

“Self-Healing” Polymers

Imagine a hip replacement made of materials so tailored that only a thin layer on the outer surface the part in contact with the body is biocompatible, while the rest of it is designed to be strong and stable to cope with any stress the body might put on it. Or imagine a material designed to coat a doorknob, in which the outer layer is designed to be microbially resistant, while the rest of it, that which holds it to the doorknob, is tailored for adhesive properties. When someone with a cold touches the doorknob, the antimicrobial agents immediately kill the

bacteria, while the adhesive properties in the matrix material keep the coating in place. A collaboration of polymer scientists at ORNL is using the SNS Liquids Reflectometer to study the dynamics of polymer mixtures that hold promise for applications from biocompatible films for human implants to semiconductors, substrates for electronic displays, toys for children, and durable, self repairing aircraft body materials.

Polymers in nature include cellulose, the main constituent of wood and paper. Some familiar synthetic (man-made) polymers include nylon, Teflon, and silicone. Mark Dadmun, a chemistry professor at the University of Tennessee and a joint faculty member of the Chemical Sciences Division at ORNL, is studying what he calls “self-healing materials,” polymer mixtures in which one critical component moves quickly to the surface while the matrix (the understructure) gives structural rigidity. Specifically, he is looking at the dynamics of a copolymer (the targeted, surface material) in a matrix (the homopolymer, the bulk of the material). “We design it so that the copolymer comes to

Depiction of the aggregation of random copolymers in a homopolymer matrix as observed in Monte Carlo simulations. The presence of these aggregates impacts the dynamics of the copolymer in a homopolymer matrix and demonstrates the importance of thermodynamic interactions in understanding the dynamics of miscible polymer blends.

Polymer studies will open up development of a whole new field of biologically dynamic materials that can be used for improved implants and antimicrobial agents.

the surface and saturates the surface, and then we retain some in the matrix so that if we lose it at the surface, we can just force it to come to the surface again.”

Dadmun works with instrument scientist John Ankner at SNS, materials scientist Joe Pickel at the Center for Nanophase Materials Sciences at ORNL, and UT and ORNL distinguished scientist Jimmy Mays. Pickel and Mays synthesized the polymer samples. In the self-healing materials, the key properties that are targeted include biocompatibility, microbial resistance, adhesion, and flammability, Dadmun said.

“The idea is that we design a system where the majority of the component has the stability we need, the strength to be a suitable matrix. But we have another polymer we designed to bloom to the surface. And then it would potentially provide the surface-sensitive property that we are looking for. And even if it got washed off, because we started with a mixture and forced it to come to the surface, there would be a reservoir of this material that would continue to come to the surface.”

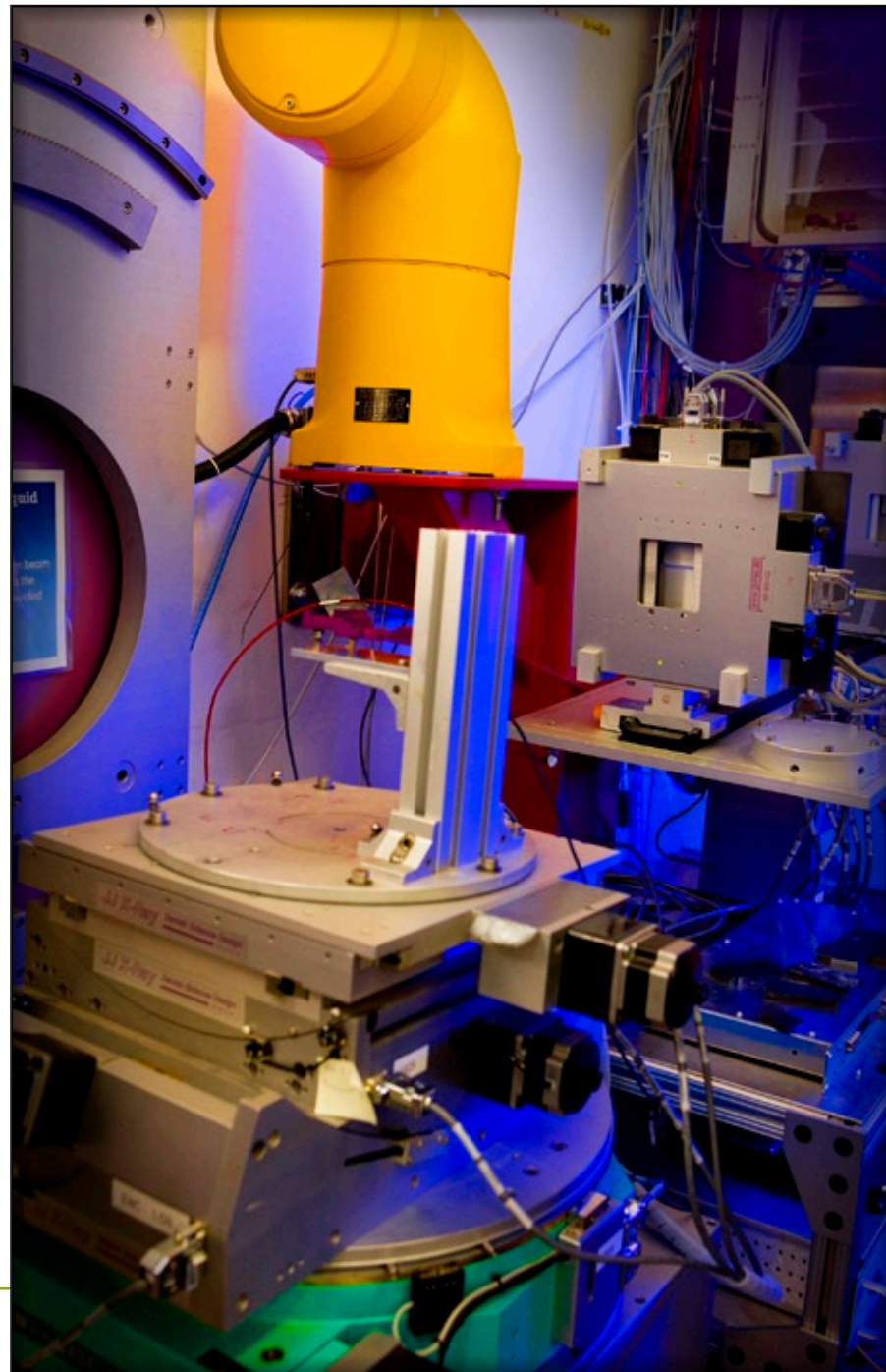
Dadmun says that finding a copolymer that migrates to the surface is not difficult. What is difficult is finding one that gets there fast enough. This has to do with the thermodynamics of the material, how its structure reacts to a change in temperature. What they need to learn, he says, is how the specific structure of the copolymer affects how quickly it migrates to the surface.

In their experiments, the researchers begin with a silicon wafer, which they coat with a thin film that is a mixture of deuterated poly(methyl methacrylate) as the matrix polymer, and a branched copolymer of methyl methacrylate and ethylene oxide. As they heat this sample, allowing the mixture to approach

thermal equilibrium, the graft copolymer (containing ethylene oxide) diffuses to the surface so that they can measure the water contact angle to verify that the copolymer segregates to the surface. “We can see that we’re getting more ethylene oxide (from the copolymer in the mixture) at the surface then when we first started. But what we really want to do is extract information on how quickly it gets to the surface,” Dadmun explained. This information is obtained using the Liquids Reflectometer at SNS.

Neutrons are ideally suited to study the dynamics of the copolymer, Dadmun said, “because with neutrons we’re able to selectively label the material.” In Dadmun’s samples the matrix is deuterated poly(methyl methacrylate) and the copolymer is an undeuterated poly(methyl methacrylate), grafted to undeuterated ethylene oxide. Because of the different neutron scattering properties of the deuterated and undeuterated materials, they can observe the location and movement of the copolymer in the composite material as a function of the annealing time (heating and slow cooling).

SNS Liquids Reflectometer.



As it is heated, the copolymer tends to migrate to the surface. The experimenters observe the time dependence of the intensity of neutrons scattered from the copolymer near the surface, which can be analyzed to provide detailed dynamics of the copolymer diffusion process. "And so we can analyze that data to work out the diffusion coefficients, other precise dynamic information about this surface segregation process, how much of it gets there, and how quickly."

Dadmun says they know from previous work that the polymer chain is actually collapsing. "It's changing its conformation away from its behavior in the homopolymer because of the repulsive interaction between the polymers. And that change in repulsive interaction—and change in conformation—alters the dynamics, which alters the properties. So it's that cascading effect which allows us to correlate the structure and thermodynamics of the copolymer to its dynamics."

"If you think of this polymer chain with the long arms, those long arms make it very difficult to move. But because of this repulsive interaction, they might actually be retracted in,

and therefore could be moving faster... we don't have evidence of this yet, but this is one of the things we're trying to find out."

How does Dadmun predict the future? Is he hopeful for these polymers? "Potentially, these are going to be too slow. All of the

applications may not be commercially viable, because it may take too long to get to the surface. If it does though, there will be a wide range of applications that we can utilize this concept for. That's why we do the research, to figure out what works and what doesn't."

Reflectivity profiles of a miscible polymer blend of a linear and branched polymer as a function of annealing time. The curves represent changes in the structure of the material. The challenge in this research is finding a copolymer that separates from the matrix quickly enough to be useful.

