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Green Polymer Field Blossoming

Progress reported in making new materials from renewable feedstocks such as soybean oils

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The opportunities for designing polymers and developing polymerization processes that are safe, prevent pollution, and are more efficient in the use of materials and energy are enormous, judging by the breadth of topics discussed several weeks ago at a symposium on green polymer chemistry.



Photo By Zhuoyang Lian

Under Stress Zhu tests the stress and strain of a biobased elastomer.

The symposium, held at the American Chemical Society's national meeting in Washington, D.C., was sponsored by the Division of Polymeric Materials: Science & Engineering and organized by Elliot P. Douglas, associate professor of materials science and engineering at the University of Florida, Gainesville.

“The number of presentations that combined different aspects of green polymer chemistry or that combined green polymer chemistry with another ‘hot’ topic suggests that we are moving into a new phase of green polymer chemistry in which the end goal is not the green chemistry,” Douglas remarked. “Rather, the green chemistry is just another available tool that can be used to address a variety of problems.”

Jennifer L. Young, a senior research chemist at ACS's [Green Chemistry Institute](#) in Washington, D.C., presented the opening lecture. She observed that green polymer research can be seen increasingly in academia, industry, and government. “The research tackles all aspects of polymers and polymerization—everything from chemical feedstocks, synthetic pathways, and reaction media to the nature of the final polymer as related to its inherent nontoxicity or degradability,” she said.

Following Young's presentation, Dejan D. Andjelkovic, a graduate student working with organic chemistry professor [Richard C. Larock](#) at Iowa State University, Ames, described how novel rubbers can be prepared from a renewable feedstock: soybean oil. “Recent years have witnessed an increasing interest in biomaterials derived from renewable resources,” he said.

One of the major initiatives has focused on utilizing renewable and environmentally benign starting materials obtained from agricultural, animal, and microbial resources for the synthesis of a wide range of bioplastics. Deploying such biodegradable starting materials protects the environment by partially or completely substituting for petroleum-based inputs. Furthermore, Andjelkovic pointed out, polymers made from biorenewable materials have been shown to have properties that are comparable with or better than those of widely used industrial polymers.

“Soybean oil is available in large quantities from soybean oilseeds and

represents one of the cheapest and most abundant annually renewable natural resources,” Andjelkovic said. “We have recently shown that a variety of promising new polymeric materials-ranging from soft rubbers to hard, tough, rigid plastics-can be prepared by cationic copolymerization of readily available soybean oils with styrene and divinylbenzene.”

This approach, developed by Larock's group, relies on the catalyst boron trifluoride diethyl etherate to initiate the cationic polymerization of the oil. To facilitate homogeneous copolymerization, the researchers modify the initiator with a fatty acid ester from Norway fish oil.

The approach can be used to copolymerize soybean oil triglyceride with dicyclopentadiene, a cheap, readily available comonomer. Dicyclopentadiene “is a good cross-linker that imparts rigidity to the resulting thermosetting materials,” Andjelkovic noted. “Our results show that the yield of the cross-linked polymers increases very slowly with increasing amounts of the dicyclopentadiene. All the copolymers formed appear as dark brown plastics with a slight odor. Almost all of them have glass-transition (softening) temperatures below ambient temperature and are therefore in their rubbery states.

“As much as 85% by weight of soybean oil is used for the synthesis of these biomaterials,” Andjelkovic added. “The results show that our approach offers a simple route toward a range of new and exciting biobased rubbery materials.”

At the University of Delaware, Newark, Ph.D. student Lin Zhu and professor of chemical engineering [Richard P. Wool](#) have prepared a series of polymeric materials from plant oils such as soybean oil. “Triglycerides are the main components of plant oils,” Zhu told C&EN. “Our research group has successfully developed triglyceride-based composites, adhesives, foams, coatings, and elastomers from plant oils.”

She described the use of acrylated oleic methyl ester monomers derived from plant oil triglycerides to synthesize biodegradable elastomers. The group first prepares high-molecular-weight linear polymers by free-radical polymerization of the monomer. The elastomers are then prepared by cross-linking the polymers.

The mechanical and thermal properties of the elastomer are improved by adding methyl methacrylate to modify the molecular structure of the rubber chain. The mechanical properties can also be dramatically improved by mixing the acrylated monomer with an organoclay: natural montmorillonite modified with a quaternary ammonium salt.

“The organoclay has a nanolayered structure that works as physical cross-links and improves the tensile properties of the elastomers,” Zhu explained. “Mechanical recovery of the nanocomposites is slow, but the layer structure has potential for self-healing materials. We showed that the clay-loaded elastomers are biodegradable and biocompatible.”



Courtesy of Richard C. Larock

Biomaterialists Larock (back, left) poses with members of his research group: Andjelkovic (back right), postdoc Yongshang Lu (front, left), and graduate students Marlen Valverde and Phillip Henna.

In related work, a group in the Netherlands has shown that microwave irradiation provides a green alternative to conventional heating for the cationic ring-opening polymerization of 2-oxazoline monomers from soybean oils. The monomers are synthesized by coupling soybean fatty acids with ethanolamine followed by ring closure in the presence of a titanium catalyst. The resulting soy-based 2-oxazoline is a mixture of 2-oxazolines with different fatty acid side chains.

“The process is green because microwave irradiation provides efficient, energy-saving heating and also because the monomer is based on a renewable source: soybeans,” explained Ph.D. student Richard Hoogenboom, who carried out the work with professor of macromolecular chemistry and nanoscience [Ulrich S. Schubert](#) and coworkers at Eindhoven University of Technology, in the Netherlands, and the Dutch Polymer Institute.

Aqueous solutions of poly(2-oxazoline) block copolymers aggregate into

micelles that could potentially be used in applications such as micellar catalysis and drug delivery, Hoogenboom noted.

“Polymerization of 2-oxazolines takes from several hours to several days,” Hoogenboom observed. “These long reaction times have prevented widespread industrial applications of poly(2-oxazoline)s. Under superheated microwave conditions, the polymerizations are completed within 15 minutes. The process allows the use of higher monomer concentrations while retaining the living character of the polymerization. We have also shown that it is possible to carry out the polymerization in bulk without volatile organic solvents.”

A group at the University of Nottingham, in England, led by chemistry professor [Steven M. Howdle](#), combines two green approaches to polymer synthesis. “We use a clean solvent-supercritical carbon dioxide-and a natural catalyst, that is, an enzyme, to make unusual block copolymers,” Howdle explained. “Supercritical fluids are environmentally acceptable replacements for organic solvents. Supercritical CO₂, for example, is nontoxic, inert, nonflammable, and inexpensive. Enzymes are used as catalysts in a wide variety of reactions because of their high activity and selectivity and also because they are more environmentally acceptable than some conventional catalysts.”

In a recent paper, the group reported the use of the two-pronged green strategy for a single-step, simultaneous, one-pot synthesis of block copolymers of polycaprolactone and poly(methyl methacrylate) by combining enzymatic ring-opening polymerization of caprolactone with atom-transfer radical polymerization of methyl methacrylate ([J. Am. Chem. Soc. 2005, 127, 2384](#)). The enzyme used in the synthesis was lipase B from *Candida antarctica*.

These block copolymers “could not be made using enzymes in conventional solvents,” Howdle said. “Using supercritical CO₂, the reaction works exceptionally well,” he remarked. “We believe that the strategy can be extended to provide a simple route to a wide range of block copolymers incorporating monomers with very different physical and chemical properties.”

[John R. Dorgan](#), professor of chemical engineering at the Colorado School of Mines, Golden, presented a paper on a new class of green materials that he refers to as “ecobionanocomposites.” “The materials exploit the triple convergence of industrial ecology, biotechnology, and nanotechnology,” he said. “Ecological concerns are a predominant theme of the 21st century. Humanity must develop sustainable systems for materials and fuels. Biologically derived and inspired materials offer hope for achieving this

important goal. Also, nanotechnology is rapidly expanding, and its convergence with both biology and ecology is now being recognized.

“We have shown that it is possible to create polymeric ecobionanocomposites based on 100% renewable resources that have properties and costs that make them viable replacements for conventional petroleum-based plastics,” he added.

The composites consist of poly(lactic acid), derived from cornstarch, grafted onto cellulosic nanowhisker fillers produced by acid hydrolysis of cellulose. “Our approach uses reactive groups on the surface of the nanocellulosics to initiate the polymerization reaction of lactide,” Dorgan said.

The lactide monomer is obtained from lactic acid produced by fermentation of unrefined dextrose obtained from cornstarch. “In the future, it should be possible to produce poly(lactic acid) and other biopolymers by fermenting wood sugars,” Dorgan observed.

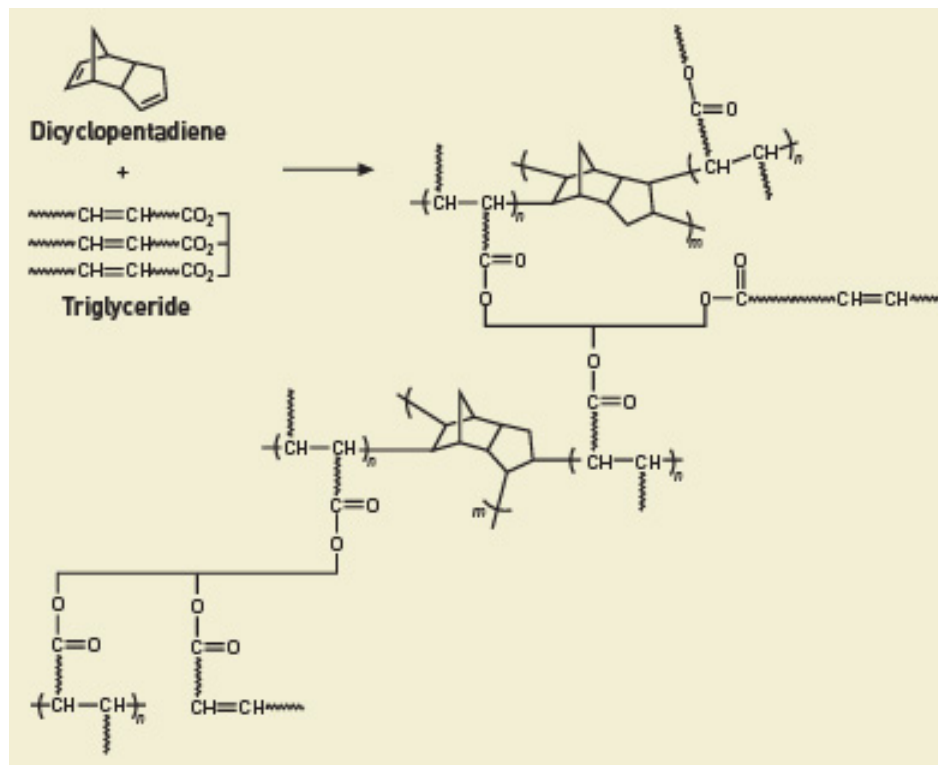
He noted that the use of poly(lactic acid)s is currently restricted to low temperatures because the polymers have relatively low glass-transition temperatures of around 55–60 °C. This property precludes the use of the polymers in applications such as plastic cutlery for hot foods, coffee stirrers, and foamed cups for hot liquids. Dorgan's group has shown that ecobioanocomposites prepared from poly(lactic acid) and microcrystalline cellulose fillers have higher glass-transition temperatures.

“Our technical approach will likely work on other plastics, thereby opening a vast market for cellulosic nanowhiskers as specialty fillers for plastics,” Dorgan remarked. “The renewable nature of the materials provides a means of reducing dependence on foreign petroleum and providing a relative sequestration of carbon dioxide, an important consideration in global warming.”

Researchers at NEC's [Fundamental & Environmental Research Laboratories](#), Tsukuba, Japan, have developed a thermo-reversible cross-linked poly(lactic acid) plastic with a rewritable shape memory. Shape-memory polymers are called “intelligent” or “smart” polymers because they are able to change their shape in response to an external stimulus.

The NEC plastic has a permanent “memorized” shape that deforms easily at 60 °C. The deformed temporary shape can be frozen in place by cooling. Heating to 60 °C rapidly restores the original permanent shape. The memory of the shape is erased by heating the shaped piece to 160 °C. The molten plastic can

then be molded either into the original shape or into a new shape. Petroleum-based shape-memory plastics currently on the market cannot be melted and restored in this way.



Rubbery Dicyclopentadiene and soybean triglyceride copolymerize to form cross-linked material.

The Japanese team introduced a thermo-reversible bond into the molecular structure of the plastic, NEC researcher Kazuhiko Inoue explained. The bond controls the crystallinity of the poly(lactic acid) and produces the rewritable shape memory. The bond acts like a thermo-switch, providing two normally incompatible characteristics: shape memory and rewritability. When the thermo-switch is turned on at low temperature, the biomass-plastic “memorizes” its original shape and can completely recover from a deformed shape like a cross-linked polymer. When the switch is turned off at high temperature during molding, the memory is easily erased, and the plastic becomes rewritable.

“Apart from biodegradability, the properties of biomass-plastics, such as those based on poly(lactic acid), are normally inferior to those of petroleum-based plastics,” Inoue remarked. “Our intelligent biomass-plastic with a rewritable shape memory has advantages over petroleum-based plastics that should help

to expand the use of biomass-plastics in durable goods.”

In Kanpur, India, chemists at [Chhatrapati Shahu Ji Maharaj \(CSJM\) University](#) have been investigating the use of naturally occurring polymers as flocculating agents for the removal of suspended solids and dissolved dyes from industrial textile effluent. “The work involves the use of fenugreek mucilage—a biodegradable, renewable, naturally occurring polysaccharide,” explained Rajani Srinivasan, a postdoc at CSJM University. “The polymer has no adverse impact on human or environmental health.”

Fenugreek mucilage is a partially water-soluble polysaccharide consisting of D-galactose and D-mannose units. It is extracted from the milled seeds of the fenugreek plant. “Fenugreek, botanically known as *Trigonella foenum-graecum*, is a leguminous plant, very similar to clover in appearance, grown in North Africa, Asia Minor, India, and Pakistan,” Srinivasan said. “An extensive literature review shows that fenugreek has never been used as a flocculant for industrial effluent treatment.”

The group demonstrated that, at concentrations as low as 0.04 mg/L, the mucilage is capable of removing around 94% of suspended solids, about 44% of total dissolved solids, and 6–35% of color.

“The natural flocculants are superior to their synthetic counterparts because of their nontoxicity, biodegradability, inertness to pH changes, easy availability, and cost-effectiveness,” Srinivasan said. Their use commercially “could be a landmark in ecofriendly treatment of textile effluents.”

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