research and Education***

<u>Vision and Goals</u>

CLiPS' vision is to be the global leader for integration of research and education in polymer science and engineering. In order to accomplish this, CLiPS integrates its research with multi-level educational programs to stimulate and prepare American students to pursue professional careers with advanced degrees in polymer science and engineering. The multidisciplinary resources of the Center are employed to develop focused programs that connect and educate a diverse range of American students from middle school through the PhD level.

Just as CLiPS research is based on multilayered structures, CLiPS education programs are called Layered Research Teams (LRT) which are multi-level and interactive in nature.




- Faculty members provide guidance and instruction. They develop project ideas and ensure the efficient operation of the LRT and serve as role models.
- Postdoctoral Associates work under the direction of a specific senior faculty advisor within the LRT. Mentoring is tailored to the career interests of each postdoctoral researcher and includes grantsmanship, interactions with industry and funding agencies, and collaborations with researchers across CLiPS. Postdoctoral associates also fulfill a teaching role interacting with graduate students, undergraduate students and Polymer Envoys on CLiPS research projects.
- Graduate Students conduct research on a project within the LRT. They teach research methodology to more junior students. This combination of teaching and learning activities, with mentoring by the faculty, prepares graduate students to become leaders in the polymer field
- Undergraduates in the LRT are mentored by graduate students on a research projects. They also serve as role models and ambassadors to the Polymer Envoys
- CLiPS program for high school students is the Polymer Envoys program. They are each taught by a graduate student on a longitudinal STEM related project. They share their research and enthusiasm with younger students through activities in the university and local schools.
- Pre-High School Student programs in CLiPS provide opportunities at the university and in the community, for younger students to become excited about science and engineering, and to learn about STEM-related opportunities, such as the Polymer Envoys program.

Mentoring

CLiPS educational programming includes a comprehensive, multi-level mentoring plan which includes Postdoctoral Researchers. This plan is further discussed in the Education section of this report and is found in its entirety in Appendix F.

Postdoctoral Associates

The goals for postdoctoral associates in the Layered Research Team are to:

- Gain experience in identifying best practices and grantsmanship
- Learn the skills to take a leadership role in developing publications, presentations and other knowledge transfer activities
- Enhance their professional skills through teaching, interactions with industrial representatives, and with professional organizations

Postdoctoral associates also serve as teachers, mentors and role models for graduate students, undergraduate students and Polymer Envoys in the program.

The success of the postdoctoral associates plan is assessed by monitoring the progress of each associate toward his or her career goals after completing the postdoctoral program. This year, two of CLiPS postdoctoral fellows went on to new careers – one in government research (Roberto Aga to Wright Patterson Air Force Base) and one to an academic career (Sanghyuk Park to a faculty position in South Korea.) In the fall of 2011, Guilin Mao, who was a postdoctoral researcher in the CLiPS program at Youngstown State University, will join the faculty at CWRU as a member of the Department of Physics. In addition, postdoctoral fellow, Mike Ponting, is the Director of Engineering for PolymerPlus LLC, the CLiPS spin off company located in Cleveland.

Graduate Programs

The goal of CLiPS graduate education is to prepare students as professionals and future leaders in the polymer field. To accomplish this goal, graduate students working in Layered Research Teams enhance their professional development by:

- learning research ethics, safety procedures and skills
- developing professional communication skills
- meeting and collaborating with industrial and academic partners
- participating in regional and national meetings and conferences
- learning to teach by mentoring undergraduate and high school students
- designing and implementing community outreach activities for pre-high school students

This year graduate students were co-authors on 32 of the 41 CLiPS publications and gave 30 presentations at professional meetings (including one student winning the award for Best Paper at ANTEC 2010.)

A key indicator of the Center's success is the production of students who enter STEM careers. During this reporting period, CLiPS graduated three PhDs (for a total of twelve since the beginning of the Center.) Two of the 2010 graduates are in the STEM workforce; one is undecided. In addition, one of our post-doctoral researchers has accepted a faculty position upon the completion of his training.

Masters candidates at Fisk University fulfill the same teaching-learning role in the LRT as the PhD students. This initiative – CLiPS@Fisk - is addressed in the section on Diversity both here and in the body of the report.

Undergraduate Programs

The CLiPS programs for undergraduate students are the *Affiliates Program* and the summer *REU Program*. These activities expose undergraduate students to polymer research and to opportunities in CLiPS.

CLiPS Affiliates are primarily undergraduate institutions in the states surrounding CWRU which have a strong undergraduate teaching focus and that do not offer PhD programs in CLiPS fields. CLiPS Affiliate institutions are Ohio Northern University, Rose Hulman Institute of Technology, Youngstown State University. In order to help fulfill CLiPS's goal of increasing diversity, we are in the process of adding three HBCUs to the Affiliates Program. The University of Texas has associations with the UT border schools, UT-Pan American and UT-Brownsville.

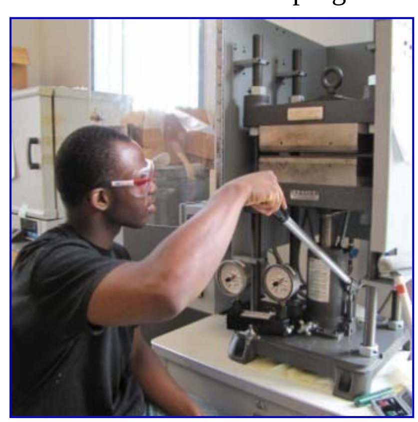
The REU program introduces CLiPS technologies, polymer science and STEM research to a diverse group of American students. It is also an important pipeline for American students into CLiPS graduate programs. This year the first four American students accepted into the CWRU PhD program in Macromolecular Science & Engineering were REU alumni, including James Aldridge, graduate of Youngstown State University, who joins the Baer research group in June, 2011. The program has grown this year. Historically there are eighteen students enrolled per year. This year there are twenty-seven REU students - eleven are women, six are from under-represented minority groups, and nine are from CLiPS Affiliate or former-Affiliate schools.

Students work as members of CLiPS Layered Research Teams for ten weeks under the mentorship of a graduate student. In addition to daily research activities, REU students participate in weekly program meetings during which they hone their presentation skills, attend lectures in various areas of polymer science and engineering, and discuss professional ethics. The summer program culminates in the Northeast Ohio Undergraduate Polymer Symposium, an event showcasing the summer research work of undergraduates from CWRU, the University of Akron, Kent State University, and NASA.

High School Program

CLiPS' program for high school students is the Polymer Envoys. This program matches one high school student with one graduate student in a longitudinal relationship that may last two or three years. As a result of this continuity structure, the program provides significant hands-on research experience and mentoring to a small number of high school students. It has a tremendous impact on the individual student participants, and allows CLiPS to more closely track students to determine short- and long-term impacts.

The program was initiated with the beginning of CLiPS in the fall of 2006. At that time six students from the Cleveland Metropolitan School District (CMSD) were recruited to become the first class of Polymer Envoys. The University of Texas followed suit, enrolling four students from the Austin Independent School District in the spring of 2007. This year there are thirteen students in the program – eight in Cleveland and five in Texas. Over the next reporting period the program will grow to number twenty-two students, including new Polymer Envoys programs at Fisk University (three students) and the University of Southern Mississippi (two students). In addition, at CWRU, recruiting efforts will cast a wider net and will recruit students from East Cleveland and Cleveland Heights-University Heights schools, as well as CMSD. All of these school districts have a high percentage of students who come from under-represented minority groups. The program in Texas also includes students from Texas School for the Deaf in Austin.



To date there have been forty-one Polymer Envoys and all but two of them have come from under-represented minority groups.

Thirteen students are currently enrolled in the program. Eighteen students have graduated from the Polymer Envoys program; all of them are in college. Fifteen are studying STEM fields. This spring we will have two more graduates; both of whom are attending college, one in a STEM field. Four of the program graduates are enrolled at CLiPS institutions.

In 2008 CLiPS partnered with the Kent State University Research and Evaluation Bureau to study the Polymer Envoys Program. The analysis of the first year's results contained some interesting highlights that will help in planning for the future. A significant finding was the influence of the graduate student mentors on the Envoys. The Envoys reported feeling supported by their graduate student mentor and motivated by the graduate student's academic achievement. They look upon the graduate students as role models both socially and academically. The Envoys reported that they have a long-standing interest in science, but that their high schools do not offer the coursework they need to prepare them for college studies in a STEM field. Tutoring in math and science has been integrated into the Envoys program to help the students in their work in the lab. With the expansion of the Polymer Envoys program, the study will also be expanded.

Pre-High School Programs

CLiPS is currently engaging youngsters across the Center in activities such as:

- Science Sundays at the Austin Children's Museum reaching greater than 1000 visitors annually
- The Middle School Science Club at Fisk University engaging 30-40 student per year
- Introduce a Girl to Engineering at CWRU, reaching 75 middle school young women
- The Martin Luther King Day activity at the Cleveland Museum of Natural History reaching ~150 children and families
- Summer Science Camp at UT – enrolling 25-30 middle school age students for 2 weeks during the summer
- Future Science Stars at CWRU – reaching 80-100 students middle-school age youngsters from local community groups with interactive science activity sessions held each summer

***Integration of Diversity into CLiPS Programs, Projects and Activities***

Diversity Vision and Overall Goal

CLiPS aims to become a national resource for broadening participation of women, under-represented minorities, and persons with disabilities in polymer science and engineering and related fields. In order to accomplish this, CLiPS has developed and will continue to develop initiatives that attract, train, and graduate diverse American students into polymer science and engineering, and related fields. The three goals for diversity are:

- To encourage a diverse range of students to pursue STEM careers through pre-college outreach programs and through collaborations between research universities and minority-serving institutions
- To engage Fisk University graduate students in CLiPS research projects through CLiPS @ Fisk activities
- To positively impact the diversity of faculty, staff, and students at all CLiPS Institutions

Engagement of Diverse Students

The Polymer Envoys Program is a key program through which CLiPS engages pre-college students. Working with the Cleveland Metropolitan School District and the Austin Independent School

District gives the program ample access to our target populations. Although this program was described elsewhere, it should be noted that all but two of the forty-one participants to date have been from under-represented minority groups and half of them have been young women.

Guided by experience with the Case-Fisk Alliance, CLiPS is exploring opportunities to engage with other minority-serving institutions. At the University of Texas, CLiPS has developed similar relationships with UT-Pan American and UT-Brownsville, two primarily Hispanic-serving institutions. The University of Texas also has an association with Texas School for the Deaf and have engaged students there in the Polymer Envoys program and other outreach activities.

CLiPS @ Fisk

Building on the earlier Case-Fisk Alliance, the CLiPS program at Fisk has been broadened and renamed CLiPS @ Fisk. The key components of the program are (1) student involvement focused on MS candidates, and (2) student research involvement with CLiPS projects.

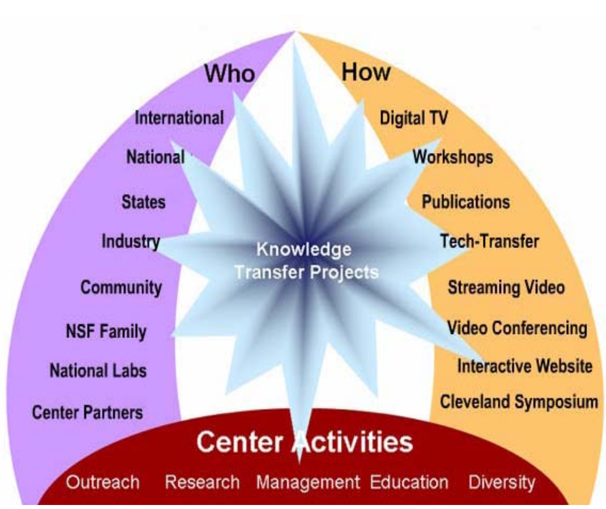
Because Fisk does not have a PhD program in polymer science, faculty members often rely on post-doctoral associates for their research. The change of focus to Masters Degree candidates, identified as CLiPS-Fisk Scholars, is allowing CLiPS research to move forward and will provide a new pool of candidates for PhD programs at CWRU and UT. Programs at Fisk include outreach to pre-college and pre-high school students through Saturday Science Academy and middle school Science Club. Finally, coordination of the 3-2 dual degree program between Fisk and CWRU is an important component of the relationship.

Impact on CLiPS Institutions

The Polymer Envoys program is an outstanding example of CLiPS' impact on the institutions involved and is helping add to the diversity of the student body at CWRU and UT (under-represented minority students and deaf and hearing impaired students.) In support of Fisk students interested in attending CWRU, two Provost Special Scholarships have been secured to provide financial aid to binary students from Fisk. In addition, CLiPS has actively championed the hiring of women and under-represented minority faculty members (Korley at CWRU; Arnett at Fisk) and will continue to follow that course of action when considering new faculty hires. With CLiPS faculty involvement, the Case School of Engineering has committed to establishing a program addressing engineering education and outreach, which includes diversity and inclusion components. CLiPS is committed to support such efforts as much as possible.

***Partnerships and Knowledge Transfer***

CLiPS goal for Knowledge Transfer is to be a unique global resource for the dissemination of knowledge in the area of layered polymeric systems. This requires a complex network of interactions illustrated in the figure at the right. Knowledge Transfer activities are organized from the standpoints of the: (1) CLiPS participants, (2) Center-related external audiences of government, academic and industrial contacts, (3) and the broader scientific community and the public.




CLiPS Participants

*Meetings*

For CLiPS participants, regularly scheduled administrative and research platform meetings meet the goal for knowledge transfer. Web meetings allow for effective communication across the

Center. Regularly scheduled meetings include:

- Weekly or bi-weekly meetings of the platforms
- Monthly meetings of the Executive Committee
- Weekly staff meetings
- Monthly meetings of the Polymer Envoys, liaison teachers and graduate students

Larger meetings, which are critical to accomplishing our knowledge transfer goal, include:

- CLiPS Annual Meeting of the Center involving CLiPS participants (faculty members, staff members and students) from all sites; held June 8, 2010 and March 17, 2011
- External Advisory Board (EAB) meetings on June 8, 2010 and March 17, 2011, coinciding with the CLiPS Annual Meetings. EAB members also participated in the CLiPS Industrial Showcase on October 19, 2010.

*Seminars*

Initiated under the ACES program, CLiPS continues to sponsor two seminars on the Case campus each academic year. The speakers for these symposia are either women who are active in academic polymer science and engineering fields or male researchers who have been active mentors to women. This year's speakers were Peggy Cebe from Tufts University (November 12, 2010), and Tobin Marks from Northwestern University (February 25, 2011).

*Educational Assessment*

CLiPS educational partnership with Kent State University's Research and Evaluation Bureau was established to study the Polymer Envoys Program. This comprehensive study is investigating the characteristics in these high school students' environments that may promote their choice of a STEM career. The initial results have been compiled and analyzed and is being used in our plans to expand the Envoys program within CLiPS and beyond.

*Website*

The CLiPS website was redesigned by a professional web designer who has been retained as webmaster.

<u>Governmental, Academic and Industrial Communities</u>

*Industrial Showcase*

The first CLiPS Industrial Showcase was held in October, 2008 and drew fifty participants representing twenty-six different companies. CLiPS's second Industrial Showcase took place on October 19, 2010. Inquiries generated by the Industrial Showcase and other means are coordinated by CLiPS's Director of Development who works closely with Development and Technology Transfer offices at Case Western Reserve University (and across the Center for multi-institutional projects) on technology, licensing and joint research opportunities.

*Outside Funding - Industry*

CLiPS originally projected a goal for outside industrial funding of $2.5 million annually by the end of the Center's five-year period. Research funded by industrial partnerships currently exceeds that amount.

*Outside Funding – Government*

CLiPS outside funding from government sources also increased. In 2009-2010 the total was $1,188,333. In 2010-2011, the amount of government funding almost doubled for a total of $2,278,333.

Broader Scientific Community and the Public

*Professional Meetings and Publications*

CLiPS faculty members regularly lead and participate in technical sessions and symposia at scientific society meetings, particularly those of the ACS, SPE and APS. Over the past year CLiPS faculty members and students have had 41 papers published in peer-reviewed journals. CLiPS participants (faculty members, post-doctoral associates, graduate and undergraduate students) accounted for 68 presentations at professional meetings over the past year.

*Intellectual Property*

During the past year, the *all-polymer laser technology* was granted a patent. A divisional application related to this technology was also filed. Originally covered by provisional patent applications, the technologies for *confined crystallization multilayer films* and *axially oriented confined crystallization multilayer films* were converted to full patent applications. Four new provisional patents applications were filed covering *aspherical GRIN lenses*, *a controlled stress extensional rheometer*, *an advanced multilayer die*, and *multilayer films with high flux and high selectivity*. In addition, the review of two provisional applications resulted in decisions not to proceed with conversion to full patent applications.

Patent activity for the 2010-2011 reporting period is described below:

Patent Issued

1. ***Co-Extruded Multilayer Polymer Films for All-Polymer Lasers, U.S. Patent 7,396,802 -*** *Kenneth Singer, Eric Baer, Anne Hiltner and Christoph Weder*
   This patent covers films which can function as lasers. It is a potential low cost laser technology with a wide variety of applications.
2. A divisional application related to this patent was submitted as a part of its approval.

Full Patent Applications

3. ***Confined Crystallization Multilayer Films -*** *Eric Baer and Anne Hiltner*
   This technology results in high gas diffusion barrier films which potentially are cost effective relative to films currently used commercially. Significant interest exists in this technology for food packaging and other market areas.
4. ***Axially Oriented Confined Crystallization Multilayer Films –*** *Eric Baer, Anne Hiltner, Yijian Lin*
   This patent application is an expansion of the Confined Crystallization application and is a part of the patent estate covering this technology.

Provisional Applications

5. ***Aspherical GRIN Lens -*** *Eric Baer, Ann Hiltner, Michael T. Ponting*
   This application expands the scope of the multilayer technology for GRIN lenses covered in a previous application. It is a key element in the technology being developed for DARPA by the spin-off company, PolymerPlus LLC and has already been licensed to this company.
6. ***Controlled Stress Extensional Rheometer -*** *João Maia, Ricardo Andrade, Patrick Harris*
   For polymer scientists and manufacturers this device significantly expands the capability to characterize polymer melts at a reasonable cost. Its potential users range from research laboratories to manufacturing quality control laboratories.

7. ***Layer Multiplier Die** - João Maia, Jorge Silva, Patrick Harris*
   This represents a new design which significantly improves the flow characteristics of polymer melts in these types of systems. It will provide more stable operations and improved quality films and potentially the ability to extrude materials with different rheologies which currently cannot be coextruded.
8. ***High Flux, High Selectivity Multilayer Membranes** – Benny Freeman, Eric Baer, Don Paul, Grant Offord, Shannon Armstrong*
   This invention creates films which can be used for selective gas diffusion. These films will have value in food packaging, where selective gas diffusion results in increased shelf life for the packaged food.

Ultimately, the goal of this work is to create commercial technology based on the research and intellectual property developed from the work being carried out in the Center. To this end, two businesses have been created based on work done within the Center. The first, Advanced Hydro in Austin, Texas, is focused on commercializing the patent pending technology to reduce fouling of membranes used for water purification and filtration systems. The second, PolymerPlus LLC in Cleveland, Ohio, is focused on creating GRIN lens technology based on polymer multilayer films and on developing commercial technology and applications for additional patents generated by the Center. PolymerPlus LLC holds a license from CWRU for the Aspherical GRIN lens patent application and for the GRIN lens patent generated by research on multilayer films at CWRU prior to the inception of the Center.

The research and education platforms are actively seeking to leverage their activities through additional support from various funding sources. In 2010-11, CLiPS received an additional $1 million for continuing research and development of CLiPS patented technology in the areas of energy and defense.

***Data Management Plan***

CLiPS is a complex Center with many sources of data. To manage the data, CLiPS has elucidated a data management plan that encompasses, among other strategies, the regular channels of peer-reviewed publications and presentations at professional meetings, control of student laboratory notebooks, and the CLiPS website which chronicles publication activity and provides an overview of CLiPS' research and educational programs. The Center's data management plan is discussed further in the Knowledge Transfer section of this report and may be found in Appendix G.

***Value-Added of CLiPS***

The field of interdisciplinary macromolecular science and engineering has rapidly emerged over the past ten years at the crossroads of polymer science, materials science, engineering disciplines, chemistry, physics and biology. This field of "polymers plus" enjoins inspiration from nature, innovative processing of microlayer and nanolayer polymeric assemblies (forced assembly), and revolutionary new synthetic polymers with greater control of macromolecular and supermolecular architecture (self assembly). A critical need exists for innovative microprocessing and nanoprocessing technologies to achieve the envisioned materials systems.

The potential application and economical impact of hierarchically organized polymer and hybrid polymer/inorganic layered systems with length scales ranging from a few nanometers to many microns are extremely broad and encompass diverse areas such as healthcare, energy, defense and environment. The expansion of Platform I to include research on understanding and control of polymer rheology will enable combinations of materials previously not possible and lead to structures which can meet performance properties not previously achievable with extrusion technology. This will accommodate the diverse needs of Platforms II, III, and IV and enable them to expand their scope in areas such as membranes and optical/electronic systems and others that are not currently addressed in Platforms II, III and IV.

The broad scope of these research activities requires participation of outstanding researchers and educators in many disciplines, including polymers, optics, electronics, material science, transport, and engineering. CLiPS is uniquely positioned to meet this challenge and has assembled a multidisciplinary, multi-institutional team of investigators. The work of these groups of scientists and engineers is disseminated through the CLiPS Knowledge Transfer program, which provides a vehicle for intellectual exchange with the public and the links to industry will allow for significant technology impact, fostering science and technology in service to society.

Research and education aspects are integrated to create a special environment for discovery, learning and innovation by students at a wide range of levels from elementary grades through graduate level, faculty and associated researchers. Emphasis is placed on teamwork, communication and engagement of students in the research and education activities to make CLiPS a unique place for training a well-qualified academic and industrial workforce. Enhanced diversity and engagement of underrepresented groups is considered a critical component of well-balanced programs and workplaces. CLiPS aim is to exploit the features of modern U.S. society with an emphasis on teamwork, communication, and workforce diversity, in addition to excellence in research and education.