#### **CENTER FOR LAYERED POLYMERIC SYSTEMS** CLIPS

# SPLIT IT, SPREAD IT, AND **RECOMBINE IT:**

## STRATEGY FOR MAKING MULTILAYERED MATERIALS WITH NOVEL PROPERTIES



Anyone who has made croissant dough or puff pastry knows the process: roll the dough very thin, spread it with butter, fold it over, roll it again and repeat many times to produce a flaky pastry.

That's the central idea of the enabling technology behind the Center for Layered Polymeric Systems (CLiPS), headquartered at Case Western Reserve University. The center is using a co-extrusion process that takes two polymer melts and combines them as two layers, multiplies the layers to four, and doubles that again as many times as desired.

"Pretty soon you have thousands of layers of alternating polymers—as many as perhaps 4,000, and these layers can be as thin as 50 angstroms," says center director Anne Hiltner, the Herbert Henry Dow Professor of Science and Engineering in the department to the commercial sector through partnerships with of macromolecular science and engineering at Case. Serving as research chair of the center at Case is Eric Baer, who holds the Leonard Case Professor of **Engineering.** 

When polymers are combined in this so-called "forced assembly," magical things can happen. The multilayered material can behave guite differently than the starting ingredients. What was once brittle becomes ductile in a multilayer. Colorless ingredients now give off a color without the presence of dyes.

As layers become thinner and thinner, the effect of the interface between these materials begins to dominate, says center investigator Donald Paul, professor of chemical engineering at the University of **Texas at Austin and director of the Texas Materials** Institute, "What happens is not so well understood," he admits. "Therein lies the frontier."

**CLiPS** researchers are working at the intersection of polymer science, engineering, chemistry, physics, and biology to catalyze research and application of this nanoscale technology and facilitate its translation industry and other organizations.

In addition to fundamental research on the polymer science and engineering, one research thrust at **CLiPS** focuses on optical and electronic materials. Multilayered polymers are being developed for use as impermeable films on flexible screens and electronic devices, which must be protected from water and oxygen.

Preliminary results on a melt processable glass that can be incorporated into layered materials to



provide such a barrier were described by center researcher David Schiraldi at a meeting of the American Chemical Society in March 2007. Schiraldi is associate professor of macromolecular science and engineering at Case. His goal is to develop a glass with excellent barrier properties and that melts at a low enough temperature to be fluid at the processing temperature of the polymer.

Another thrust deals with barriers and membrane systems that have applications, for example, in the food industry. Keeping vegetables fresh requires that the packaging material allow the right exchange of gases in and out of the package. Because each vegetable has unique needs in terms of gas transport, researchers are exploring the possibility of tailoring the performance of multilayered materials to extend shelf life of produce and perhaps even control the timing of ripening of packaged fruit.

The co-extrusion process offers the advantages of simplicity, compatibility with existing polymer materials, and scale of production, "We can take a polymer off the shelf and do it—and we can make miles of the stuff," says Hiltner. "None of this 'little milligram quantities' and laborious synthesis and worrying about scale-up," she notes. "We have two co-extrusion lines and it's not a particularly difficult process once you have it set up and know how to work it—so it's really good for students. The students run it and we have undergraduates who can help and even have had high school students help. So it's a process that can be very hands on for the students."

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- CLIPS DIRECTOR ANNE HILTNER

## KNOWLEDGE TRANSFER

#### LAYERED LENS TECHNOLOGY FOR **ADVANCED CAMERAS**

Researchers at the center have taken inspiration from nature in the development of nanolayered lenses that are not unlike the lenses in the eyes of fish.

In fish lenses, the material's ability to bend light, or refractive index, gradually changes with depth inside the lens: in other words, they have a refractive index gradient. "We are able to copy that using the nanolayer approach," says center research chair Eric Baer.

Lenses of this type exhibit a wider field of view with less aberration than conventional lenses having no index gradients. The "gradient refractive index" or GRIN lens shown in the figure below mimics a segment of the octopus lens. It contains more than 500,000 nanolayers.

Baer notes that the technology is being considered by public and private sector organizations for use in advanced cameras.



**Gradient Refractive** Index (GRIN) Lens



#### SURFACE EMITTING LASERS

Center researchers have recently demonstrated use of multilaver films in all-plastic lasers. The approach provides a new way to make lasers in which the light is emitted from the surface of the material. These "surface-emitting" lasers are important because they can be used in display technology, notes center investigator Kenneth Singer, professor of physics at Case Western Reserve University and leader of the research platform on optical and electronic materials. Inexpensive and easy to make, these multilayer lasers are flexible and can be made to produce ight of different colors.

#### **REFLECTIONS ON STARTING A CENTER**

Established in August 2006, CLiPS is new enough that the experience of planning a center and competing for funding is fresh in the minds of participants.

Center director Anne Hiltner reflects upon the center's origins: "Eric Baer and I have been involved with lavermultiplying coextrusion since the1970s when The Dow Chemical Company invented the process. Recognizing the novelty and potential of the process, we installed our own, highly flexible coextrusion line in the 1990s to explore some of our ideas.

"It became obvious to us that there were more opportunities than two people could handle, and that some of these (in optics and electronics, for example) required expertise that we did not have. In concept and even operation, the process was accessible to students at all levels. It was clear that it would be the ideal enabling technology for an interdisciplinary, multi-investigator program.'

"I think none of us anticipated that the STC competition would be the one that we would win," says Hiltner. "Each time we passed a gate, I, for one, felt thrilled and challenged. However, essentially all the parts of the proposed center were there from the beginning: the research platforms, the education programs, the Case-Fisk Alliance, the Envoys Program. I do know that our confidence in our vision grew as we continued to flesh it out for each phase of the competition, and responded to reviews from the previous phase."

David Schiraldi, associate professor of macromolecular science and engineering at Case Western **Reserve University, reflects upon the planning effort to** coordinate with partner institutions. "Once we had the idea, we had to organize it. Line up all the players, get the commitments," says Schiraldi. He remembers "getting in the car and driving through the snow drifts of Ohio in the middle of winter to meet with institutions and share the vision, get their input."

The process involved a preproposal competition, notes Schiraldi. "When you make it through the first cut, vou're both relieved and horrified simultaneously. Relieved. because you were successful; and horrified, when you realize you have to do ten times as much work in the next level," he laughs. There were about 160 preproposals, he recalls, of which some 37 were selected to go forward with full proposals. Twelve were selected to receive site visits, and of those, six were selected for funding, two during 2005 and four in 2006.



### **FACULTY VIEWPOINT**

## Kenneth Singer & Donald Paul

Q: How do you like participating in the center?

**Singer:** You have all these people working together, doing things I can't even imagine doing alone . . . . So it really is a team. We have very frequent meetings, pretty much every week, between the faculty and students. We're trying to get the students to collaborate with each other.

Whenever you have a large group working on something, there's a lot of overhead in communication. You meet more, but the payoff is you have many hands helping with the work.-you just have to coordinate all the hands.

The laser is a great example of why the team mode is needed. I brought the idea of doing this to the group. Eric and Anne had been working on the process for many years without knowing what the possibilities for lasers were. Then Chris Weder made the dye that goes into the laser to make it work, and he had a key idea on how to get a result quickly. It's not just individual expertise—there's a real synergy there.

It's a creative force; a forcing function that helps people to be better or more creative than they were. What team science does is to take you beyond the cutting edge-when you get together with somebody has an idea that you haven't thought about before, it increases the creativity. By yourself, you can only be so creative; you can't

imagine things you haven't thought about. Everybody improves upon each others' ideas, and there's a certain element of competitiveness—a good kind. Everybody brings their little corner of science and you end up with a big room.

#### Q: Why a center?

**Paul:** Case Western Reserve University has the capability of making laminated thin layer systems. We don't have that at the University of Texas at Austin (UTA) but we have measurement and theoretical expertise that complements expertise at Case.

This is research that would not have happened individually just because of the different skill sets and capabilities that are involved.

I think the students are really excited about the center because it offers a rather different kind of project than just a normal Ph.D. student would pursue. They really do have to interact with these other people, and we envision that UTA students will probably have to go to Cleveland and interact with people at Case, and that's an enriching experience that normally doesn't happen.



Donald Paul

To make progress in science and technology, we really need both modes of operation—team and individual. We need an appropriate balance. There are some ideas that happen by only one mode or the other...

You can't be interdisciplinary until you're disciplinary. You have to learn your area first before you have anything to offer to interdisciplinary efforts.



#### **EDUCATION AND DIVERSITY**

CLiPS works to broaden participation in engineering and science through pre-college outreach programs and partnerships with historically Black and non-Ph.D. granting institutions.

Overseeing all of the education and diversity programs in the center is LaRuth McAfee, who has bachelors and doctoral degrees in chemical engineering and postdoctoral research experience on engineering education funded by the Center for Advancement of Scholarship on Engineering Education.

Through its affiliates program, the center works with several non-Ph.D. granting institutions and regional schools. Each receives funding for educational as well as research activities that are aligned with the CLiPS research agenda. Faculty and students take part in exchanges and extended visits to Case. Schools currently participating in the program include Rose Hulman, Indiana; Ohio Northern in Ada; Penn State, Erie; SUNY Fredonia, and Rochester Institute of Technology, NY.

McAfee also notes that the "Polymer Envoys" program brings high school juniors and seniors from Cleveland Municipal School District to CLiPS for research experiences during the school year and summer.