IREE: Center for Advanced Engineering Fibers and Films (CAEFF)

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Through the IREE program, CAEFF enhanced its programs by building upon collaborations established by Clemson University with the University of Bradford (United Kingdom) and the University of Minho (Portugal). Both of these institutions have internationally recognized programs in polymer science and engineering. They have an extensive array of online experimental measurement techniques that (1) led to substantive enhancements to, and extensions beyond, the core CAEFF fiber/film research, and (2) offered the CAEFF researchers the opportunity to learn and apply novel experimental techniques to emerging areas of microscale polymer processing. The researchers included an early career faculty member, a graduate student, and an undergraduate student. At Bradford, CAEFF researchers engaged in ongoing micromolding research activities, particularly how small length scales, and the consequent high shear (strain) rates, impacted micromolding. At Minho, research focused on online rheological measurements. The interactions with international institutions fostered more productive partnerships, provided CAEFF researchers the opportunity to work with leading scientists, prepared the students for careers in a more global market, and served to make the students more aware of the opportunities in business and culture worldwide.

INTRODUCTION

The Center for Advanced Engineering Fibers and Films (CAEFF) is a National Science Foundation Engineering Research Center that comprises a partnership between Clemson University (lead institution), the Massachusetts Institute of Technology, and Clark Atlanta University. The Center provides an integrated research and education environment for the systems-oriented study of fibers and films. CAEFF's vision is to *become the international leader in the development of fibers, films, and related functional materials through integrated systems research and education programs that combine molecular understanding, process innovation, and multi-scale modeling to impact industry, academe, and society.*

CAEFF is spearheading the transformation of the fiber and film industry's approach to developing processes and products – from traditional trial-and-error to computer-based design. FiSim, the integrated model that is being developed by CAEFF, has advanced the state-of-the-art in modeling polymer processes beyond any existing model in the world. Center-developed software will allow users to design an entire fiber or film system by inputting precursor specifications, processing parameters, and desired properties. This virtual testbed will bring design improvements to current manufacturing systems, and also significantly reduce, if not alleviate trial-and-error experiments needed for the design of next-generation fiber and film processes. CAEFF has created state-of-the-art fiber and film processing testbeds for verification of the models. Our integrated education program recognizes the need for a workforce with a global perspective on polymer processing, in particular the uses of computer-based polymer process design in industry.

CAEFF proposes to enhance its research and education program by building upon collaborations established by Clemson University with the University of Bradford (United Kingdom) and the University of Minho (Portugal). Both of these institutions have internationally recognized programs in broad aspects of polymer science and engineering. Bradford, along with the Universities of Sheffield, Leeds and Durham, is a participant in the International Research Centre in Polymer Science and Technology. The Polymer IRC at Bradford has an extensive program in a wide range of polymer processing applications, and unique facilities for material characterization. The University of Minho is home to the Institute of Polymers and Composites (IPC) and the Biomaterials, Biodegradables and Biomimetics (3Bs) Research Group. These centers' research on complex processing flows coupled with continuum-level modeling of similar geometries complements CAEFF studies on the rheological behavior of materials. Collaborative research projects will be augmented by exposure to international models for technology transfer and immersion in foreign cultures.

Graham Harrison and Jason Conrad, a graduate student, spent three months in the Bradford laboratory of Professor Phil Coates working on high shear rate rheology for micromolding applications. Subsequently, Harrison and an undergraduate student, Mallory Armfield, spent three months in the laboratory of Professor Jose Covas at the University of Minho in Guimaraes, Portugal, investigating the degradation of bio-based polymers in a custom-built microextruder, all over the period January to July 2008.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

Micromolding is a relatively new technique now being used for manufacturing micro-sized parts for many applications, including medical, electronics, telecommunications, automotives, and microfluidic devices. The Coates laboratory at Bradford is an acknowledged leader in polymer processing in general and micromolding in particular. Available facilities include five different micro-injection molding machines. The flow conditions encountered in micromolding cannot be reproduced using conventional rheological equipment. This is because micromolding typically incorporates small length scales and high velocities – conditions that lead to extremely large shear and strain rates. We used a modified injection molding machine to perform high shear rheological measurements for several polymers. The apparent shear rates exceeded 10^6 s^{-1} – values that may be encountered in micromolding applications. Thermal measurements made using an infrared camera were used to monitor fluctuations in temperature as a result of the viscous heating experienced by the polymer melt during extrusion at these extreme rates. A high speed camera allowed flow instabilities to be captured during the injection process.

Shear rheology results were obtained over a broad range of shear rates. As in conventional capillary rheometry, the viscosity was obtained using the pressure drop measurement in the die. The shear rate was calculated using standard techniques. At rates up to 10^4 s^{-1}, a capillary rheometer was used to it provide comparison to the results obtained using the injection molding machine. It was found that the polymers exhibited typical shear thinning behavior at shear rates approaches 10^5 s^{-1}. However, as the rate approached and exceeded 10^6 s^{-1}, the shear viscosity began to plateau and was effectively independent of the shear rate.

The thermal analysis indicated that viscous heating of the polymer can be an issue in polymer processing at the high shear rates encountered in micromolding. We observed an increase in the temperature of the extrudate with increasing shear rate. However, at the very high shear rates (exceeding 10^5 s^{-1}), the temperature difference between the barrel setpoints and the extrudate reached a plateau value. We attribute this to the short residence time within the barrel.

The results obtained in this work have significant implications for the experimental processing and numerical simulation of polymers in micromolding applications. A manuscript is in preparation for submission for publication.

Biobased polymers such as PLA and PHA show the potential to replace conventional, fossil-fuel derived polymers in a variety of applications. However, a well-known limitation of these biobased materials is the fact that they can degrade at typical processing temperatures. The Harrison group at Clemson has published extensively on biobased polymer degradation under well-controlled, rheological flows. An obvious extension of this work was to investigate polymer degradation in a more realistic polymer processing geometry. To accomplish this, a collaboration with the Covas group at the University of Minho was initiated. The Covas group is a world leader in fundamental extrusion studies. Facilities include multiple single- and twin-screw extruders coupled with advanced characterization equipment. The equipment we were working on was a custom built, mini extruder. This equipment had several advantages: it required small sample volumes; was modular so that different screw elements could be employed; and most importantly enables the investigator to extract samples from different positions in the barrel for subsequent analysis.

In this work, we studied the degradation of PLA and PHA polymers as a function of processing conditions and position within the custom extruder. Processing conditions such as temperature and screw rotation rate can be compared with variables in our (prior) rheological studies. Likewise, the position at which the polymer is extracted from the extruder can, through residence time studies, be compared to the experimental time in a rheological experiment. After collecting the extracted samples, we performed rheological and GPC experiments to determine polymer degradation in the extruder. We observed that with increasing distance down the extruder or barrel temperature, the polymer molecular weight decreased. These results are currently being evaluated and compared to our prior rheological experiments. We anticipate submitting a paper for publication in the months ahead.

BROADER IMPACTS OF THE INTERNATIONAL TRAVEL

In addition to the research outcomes of this work, the IREE grant supported initial international experiences for both a graduate and undergraduate student. Jason Conrad had traveled overseas briefly prior to this research experience, whereas Mallory Armfield had never left the US. Both students had the opportunity to work in a worldclass international research environment with students from all over the world. In addition, Armfield was the sole American living in a Minho university dormitory, and quickly became the reference by which her fellow students evaluated America and Americans. Harrison gave invited lectures on his research activities at both Bradford and Minho. In addition, at the University of Minho he was a keynote lecturer in a university-industry short course entitled “Rheoprocessing”.

Collaborations and faculty/student exchanges with international institutions: (1) enhanced knowledge transfer and exchange across borders; (2) fostered research partnerships and achievements by bringing together expertise in related fields; (3) strengthened American academic research and education through discussions with leading scientists worldwide; (4) prepared students for careers in a more global market; and (5) served to make the students more aware of the opportunities in business and culture worldwide. The proposed projects provided an opportunity for CAEFF researchers to expand their knowledge of different approaches to collaborative research, and further developed the Engineering Research Center’s primary deliverable to the international polymer processing community.

DISCUSSION AND SUMMARY

CAEFF-developed software (FiSim) predicts fiber and film properties as a function of material and process parameters. The software package and its associated properties database would be improved by the inclusion of rheological data related to three-dimensional polymer processes such as injection molding and to processing of bio-based polymers. The Harrison group focuses rheological characterization of polymeric materials, which establishes fundamental flow properties in well-defined geometries and provides input parameters for the constitutive models built into the FiSim software. The group also experimentally investigates the effect of rheology and process conditions on film casting. The IREE experience provided an opportunity for CAEFF researchers to expand their knowledge and further develop the Engineering Research Center's primary deliverable to the polymer processing community.

The visits to both Bradford and Minho offered a wealth of opportunities beyond the specific research projects discussed above. Clemson visitors traveled to Durham, Sheffield, and Leeds to meet with other IRC researchers. In Minho, there was opportunity for substantial engagement with faculty in IPC and the 3Bs Research Group. These faculty and associated researchers investigate polymer processing applications beyond the film expertise of the Clemson visitors.

As in the mission of an ERC, the IRC and the IPC have substantial industrially driven research programs. Their industry connections afforded opportunities to learn how to better develop and cultivate academic/industrial collaborative research environments. At Bradford and Minho, Harrison was a resource and advocate for the adoption of FiSim by the next generation of polymer scientists and engineers.

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BRIEF BIOGRAPHIES OF RESEARCHERS

Graham Harrison received his B.S. degree in chemical engineering from Stanford University in 1991. He received his Ph.D. degrees in chemical engineering from the University of California, Santa Barbara in 1997. He then served as a Postdoctoral Fellow at the University of Melbourne from 1997-99, after which he joined the chemical engineering faculty at Clemson University. Professor Harrison's primary research interests are in the general areas of non-Newtonian fluid mechanics, extensional flow, and renewable resource polymers.

Mallory Armfield is an undergraduate student in the Department of Chemical and Biomolecular Engineering at Clemson University. She has conducted undergraduate research on biodegradable polymers for two years.

Jason Conrad received his B.S. degress in chemical engineering at Florida Institute of Technology. While an undergraduate, he participated in Clemson's

REU program. He is currently a doctoral candidate in the Department of Chemical and Biomolecular Engineering at Clemson University. Jason's research involves the shear and elongational rheology of biobased polymers.