



Kenan Center News

Kenan Center for the Utilization of Carbon Dioxide in Manufacturing
University of North Carolina at Chapel Hill and North Carolina State University

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Directors' Letter

The carbon dioxide technology platform continues to attract attention from many sectors as a tool in pollution prevention. The industrial manufacturing and service industries are dependent upon the usage of staggering amounts of water and organic solvents. It is difficult to imagine a significant reduction of this need by going to "solventless processes". Carrier media will almost certainly be needed and this is where CO₂ can play an increasingly important role.

Research teams within the Kenan Center have taken a system engineering approach to solve some of these problems. For example, a liquid CO₂ spin coater was envisioned whereby liquid CO₂ could be coated onto silicon wafers in a pressurized spincoating device. However, this necessitated the design of completely new positive and negative resist materials that not only had the requisite properties for high performance lithography, but also had one more

very important attribute—they had to be soluble in liquid CO₂ at vapor pressure. Several options for overcoming this further boundary condition were developed and it looks like this could indeed be a realistic approach to "solventless" microlithography.

But this is not where it ends! During the course of this problem-solving team approach, it also became clear that the low viscosity of liquid CO₂ might facilitate thinner, defect-free films to be applied onto silicon wafers. This is a great example illustrating

how a significant performance advantage may now be realized in the manufacturing of integrated circuits (and by the way, its environmentally friendly!).

We look forward to identifying other value-added opportunities in the various projects we pursue. If you have any question about the Kenan Center, please don't hesitate to contact me.

—Joseph M. DeSimone
Co-Director of the Kenan Center



Check out our recently updated website. www2.ncsu.edu/champagne

Faculty Profile: Saad Khan, Professor of Chemical Engineering, NCSU

Originally from Bangladesh, Professor Saad Khan came to the United States as an undergraduate and received his B.S.E. in chemical engineering from Princeton University. He continued his education at the Massachusetts Institute of Technology, where he earned his Ph.D. in chemical engineering. At MIT he developed his knowledge of rheology while studying aqueous foams. After completing his thesis, he joined AT&T Bell labs. He spent two years researching techniques to apply planar and biaxial extension to polymers using a lubricated flow channel and the rheo-optical properties of polymer solutions.

In 1987 Professor Khan began working at Bell Communications Research (Bellcore). He studied composites, polymer gels, polymer blends, and sol-gel rheology. Most notably, he developed techniques to monitor in situ curing of UV sensitive polymers and linked their microstructure & process variables of ceramic precursors to the final properties

of sol-gel derived high T_c superconductors. It was his desire to pursue an academic career that ultimately brought him to N. C. State University as an Associate Professor in January of 1993.

Prof. Khan's research group focuses on industrially relevant environmental technology. Four group members are conducting research for the Kenan Center on the plasticization of polymer melts, miscibility of blends, and the development of methods to tailor the physical properties of microcellular foams. Two of these projects were highlighted at the Fall 1998 Kenan Center Review Meeting.

Prof. Khan's group is also working with Prof. Robert Kelly to use polymers and enzymes to enhance the hydraulic fracturing process. A patent has been issued for this work in conjunction with Schlumberger Dowell Ltd.

Current research focuses on correlation of the rheological properties of UV cross-linked polymers with the underlying material chemistry and process con-

ditions.

Lastly, group members are determining how surface groups can be used to tailor the physical properties of fired silica gels. These gels are used as polymer electrolytes and will be used to develop new generation batteries.

Prof. Khan is the director of Graduate Programs and polymer options advisor. He is the co-inventor of 4 patents and has published over 25 times in the last three years. He was a visiting professor at the University of Campinas in Brazil and has been a UN Visiting Scientist to Bangladesh. In 1997, Prof. Khan was awarded the ALCOA Engineering Research Achievement Award. He is an active member of the Society of Rheology, ACS, AIChE, the Electrochemical Society, and AAAS.

In addition to mentoring graduate and undergraduate students, Saad uses his spare time to cook and travel.

-Brian Novick

Brian is a 2nd-year ChemE student at NCSU

Student Profile: Terri Johnson, Chemistry, UNC-CH

Terri Johnson's enthusiasm for a scientific education started at an early age. After attending the NC School of Science and Math, she attended Spelman College and earned her B.S. in Chemistry. As an undergraduate, Terri worked as a research assistant at the Dolphus E. Milligan Science Research Institute in Atlanta, studying the effects of lead ions on the secondary structure of proteins using FTIR. She also worked as a summer research assistant in 1993 and 1994 at Hoffmann-LaRoche measuring histamine and intracellular calcium and identifying novel targets for pharmacological intervention in mast cells.

After graduating from Spelman in 1994, Terri joined Cabot Applications Development Center. During her time at

Cabot, Terri was a member of the Industrial Blacks Team that primarily focused on the development of rubber products using different grades of carbon black. Although Terri initially went on to work after college, she always intended to continue her education, and in 1995 she entered the graduate school at UNC.

Terri's research at UNC-CH has been in a number of exciting areas. She has designed and synthesized amphiphilic surfactants composed of hydrophilic and fluorocarbon blocks for use in supercritical CO_2 applications, nanofiltration membrane technology and the stabilization of pharmaceuticals in CFC substitutes. Terri has also collaborated with Matyjaszewski at Carnegie Mellon on the synthesis of polymers in

supercritical CO_2 by atom transfer radical polymerization using homogenous and heterogenous methods. Currently, Terri is investigating dispersion polymerizations of water soluble and biodegradable polymers in compressed CO_2 .

Before Terri comes to the lab in the morning, she typically begins her day with an early morning workout. She is active in her church, where she participates in the choir and volunteers in the Community Advocate Program. In her remaining time, Terri enjoys cooking and preparing for her wedding (which will happen this Memorial Day)! Terri's friendly nature and positive attitude is a true asset to the lab at UNC-CH.

-Stephen Gross

Steve is a 3rd-year Chemistry student at UNC

Small Molecule Endeavors Make Progress

Although much of the Kenan Center's research focuses on polymer synthesis and processing in CO_2 , we have a strong commitment to impact manufacturing beyond polymer production. Two small molecule research areas have been making progress over the last year: enzymatic catalysis and solid acid catalysis. CO_2 has an important role as an environmentally friendly solvent in both of these areas.

Industrial researchers have increasingly turned their attention to enzymes as catalysts for chemical reactions because of their high chemo-, regio-, and stereoselectivity. Many of the targeted products are consumed internally, which makes the environmentally friendly nature of enzyme catalysts an additional advantage. However, in many cases, key intermediates or the products themselves are insoluble in water, which necessitates the enzymatic reactions to be performed in organic solvents. This drawback can be overcome by using CO_2 .

We have been developing the methodology for performing enzymatic reactions in CO_2 with a systematic study of esterification reactions over a wide range of pressures. Not surprisingly, our results have shown that performance parameters show pressure dependence in CO_2 . The tunable properties of compressed CO_2 , allow these parameters to be varied more easily than in traditional

organic solvents.

In addition to studying fundamental enzymatic reactions, we are designing and synthesizing appropriate solid supports to facilitate these reactions in CO_2 .

In the area of solid acid catalysis several key advantages are seen. Inexpensive, non-toxic adsorbents such as silica gel and alumina provide methods for fast, highly selective reactions that avoid the use of heavy metal catalysts. Besides the low environmental impact of these surface-mediated reactions the fact that such adsorbents are easily recyclable may decrease overall cost in manufacturing. However, the traditional organic solvents that have proven most effective in these reactions have a high environmental impact. CO_2 is an obvious solvent alternative that maximizes the environmental advantages of surface reactions.

The reactions under study in the Center focus on the high selectivities of surface catalysis. Oxidation of sulfides and amines especially demonstrate the effectiveness of adsorbents to yield high amounts of single products, thus decreasing the need for post-reaction separations. Interesting differences in the reaction rates between liquid and supercritical CO_2 conditions demonstrate both the flexibility of CO_2 as a solvent as well as the need for further study into solid adsorbent reactions in CO_2 .

In addition to continued study of these reactions under varying temperatures and pressures, we are expanding our scope to include other types of small-molecule synthesis. Along with enzymatic catalysis, solid acid catalysis is proving to be greatly benefited by the use of CO_2 as a tunable, environmentally responsible solvent for small molecule synthesis.

-John Fields and Jonathan Kendall

NSF Site Visit Update

Center Directors Joseph DeSimone and Ruben Carbonell worked hard this past winter preparing for the NSF Science and Technology Centers Program site visit. On February 21-23, the fourteen panelists came to UNC to evaluate first hand the strength of the proposal. The proposing team addressed any remaining concerns of the review panel. We would like to thank all of the faculty, staff, students, and administrators from UNC, NC State, NC A&T, and UT-Austin who participated in the site visit. Thanks to Kenan Center members for their support in this endeavor.

Our submission was one of sixteen selected from 43 full proposals to participate at this level. From these sixteen sites, the NSF will select up to ten S&T Centers for funding. Notification of S&T Center awards is expected this spring.

-Jonathan Kendall

Several Center students attended the Fluorine in Coatings III conference on January 25-27, 1999. Clay Bunyard and Jonathan Kendall presented papers on perfluoropolyether coatings and resin materials for CO_2 -based spin coating, respectively. Erik Hogan and Brian Novick also attended the event. The conference, sponsored by the Paint Research Association, was held at the Grenelefe Resort (vaguely near Orlando) in Florida and was attended by over 200 scientists from industry and academia.

Congratulations to Joseph DeSimone for winning the 1999 C. S. Marvel Award for Creative Polymer Chemistry. The Marvel Award was established to recognize accomplishments in basic or applied polymer science. It is administered by the ACS Polymer Chemistry Division and is presented biennially at the Spring ACS national meetings. Professor DeSimone will be presented the Marvel Award at the 217th ACS National Meeting (March 21-25, 1999) in Anaheim, California.

Center Meeting Past...

Dispersion polymerizations, polymer coatings, solid state polymerization, microlithography. These are just a few of the topics discussed at the last Kenan Center Review Meeting. The meeting was held at the Jane S. McKimmon Center in Raleigh, N.C. on November 8-9, 1998. Following an evening business meeting, the second day began with 10 minute research presentations by several of the students and post-docs from UNC-CH and NCSU. An hour long poster session provided the opportunity for the industrial partners representing 12 companies to speak individually with students, post-docs, and professors, discuss new ideas, exchange knowledge, and make business contacts. The poster session continued after lunch and was followed by tours of the Kenan Center laboratory at NCSU. To end the meeting, the industrial partners met to discuss the strengths and weaknesses of the research projects presented during the day.

...Center Meeting Future

The next Center Review meeting will be held Friday, May 7, 1999, at the George Watts Alumni Center on the UNC campus in Chapel Hill, N.C. If you have any questions about the upcoming meeting, please contact Vicki Haithcock by phone (919-962-5468) or email (vph@email.unc.edu).

-Jennifer Young

Jen is a 4th-year Chemistry student at UNC

Transitions

We extend a welcome to numerous new researchers at the Kenan Center. Dr. Eri Yoshida has joined the DeSimone Group to study latex coatings. She is a graduate of the Tokyo Institute of Technology. New graduate students will begin research soon: Timothy Duncan, Karen Erford, Devin Flowers, Sarah Folk, Liang Hong, Charles Jones, Clarence Murray, Dave Williams, and Wei Jun Ye at UNC and Yvon Gay and Srinivasa Siripura at NC State.

Shortly after press time, I will be departing from my position as Technical Coordinator of the Center and Editor of Kenan Center News to join Lord Corporation in Cary, N.C. My successor will be Dr. Darlene Taylor, who received her Ph.D. from Prof. Ed Samulski at UNC. She can be reached at dk@unc.edu.

-Jonathan Kendall



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