

ACADEMIC RESEARCH:

Fundamental to Advancing Sustainable Coating Technologies

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Many industries today recognize the need to improve the sustainability of processes and products. The paint and coatings sector is no exception. The development of "greener" products is no longer driven simply by regulatory changes, but also by the need to meet customer expectations and the desire to realize the economic, social, and environmental advantages that many sustainable solutions can offer. There is still much to be learned, however, and academic researchers in universities around the world are exploring many of the fundamental questions about the potential of greener raw materials and the resins and other ingredients derived from them to yield cost-effective, high-performing paints and coatings.

GREEN EVOLUTION

The concept of "green" has evolved over time into the broader context of sustainability, according to Mark D. Soucek, professor of Polymer Engineering at the

University of Akron. "The initial focus on environmental issues graduated to a focus on using greener materials and making coatings 'benign by design,'" he says. "The last frontier will be making sustainable coatings using green starting materials and processes that yield green formulations," he adds. While regulations on volatile organic compounds (VOCs) continue to drive industry, there is also a significant push to find safer materials for applications where both workers and end users may be exposed to hazardous chemicals. One example noted by Dean C. Webster, chair of the Department of Coatings and Polymeric Materials at North Dakota State University (NDSU) is the active search for alternatives to isocyanate curing chemistry.

MANY CHALLENGES REMAIN

There are challenges, of course. Any new coating technologies compete with existing commercial technologies that have been accepted by the market, according to Webster. "New coatings must be competitive with respect to performance and cost; being greener or more sustainable isn't sufficient," he



explains. Biobased raw materials face other hurdles. "There is a lot to be done yet regarding the supply chain for raw materials derived from biomass. Few of these raw materials are manufactured at large scale today, and there can be issues with the consistency of their quality and characteristics year to year and crop to crop," says Vijay Mammi, professor of Polymers & Coatings in the School of Engineering Technology at Eastern Michigan University. The limited availability is a real concern, according to Andriy Voronov, professor of Coatings and Polymeric Materials at NDSU, because the mechanisms that can be used to produce resins for coatings are typically limited to free radical or condensation polymerization. "Green coatings development is directly related to the development of libraries of monomers that can be produced cost-effectively at commercial scale," he comments. With oil prices driven much lower in the wake of the shale oil and gas boom, biobased materials currently have difficulty competing on a cost basis, even with government incentive programs.

Ghasidch Pourhashem, assistant professor in the Department of Coatings and Polymeric Materials at NDSU believes that a lack of standards for

green or sustainable coatings is also hindering their development. "Better regulations and policies, including the establishment of specific standards or mandatory regulations for green and biobased coatings that have to be followed would benefit everyone," she says. In particular, she would like to see standards that address the entire supply chain and not just the environmental and health benefits of the final coating formulations. "The impact of coatings begins long before they are made with the basic raw materials that are extracted from the earth or biomass. We, therefore, need standards that account for the entire supply chain when determining the greenness or sustainability of paints and coatings," she explains.

The conservative nature of the coatings industry is yet another challenge, according to Voronov. "While interest in more sustainable materials for use in coating formulations is definitely growing, there are only a few companies willing to take on the significant risk associated with using novel ingredients. The situation is changing, and there are numerous companies with stated plans to expand their portfolios with greener products over the next 10 years."

ONLY A MATTER OF TIME

The question, according to Sergiy Minko, Georgia power professor of Fiber and Polymer Science in the Department of Textiles, Merchandising and Interiors and the Department of Chemistry at the University of Georgia, is not if more sustainable technologies will be adopted, but how long it will take. "The future direction of the coatings sector is to be more sustainable. It will take time to address the technical, economic, and political aspects, but the time will come when sustainable materials and green chemistry are the norm," he asserts. The role of academic researchers, Webster adds, is to perform the basic research needed to understand the chemistry and properties of various new polymers and what needs to be done to develop sustainable alternatives that meet the cost and performance requirements of industrial applications. "There is always a combination of technical push and market pull, and today we are still at the technical push stage. Scientists are looking at what materials are available from biomass and how they can be functionalized, transformed, or even directly used in coatings. We are completing the essential basic research

in order to develop new materials that can then be evaluated for their benefits by actual users," he concludes.

MANIPULATION OF SOYBEAN OIL

Seed/vegetable oils have long been used by the coatings industry—alkyds are a prime example. Many academic researchers are exploring a wider range of plant-based oils, novel derivatives, and the use of different comonomers with the goal of improving the performance characteristics of biobased resins in paint and coating formulations.

Webster has been developing epoxidized sucrose soyates, 100% biobased materials generated from the reaction of soybean fatty acid with sucrose followed by epoxidation using hydrogen peroxide. The epoxidized sucrose soyates possess larger numbers of epoxy groups that can be used in curing processes to generate thermosets, which have applications in the construction, automotive, appliance, and furniture industries. "We view these epoxidized sucrose esters as a platform technology that can be converted via multiple mechanisms to many different types of resins with wide ranging properties," states Webster. For instance, they can undergo photopolymerization, thermal crosslinking with anhydrides or blocked acids, or water-assisted acid crosslinking. They can be converted to polyols that can then be used to generate polyurethanes (PUs) with unique properties. The sucrose soyates can also be derivatized into carbonates, acrylates, or methacrylates, which also have a wide range of curing options and afford resins with interesting properties.

"One major advantage we are realizing with this technology relates to the high functionality of the sucrose soyates. They provide high crosslink densities, yielding coatings that are hard and tough. One of the traditional challenges with vegetable oil-based coatings has been achieving the necessary physical and mechanical properties. We have overcome that issue with these materials," Webster notes. He has even explored their use in composites with natural fibers. In many cases, the new coatings and composites that Webster has developed using the epoxidized sucrose soyates have properties competitive to those obtained using



Dr. C. Webster (right), chair of the Department of Coatings and Polymer Materials at North Dakota State University (NDSU) and Eric Kral (left), doctoral graduate research assistant, Department of Coatings and Polymer Materials, NDSU. Photo courtesy of NDSU/ES&C.

petrochemical-based materials. Some of this work is being done through the Center for Sustainable Material Science, a National Science Foundation-funded collaboration between researchers at NDSU and several other universities with a focus on investigating chemicals derived from biomass for the preparation of polymers and composites.

Mannari's group at Eastern Michigan University is also investigating coatings based on resins made from soybean oil derivatives. In one example, the soybean oil is reacted with biobased itaconic acid to form a polyester that is used as a major component in UV-curable green UV-LED gel nail polishes. "Nail polishes are one of the most widely used products in the U.S. cosmetic industry," Mannari observes. He notes that by 2020, 122 million Americans alone are expected to use them. Gel nail polishes are attractive because, once crosslinked under UV radiation, they have much greater durability than conventional nail polishes. The gel nail polishes his group has recently developed are green for several reasons: they are cured using UV-LED radiation and are either zero-VOC solventborne or water-based formulations, including polyurethane dispersions, comprising approximately 50% biorenewable content. Mannari is not satisfied, though. "We are working to increase the biobased content by incorporating other biobased materials such as derivatives of gum/wood rosin,

cardanol, and sorbitol, to name a few, as components in the formulations," he comments.

In a separate project, Mannari is exploring the development of bisphenol-A-free (BPA-free) epoxy resins predominantly from biobased resources. "There is good demand for BPA-free products due to the increasing concerns regarding the use of BPA, especially in food packaging and consumer products," he notes. Mannari is also developing waterborne UV-curable polyurethane wood coatings based on epoxidized soybean oil polyols with varying chemical structures and hard to soft properties. These formulations also include rosin. He intends to investigate this biobased approach for the development of packaging coatings given that this market is very much interested in renewable and recyclable materials.

BIOBASED LATEXES

One of the challenges in developing waterborne latex coatings using resins based on plant and vegetable is that these oils are very hydrophobic, and it is difficult to achieve an acceptable solids content (~40%) and high molecular weight during emulsion polymerization via a free radical mechanism, according to Voronov. For commercial applications, he notes that 99% conversion with no residual monomers is needed. To

tackle this challenge, Voronov's group has established a library of vinyl monomers prepared in one step from soybean, canola, sunflower, high-oleic soybean, hydrogenated soybean, and corn oils. The researchers have been exploring how these monomers act during free radical emulsion polymerization, both for the formation of homopolymers and copolymers (with commercially available monomers such as methyl methacrylate, styrene acrylate, etc.). High-oleic soybean oil is an attractive option because it has high heat stability, improved shelf life due to enhanced resistance to oxidation, and a better controlled composition because it is monounsaturated.

"We anticipated that there would be fundamental challenges, including insufficient conversion due to the hydrophobicity of the monomers. The first step was to investigate the kinetics, reactivity, and other fundamental characteristics to identify opportunities for optimizing the polymerization to achieve better properties and performance," Voronov observes. One approach employed to increase the conversion was to perform the reaction as a mini-emulsion. This method is more suited for hydrophobic monomers because the initiator is not soluble in water but soluble in oil, which potentially causes the polymerization to take place in oil droplets rather than in micelles, as is the case with traditional emulsions. His group has been able to easily achieve 95-97% conversion,

which is not sufficient for commercial products, but is good enough for initial proof of concept testing.

"We have been able to show that the vinyl monomers are indeed polymerizable with a broad variety of vinyl counterparts, providing a versatile platform with different properties achievable depending on the choice of oil from which the monomer was derived," says Voronov. He notes that one of the advantages of these resins is that unsaturated fragments are present that allow for crosslinking. "We can realize a broad range of properties, which allows for optimization of the desired

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combination of strength, flexibility, and toughness," Voronov asserts. So far, the solids content has been sufficient too, but while close, 99% yields have not yet been obtainable. In addition to working on that goal, Voronov is exploring comonomers from the same seed/plant oils but with different chemistry to enable the production of 100% bio-based resins. He is collaborating with a French group that has synthesized a bio-based monomer containing a benzene ring that when copolymerized with the oil-based vinyl monomers provides resins that impart some strength to coatings. Voronov has also investigated acrylic monomers prepared from cardanol,

which is obtained from cashew nut shell liquid. It contains an aromatic ring functionality and has the added advantage of being commercially available (annual production volume of one million tons).

ISOCYANATE-FREE POLYURETHANES

In both military and industrial applications, there is a need to replace commonly used ingredients that are now recognized to pose a health and/or safety hazard to plant personnel and end users. The use of bisphenol A in can coatings, chromates in protective coatings, and isocyanates as curing agents for PTs are perhaps the three most pertinent examples. Bio-based materials have potential utility in the development of alternatives in some cases.

Webster, Mannari, and Soucek have all focused on the development of nonisocyanate curing agents. Webster has been exploring the use of cyclic carbonate derivatives of epoxidized sucrose soyates, which can be cured with amines. The reaction takes place at room temperature, but can also be accelerated with low levels of heat. The rate is dependent on the amine structure, with primary and less hindered amines reacting more rapidly than secondary and bulky amines.

Mannari's solutions involve the use of cyclic carbonates and diamines. "Carbonate-diamine chemistry isn't

new for making polyurethanes, but our approach using cyclic carbonates is customized to ensure that the resultant resins have desirable properties," he comments. The PUs formed in the reaction are slightly different from conventional PUs in that they possess a β -hydroxy group. The presence of a large number of such polar groups in the cured coating has the potential to impact chemical and alkali resistance and result in higher viscosities due to hydrogen bonding, according to Mannari. While higher viscosities were observed, he did not, however, see as large an impact on coating performance as expected. His group, therefore, investigated the use of different reactive diluents as a means for locking the hydroxyl groups via secondary crosslinking.

Mannari proposed two types of nonisocyanate PUs for aerospace applications—high-solids (> 60% at time of application) and single-component UV-curable solventborne systems with zero HAPs. A total of 28 UV-curable compositions were screened using conventional reactive diluents with a focus on the resultant mechanical and chemical resistance performance. This project, funded by the Strategic Environmental Research Development Program (SERDP), is currently underway, according to Mannari. He is also investigating the possibility of curing these coatings using a UV-LED source.

Soucek elected to focus on the development of waterborne/latex monomers and UV-curable reactive diluents for the formulation of nonisocyanate urethane-modified acrylic latexes containing some acrylate groups. His approach involved modifying the synthesis route used to produce urethane acrylic hybrids, which involves the copolymerization of urethane acrylic monomers and acrylates. To increase the level of incorporation of urethane groups into these polymers, Soucek mixed specially designed UV-curable reactive diluents with the urethane acrylic monomers. The diluents are produced by reacting aliphatic amines with ethylene carbonate to intermediate carbamates that are then reacted with methacrylic anhydride to generate nonisocyanate urethane functional monomers. "With this method, it is possible to add more urethane groups without increasing the formulation viscosity. Simple addition of the new monomer to the latex provides an acrylic urethane

dispersion without other processing. In the resin, pendant urethane groups hydrogen bond to increase the T_g of the latex and improve other properties, such as tensile modulus, tensile strength, and storage modulus. At the same time, the phase separation and processing issues observed with most PLDs are alleviated," Soucek observes.

CHROMIUM ALTERNATIVE

Corrosion resistance is a primary concern for any applications in which metal substrates may be exposed to harsh environments. Currently, chromium-based pretreatments are commonly used to improve corrosion prevention on aluminum surfaces used in aerospace applications. Because this form of chromium is toxic, there is an urgent desire to replace this pretreatment method with a more sustainable alternative. Mannari has developed organosilane technology that has been customized for use on structural aluminum alloys. The bis-ureasil and epoxy silanes produce stable sol-gel bath compositions that when formulated with nano-silica and organic corrosion inhibitor in varying proportions generate pretreatments that are compatible with topcoats and provide the corrosion resistance, adhesion, and mechanical properties essential for high-performing coating systems. According to Mannari, they provide the same or even greater level of protection afforded by chromate conversion coatings. One difference is the film thickness, which is slightly higher (4–6 vs 2–3 microns, respectively).

WORKING WITH LIGNIN AND CELLULOSE

To overcome the limited availability of biobased raw materials, one approach is to look for sources of biomass that are generated in large quantities as byproducts of other industrial activity. Both lignin and cellulose meet this criterion. Lignin is an important structural component in the cell walls of woody plants. It comprises approximately one-third the mass of lignocellulose, the raw material for papermaking (the remainder is cellulose). In most papermaking processes, the lignin is removed. It is often burned as fuel, but could serve as a raw material for the production of value-added products. Lignin is very difficult to work with, but Webster has discovered a process for functionalizing the material without the need to use any solvents. The product of this fairly green process is a liquid resin that, due to its highly aromatic nature, imparts attractive properties to thermosets.

Pourhashem is also exploring the sustainability of coatings based on lignin. Because it is a byproduct from another industry (paper or biofuel), it could, through its use in coatings, contribute to a circular economy, minimize waste, and essentially improve the efficiency and environmental impact of both the

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Dr. Ghassefi Pourhasseini (above), assistant professor in the Department of Coatings and Polymer Materials at NDSU. © Photo courtesy of ND EPSCoR.

coatings and paper sectors. For a similar reason, she is evaluating coatings made from materials derived from corn and corn cobs.

Minko, in collaboration with Suraj Sharma, associate professor and graduate coordinator in the Department of Textiles, Merchandising and Interiors at the University of Georgia, meanwhile, is investigating the utility of fibrillated nanocellulose, a very strong material with a high elastic modulus that comprises small fibrils of cellulose in the range of 10–100 nanometers that are produced following the chemical or mechanical degradation of plant cells walls in wood pulp traditionally used in papermaking. Due to the decline in the paper industry, wood processors have sought other applications for wood pulp, with the production of nanocellulose one option that is being explored. The material is finding increasing use in the pharmaceutical and packaging industries and in composite applications. The initial product of wood pulp degradation (exposure to high shear rate in a homogenizer) is a hydrogel containing the nanocellulose. Minko's group is exploring the combination of this

hydrogel with other green materials and monomers to form new materials with many potential applications, including high-performance functional textile coatings. "Nanocellulose is valuable because it provides improved mechanical properties while also being biodegradable and sustainable," Minko says.

One of the challenges has been improving the water resistance of formulations based on the nanocellulose hydrogel. "Cellulose is hydrophilic; plants use lignin and some waxes to make the plant wall more hydrophobic," Minko explains. His group has tried to take a similar approach, using natural products wherever possible, but in some cases small quantities of petrochemicals to make the nanocellulose more compatible with hydrophobic materials. In textile coatings, the fibrillated nanocellulose acts as a binder, providing strong adhesion between the cellulose fiber matrix and the functional coating material and ensuring retention of the coating materials on versatile fabric surfaces, according to Minko. "The coatings provide a means for introducing functionalities to textiles that can improve their performance, such as thermal energy management and launderable conductive features, and extend their lifespans," he adds. One specific project that Minko's group is working on is the development of novel thermo-regulating textiles material for military uniforms.

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CURE-ON-DEMAND

Current cure-on-demand technologies are two-component, UV-, E-beam-, or thermally cured systems, each of which has a problem, according to Soucek. "Two-component systems in general have limited processing/potlife capabilities. UV has line of sight and opacity issues dictated by Beer's law, E-beam has safety issues, and thermal curing is not possible for heat-sensitive substrates such as plastics," he explains.

To overcome these various problems, Soucek has attached a free radical initiator to a magnetic nanoparticle that can initiate polymerization or curing reactions upon oscillation of the nanoparticle and without substantial heating of the coating. "With this approach, heat-sensitive substrates can be coated without line of sight issues, while opaque composites and highly pigmented coatings can be cured without being impacted by Beer's law," he explains. "This new cure on demand technology would augment UV- and E-beam curing of polymeric materials

into composites, adhesives, and coatings and may even be useful for in vivo applications such as bone stabilization or cartilage enhancement," Soucek states.

MODELING TO EVALUATE SUSTAINABILITY

One of the challenges for researchers investigating novel materials for the development of sustainable coatings is to understand the actual level of sustainability that a technology achieves

when the whole lifecycle is considered. Pourhashem recently joined NDSU and began applying her expertise in modeling of environmental impacts for biofuel

production to paints, coatings, polymers, and polymeric materials. "We look at the ingredients in the formulation and the process conditions used to make those ingredients and the coating itself. In addition, we follow the supply chain back to the basic raw materials that are

used and consider all of the inputs and outputs that are involved," she explains. The results are compared to the performance of competitive products that are already on the market to determine if the new technology is indeed more sustainable. Her analyses are also used to identify areas for improvement and optimization so that the sustainability of new technologies can be enhanced.

The factors Pourhashem considers range from the raw materials—chemicals including solvents, catalysts, and energy used in the form of heat or electricity—to their global warming potential and contribution to ozone depletion, to the toxicity to humans and ecosystems. "We start at the beginning with the extraction of basic raw materials (mining for minerals, oil for petrochemicals, and cultivation for plants) and consider every aspect that could have an impact on the environment to determine how sustainable a coating really is," she remarks. "What we have found is that in some cases choices that were made with the intent of increasing sustainability may have unintended consequences that, in the end, actually have a negative impact," Pourhashem adds. An example output is the quantity of fossil fuel consumed to produce a ton of a specific paint or to coat a square meter of surface. This type of result makes it possible to compare the sustainability performance of different coatings. *

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