Bio-based Resins

for Paints and Coatings: Moving Beyond Basic Vegetable Oils

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Bio-based resin technology has been a staple of the paint and coatings industry for many decades. The polyol and fatty acid components of conventional alkyds have been derived from naturally occurring oils since their first introduction. Until recently, however, coating resins prepared from oil-based raw materials were selected based on their performance, with no attention paid to the renewable content. But in recent years, demand for traditional alkyds has been declining because of their high volatile organic compound (VOC) content. There is growing interest in "greener" products and a greater awareness on the part of paint and coating manufacturers and their customers that the use of renewable raw materials can help meet sustainability goals. This, in turn, is driving renewed interest in the development of coating resins developed from a variety of bio-based materials, including derivatized natural oils, proteins, and other biodegradable polymers.

Presented below are highlights of both commercial products produced using bio-based raw materials and academic research projects focused on utilizing renewable resources for the synthesis of high-performing resins for a variety of paint and coating applications.

ON THE MARKET

Polyurethane Dispersions

Alberdingk Boley is a company focused on 100% solids and water-based resins for numerous applications. Its products have been based on renewable materials since its inception—first linseed oil and then castor oil. Most recently, the focus at the company has shifted to polyurethane dispersions (PUDs) prepared using polyols derived from castor oil.

"Traditional paint and coating manufacturers have begun to embrace the idea of renewable materials, and there has also been particularly strong interest from the do-it-yourself (DIY) sector," notes Yasmin Sayed-Sweet, vice president of sales and marketing for Alberdingk Boley. However, renewable content is not enough, adds technical applications manager Markus Dimmers. "The performance characteristics have to be there. There is a big push for paints and coatings to be longer-

lasting, and products formulated with resins and/or additives prepared from renewable content must also meet that expectation," he explains.

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That is one reason Alberdingk opted to develop PUDs instead of pursuing waterborne alkyd technology; polyurethanes are generally more durable and thus offer a significantly extended service life compared to alkyds. "The renewable polyols content combined with the greater durability makes PUDs a good option, even though the isocyanate component is not renewable," Dimmers observes.

In addition, the properties of castor oil and its polyols make it ideal for use in the preparation of PUDs, according to Sayed-Sweet. Castor oil is both hydrophobic and more nonpolar than other natural oils, as well as having excellent viscosity that is beneficial for coatings applications and performance. Castor oil also contains natural OH functionality and can be reacted directly with isocyanates without any need for derivatization. "The fact that no further chemical modification is required is quite attractive, because there is no additional energy used, and the maximum renewable content can be achieved," comments Dimmer.

The company's latest PUD based on castor oil (CUR77) is a VOC- and odor-free resin designed for use in interior wall paints. It is odor-free because it is neutralized with a sodium salt, according to Dimmers. According to the company, additional features include good wet scrub resistance, excellent hiding power, excellent blocking resistance, and a high water vapor transmission rate. The resin was introduced to the European market at the European Coating Show in April 2013, and is currently being promoted to key customers in North America prior to a full launch later in the year.

Both Sayed-Sweet and Dimmer agree that it is up to paint companies to find a way to effectively market their products containing renewable content in such a way that will differentiate it from other choices on the shelves at "big box" stores. Part of that effort, they believe, will involve combating misperceptions in the marketplace, such as competition with food crops and performance and processing concerns. "Resin manufacturers have the technology to make advanced, high-performance bio-based resins. The challenge is to get consumers to realize that products formulated with these resins are viable and 'greener' options," concludes Sayed-Sweet.

Waterborne Alkyds

Reichhold, meanwhile, continues to advance its waterborne alkyd technology, and now offers several products that have received the U.S. Department of Agriculture (USDA) voluntary Biopreferred® label, which indicates that the material has a renewable content of at least 25%. The resins are also low-VOC (<~50 g/l as supplied) and APE-free, according to Jamie Dziczkowski, a chemist associate at Reichhold. The Beckosol AQ line includes a range of products with varying renewable content (35–65% renewable carbon content) from various oils and fatty acids, including soybean oil. The alkyd latex is formed using proprietary processing technology that includes the addition of a surfactant to enable dispersion of the resin. "The different levels of renewable content lead to different properties that are suitable for a range of coating applications from stains to metal primers," Dziczkowski says.

"At Reichhold, we are committed to providing our customers with waterborne alkyds that perform analogous to our solvent-based technology, with much of our R&D in the alkyd latex sector focused on new products that provide performance in both industrial and architectural applications," she continues. "We are also developing bio-based polyols for the preparation of water-based, oil-modified polyurethanes."

Importantly, she notes, the waterborne alkyds have a flow and appearance that is similar to conventional solvent-based alkyds, combined with good adhesion and long-term stability. "In fact, very high gloss rivaling that of solventborne alkyds, and much greater than acrylics, is possible with these renewable water-based alkyds," says Dziczkowski. "In addition, a variety of sheens is possible because they can also be readily flattened." Because the alkyd latexes behave like traditional latexes, they also can be processed on existing equipment.

The newest Beckosol product, Beckosol AQ 521, is an epoxy-modified alkyd latex designed and formulated for use in wet-look sealers. It provides excellent penetration and substrate wetting for porous concrete surfaces and enhances the natural color of concrete pavers and flagstone without imparting gloss, Dziczkowski notes.

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While she feels that the goal of developing renewable alkyd latexes with performance rivaling solventborne systems has been achieved, she does agree that challenges remain. The biggest hurdle for bio-based resin manufacturers is the need to educate both their direct customers and end users about the benefits of this type of technology. "In addition, people generally think that latex means acrylic. We have to overcome that assumption and also demonstrate that products with renewable content can provide both high performance and increased sustainability," Dziczkowski explains.

Vegetable Oils

Like Alberdingk Boley, Cargill has been involved in the business of natural oils for many years. While not specializing in coating resins, the company does take basic vegetable oils and develops processes that make them suitable as raw materials for various applications. According to Brent Aufdembrink, technical director for industrial oils and lubricants at Cargill, this is generally achieved via the additional acid functionality.

Many of Cargill's products are based on soybean oil. For example, the company makes a line of soy-based polyols that can replace castor oil. Although much of the work that Cargill did on soybean oil-based polyols was directed at the polyurethane foam market, the company is interested in finding additional applications for these products in polyurethane coatings. "We have polyols with hydroxyl values ranging from 56 to 260, and many of them should be appealing for coating resin applications," Aufdembrink believes. Notably, the range of functionality can be further expanded to impart different properties. "The main idea is to add value to the oils. We are happy to work with customers to develop specific vegetable-based products for specific applications, but generally, there needs to be a pretty sizeable market opportunity involved," he adds.

Like others in the industry, Aufdembrink has found that although interest in bio-based raw materials is growing, it has not yet reached the point where customers are willing to pay a higher cost for sustainability. "Either the bio-based material has to be of equal or lower cost for the same (or better) performance, or it has to offer some special functionality or performance capability not otherwise possible with petrochemical products."

One area where Aufdembrink has noted a resurgence of interest in vegetable-based products, and in particular methyl esters of vegetable oils, is as adjuvents in pesticide formulations that are sprayed onto plants. The oils help the pesticide formulation flow over and coat the leaves of the plant so that the active ingredient is uniformly distributed. This application was important in the 1990s, but shrank dramatically with the introduction of Roundup Ready® seed, which eliminated the need for sprays that required oil-based adjuvents. Recently, however, there has been some incidence of resistance to Roundup, and some alternatives have required re-adoption of oil-based adjuvents. The bio-based nature of the vegetable oil derivatives is attractive, given that the material is applied to crops.

Polylactides

NatureWorks is a company that is just beginning to explore the opportunities for its bio-based resins as binders in paints and coatings and other related materials (adhesives, inks, toners, etc.) Manuel Natal, global segment leader for lactide derivatives, is looking to identify new applications for polymers based on lactide and its derivatives. "The first response I often hear when I suggest the use of polylactide (PLA) in paints and coatings is that it is too stiff," says Natal. "In fact, while the T_g of poly-L-lactide is indeed relatively high (55–60 °C), if a mixture of the L- and D-lactyl isomers is used, the T_g could drop to 40–45 °C. By carefully selecting co monomers, lactide derivatives with T_g values as low as –20 °C can be obtained." He adds that PLA and its derivatives also exhibit excellent adhesion to a wide range of substrates, including plastics, metal, and wood.

Oligomeric lactides have, in fact, been used as binders in low-VOC paints, such as in U.S. Patent No. 7049357 B2 from Glidden (which is not part of PPG Architectural Coatings), and they provide good pigment dispersion and adhesion. Toyobo Co. in Japan, for example, has developed biodegradable film adhesives, inks, and coatings based on amorphous PLA, and is even looking to commercialize a foul-release coating for ship hull exteriors that is self-polishing (via hydrolysis of the PLA resin by the seawater). Henkel and DaniMer Scientific, meanwhile, offer hot melt adhesives with significant renewable content.

Polylactide derivatives have also been used in mono chrome and color toners that offer equal or improved printing performance compared to petrochemical-based products. In this case, the stiffness of the PLA is advantageous for the particle formation process, which can be achieved via chemical or mechanical methods.

In the agricultural space itself, PLA binders are finding use in sustained-release coatings for fertilizers, including urea, potash, and phosphates, according to Natal. The PLA adheres very well to the granules of fertilizer and then, once in the ground, slowly degrades, releasing the chemical over time so that it can be used effectively with minimal waste. In addition, there is some evidence to suggest that the lactic acid produced as a result of the polymer degradation may be beneficial for plant growth. However, more research is needed on this front. This product is currently in the validation stage.

Natal points to academic research at the University of Minnesota by Steven Severtson, who has found that acrylate resins (2-ethyl hexyl acrylate or n-butyl acrylate) grafted with bio-based lactide and caprolactone side chains are effective latex based, pressure-sensitive adhesives (PSAs). In addition, by varying the amount and composition of the grafted side chains, the properties of the PSA can be adjusted. Importantly, these PSAs can contain up to 60% renewable content, and scale up is possible using conventional emulsions polymerization equipment and manufacturing processes. The university is seeking licensees for the technology.

NatureWorks itself continues to seek out partners for the development and commercialization of binders based on lactide derivatives, and welcomes any opportunities to work with companies to bring new products to market.

Two other companies have committed to developing PLA-based binders for coating and adhesive applications. Purac and Perstorp have formed a research and business development partnership for caprolactone lactide copolymers that have potential use as polyols for coatings, adhesives, sealants, and elastomers, and as hot-melt adhesives. The unique composition of the copolymer makes it possible to control both its melting point and mechanical properties and to reduce the crystallinity of the polyols, according to the two companies.

"The first jointly developed caprolactone lactide co products show that the modification of existing resins with bio-based Puralact® lactide adds value to the value chain by combining increased sustainability with enhanced performance," notes Marco Bootz, vice president for Chemical & Pharma. The copolymers were first presented at the European Coatings Show in April 2013. Customer sampling has been under way, and use of the new lactide copolymers has been approved in some final products.

Pigments, Resins, and Additives

Paper manufacturers are also looking for bio-based and biodegradable coatings. In response, German company Solam has developed a low-viscosity, pregelatinized biopolymer that functions as a pigment binder with optimum color properties in paper coatings, according to the company. Unlike dextrin, which is a common biopolymer used as a pigment binder in topcoats for paper, the new cold-water-soluble, starch-based resin aids in water retention and does not affect the whiteness of the coating. As a result, a greater quantity of less expensive starch can be used, while the amount of expensive water retention agents can be reduced. Solam, in partnership with a graphics company, has demonstrated the performance of the coating on the pilot scale and confirmed that the runnability of the new starch-based coating is suitable for high-speed operations and provides good print quality. The coating has been introduced at full scale.

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Even additive companies are getting involved in the development of bio-based products. BYK Additives & Instruments, in fact, introduced an interesting product in 2012 based on a resin produced by a bio organism. BYK began investing in biotechnology about four years ago, including the use of enzymes for the manufacturing of chemicals and other bio based technologies, according to Kevin Lassila, director of technology for the company's Paint Additives Division. "We have had a growing number of customers asking about 'green' additives," he says. "Our investment in biotechnology, as well as our recent efforts to take product life cycle analyses into account, is part of how we have responded to this customer expectation."

These efforts have resulted in Ceraflour 1000 Biodegradable Polymer, the company's first bio-based additive. The resin is actually isolated from an organism engineered to produce the product and then micronized. As a result, it is 100% sustainable and 100% biodegradable, according to Bruce Seeber, business line manager for BYK USA's Paint Additives Division. Although it is not a wax, it has wax-like properties, and is effective for improving matting and imparting attractive haptic (soft touch) properties, but is transparent. It also improves scratch and blocking resistance and leveling properties, although it has no influence on slip performance and does not affect the foam stabilization or formulation viscosity.

The product was originally developed for interior wood coatings, including kitchen cabinets, countertops, and furniture, and is particularly effective in UV-cured formulations. Currently, BYK is looking to expand its use in more application areas, including industrial and architectural coatings, overprint varnishes, plastic and paper coatings, and leather finishes.

Like other companies involved in the development of new bio-based material for paint and coating applications, BYK has found that one of the biggest challenges in introducing a new product into the marketplace is educating the end-user. In this case, according to Seeber, a key issue is getting potential customers to understand that the resin is not a wax and is biodegradable, even though it has many of the properties of a wax. "The coatings industry is very methodical when it comes to the adoption of new technology. We expect, though, that as greater numbers of bio-based products are introduced and their performance is demonstrated, the potential opportunities will increase dramatically," he concludes.

Reactive Surfaces has taken a different approach, developing bio-based additives using naturally occurring biomolecules including enzymes, peptides, and proteins. In May 2013, the company launched its latest product, WMDtox™, a self-decontaminating coating that protects firearms, vehicles, equipment, and uniforms by neutralizing organophosphorous chemical agents such as sarin, according to chief innovation officer Steve McDaniel. The coating includes the company's additive OPDtox™, which contains organophosphorous hydrolase, an enzyme that specifically cleaves the P–O, P–F, and P–S bonds in organophosphorous compounds, producing nontoxic byproducts.

Other products from the company based on enzymes include DeGreez™, which contains lipases, or hydrolytic enzymes, that catalyze the breakdown of natural greases, fats, and oils known as triacylglycerols. DeGreen™ consists of a mixture of enzymes known to inhibit the growth of algae. In addition, Reactive Surfaces' ProteCoat® additives are based on antimicrobial peptides (AMPs) that selectively target the cell membranes of microorganisms but are inactive toward plant and animal cells. Because they focus on characteristics common to microorganisms, they offer true broad spectrum activity against many different types of bacteria, yeast, mold, fungi, and some viruses and algae, yet are selective only for these microbes.

JOINT INDUSTRY/ACADEMIC EFFORTS

In addition to the individual resin manufacturers and other raw material suppliers working on the development of bio-based products for use in paints and coatings, numerous joint development efforts are under way that involve both companies and research institutes or academic research groups.

At the VTT Technical Research Center of Finland, several scientists are investigating the use of different types of biomass for the production of industrially relevant bio based materials. Ali Harlin, a research professor in bioeconomy, chemicals, and materials, is focused on developing waterborne binder systems based on PLA dispersions and hemicelluloses. After developing crosslinkable polyhydroxyacid dispersions, he more recently has focused on water-soluble xylan ether derivatives produced from high molecular weight xylan present in bleached birch Kraft pulp. The xylan ethers can be produced either from extracted, nondried xylan or the birch pulp by reactive extraction.

These xylan ethers were demonstrated by Harlin's team to be effective binders in inks, barrier coatings, pigment coatings, hot-melt adhesives, and films. Harlin notes that, unlike starches, hemicelluloses present no conflict with the food supply, being nonfood polysaccharides and the second most abundant plant material in nature. "Xylans are the main hemicelluloses in hardwoods, and the global annual growth of wood and other bio based raw materials will provide an annual maximum availability of hemicellulosic raw materials of approximately 35–70 billion tons, making them a practically unlimited resource," Harlin observes.

Xylan can be produced from different types of wood or agricultural materials using a variety of extraction methods, such as treatment under alkaline conditions following bleaching for whiteness, if required, and removal of the lignin, or—more preferably—extraction of bleached pulp used later, e.g., for fluff. The xylan then can be chemically modified to adjust its properties, including, but not limited to, the hydrophobicity–hydrophilicity balance, solubility, thermoplasticity, and film-forming behavior, according to Harlin. Typical reactions include esterification and etherification, such as alkoxylation or carboxymethylation, and methacrylation.

To increase the solubility of the unacetylated but amorphous xylan in birch Kraft pulp in water, Harlin subjected the natural polymer to hydroxyalkylation at a suitable substitution level to achieve internal plasticization and to form water-soluble, film-forming compounds. These polymers were then further converted to xylan ethers using propylene oxide or glycidyl ether via reactive extraction, which avoids difficult intermediate separation and concentration steps.

The hydroxypropylated and butyl-allyl derivatives of xylan were found to be particularly suitable as binders for water-based and UV-curable flexo inks for paper, coated board, liquid packaging board, and polypropylene top white laminate with increased water repellency. Inkjet inks were also formulated and tested, and VTT is conducting further investigations in cooperation with various companies in the supply chain, including raw material, binder, and ink manufacturers, pigment producers, converters, substrate manufacturers, and brand owners.

Harlin's group has also demonstrated that the xylan ethers are potential replacements for styrene-butadiene latexes and starch in pigment coatings for offset grade printing papers. Formulations containing 70% calcium carbonate and 30% kaolin were applied with success, even though the xylan systems had a higher viscosity than the synthetic latex and the solids content was lower in the paste.

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Also in Europe, six industrial and seven academic partners involved in the E.U.-funded Surface Functionalization of Cellulose Matrices Using Cellulose Embedded Nanoparticles (Surfuncell) project announced in May 2013 that they have developed a new class of bio-based materials made up of extremely small layers of polysaccharides coated with nanoparticles comprising other biological or mineral matter. When formed into a composite with other materials, the new polymers have certain characteristics, such as selective adsorption, flame resistance, electrical conductivity, anti-microbial activity, and barrier properties. According to the Surfuncell group, these are attractive properties for pulp and paper, cellulosic yarn, cellulose film, and filter membrane products used in medical and hygiene devices, water-purification systems, and electronics.

ACADEMIC RESEARCH HIGHLIGHT

Dean Webster at North Dakota State University (NDSU) is investigating derivatives of low-viscosity, sucrose-based fatty esters. The starting esters (Sefose®, developed by Procter & Gamble) are 100% renewable materials prepared by esterifying sucrose with fatty acids in a solvent-free process. Typically, all eight hydroxyls on the sucrose molecule are esterified.

Webster epoxidizes the sucrose esters and then derivatizes them through reaction of the epoxy groups, leading to bio-based resins with a high degree of functionality. He has, for example, developed derivatives with a high degree of hydroxyl functionality and used them in the synthesis of polyurethanes and melamine resins. Initial evaluations have suggested that the technology should be fairly competitive in terms of cost. The work has attracted the interest of a number of companies who are in discussion with Webster regarding potential licensing opportunities.

With respect to the future of bio-based resins for paint and coating applications, Webster is quite positive. "Interest in this area is growing exponentially, and there are a lot of interesting developments occurring with respect to bio-based building blocks, such as succinic acid, levulinic acid, isosorbide, furan dicarboxylic acid, and even 1,3-propanediol. In addition, unique work is being done in the area of vegetable oil derivatization that is yielding bio-based resins with interesting properties," he observes.

NDSU colleague Bret Chisholm is one of the researchers developing derivatives of soybean and other plant oils. He esterifies the base oil with a vinyl ether alcohol (butylene glycol monovinyl ether or ethylene glycol monovinyl ether), removing the glycerol byproduct (in a process similar to that used for the production of biodiesel) and then polymerizes the new vinyl ether, obtaining polymers with the sites of unsaturation located in the plant oil-derived pendent groups which can be used for curing. These polymers can be used directly in coatings or can be epoxidized for use in UV-cured coatings or further derivatization to polyols or polyacrylates. In addition, the fatty acid-substituted vinyl ethers can be copolymerized with water soluble monomers to form polymers that can be dispersed in water without the need for an added surfactant. The use of monomers with side changes of varying steric bulk enables control of the T_g of the final polymers, which in turn enables formulation of coatings with varying degrees of hardness.

As with Webster, there is significant interest from the industry in Chisholm's work, and a number of companies have been requesting samples for evaluation. Chisholm believes that, as a bio-based starting material, plant oils have an advantage because they do not require extensive downstream processing to be used in paints and coatings. He notes that significant advances in technology would be needed before cellulose and lignin, for example, could be used as bio-based resin materials.

At Pittsburg State University in Kansas, Petrović Zoran is also developing resins based on soybean in oil. In his case, though, he is focused on the cationic polymerization of soybean oil with superacids, such as triflic acid (CF3SO3H) and tetrafluoroboric acid (HBF4). He has demonstrated that the polymerization proceeds under mild conditions (80–100°C and atmospheric pressure) in high yield to produce viscous liquids or solid polymers depending on the reaction time, and that it is more economical than conventional thermal and "air blown" processes. In addition, because a large percentage of the double bonds are retained in the final polymers, they can be further crosslinked for use in a range of applications, including printing inks.

Researchers at Iowa State University (ISU) are also achieving noteworthy advances with respect to bio-based polymers for coating applications. Michael Kessler developed antibacterial soybean-oil-based cationic (through incorporation of ammonium) polyurethane coatings prepared from five different amino polyols. The particle morphology, mechanical properties, thermal stability, and antibacterial properties of the coatings are determined by the structure and hydroxyl functionality of the amino polyols, which are derived from soybean oil. The ammonium ions bind to bacteria and other microbes and disrupt their structure, leading to cell injury or death. Also in conjunction with Richard Larock, Kessler has developed a variety of vegetable oil-based polymers via free radical, cationic, olefin metathesis, and addition polymerization reactions that exhibit a range of thermophysical and mechanical properties from soft and flexible rubbers to hard and rigid plastics.

Meanwhile, David Grewell, also at ISU, has focused on the use of proteins as natural resins for coating development. "It seemed reasonable to choose a naturally occurring polymer rather than to take a polysaccharide, break it down into its sugars, and then repolymerize it," he explains. Plant-based proteins are attractive for temporary coating applications because they eventually biodegrade. One example of a coating developed by his group that is attracting a lot of interest is a barrier coating for paper and paperboard that can replace nonbiodegradable waxes. Food packaging manufacturers have been actively seeking just such a technology.

Even more interesting is the coating that Grewell has developed for hay bales. Large round bales are generally wrapped in a polyethylene plastic wrapper for storage, and this wrapper adds significant cost to hay production and a large amount of nonbiodegradable waste product. Grewell's protein-based coating alternative, on the other hand, is sprayed directly onto the hay and lasts for several months—about as long as is needed to store hay for winter feeding. Because the cows can eat the hay directly, there is no waste plastic to dispose of, and the cost, time, and inconvenience to the farmer are significantly reduced.

Separately, Grewell recently received a planning grant from the National Science Foundation for the establishment of the CB2 Center for Bioplastics and Biocomposites as an Industry & University Cooperative Research Center, which will be organized by ISU and University of Massachusetts-Lowell. Although most of the work will be focused on bioplastics and biocomposites, he anticipates that some research will involve the development of resins for coatings applications.