Better Bonding with Beans

Formaldehyde is an extremely useful industrial chemical but also one that has long been known to cause environmental health problems in some circumstances. A major route for human exposure is inhalation of formaldehyde gas emitted from urea- and phenol-formaldehyde resins used as adhesives in engineered woods such as plywood and particleboard. Industrial workers are exposed to significantly higher amounts of formaldehyde than the general public, although residents of new homes built with engineered wood materials often experience symptoms, especially soon after moving in. Formaldehyde concentrates in indoor air, with known and suspected human health effects ranging from eye irritation to cancer.

Now a new adhesive using soy protein, processed to resemble the protein that allows mussels to cling to rocks, is enabling some manufacturers to make formaldehyde-free engineered woods. Developed by Kaichang Li, an associate professor in the wood science and engineering department at Oregon State University in Corvallis, the soy adhesive is being hailed by many as a nontoxic, economically attractive, and renewable solution to a long-standing environmental health issue.

Formaldehyde Figures

Soy adhesives are not new, having been used in commercial wood products as early as the 1920s. But like other vegetable glues, they were water-soluble and too chemically unstable to provide the necessary durability. The 1930s saw the introduction of urea- and phenol-formaldehyde adhesives derived from petroleum and natural gas. When cured using heat and pressure, these formaldehyde adhesives easily outperformed the soy glues of the time. The construction and wood products industries embraced the formaldehyde-based adhesives wholeheartedly.

According to the National Toxicology Program's 2004 *Report on Carcinogens, 11th Edition* (*ROC*), the amount of formaldehyde manufactured has steadily risen over the last 75 years, and in 1998 (the latest year for which figures are available), 11.3 billion pounds of formaldehyde were produced in the United States. An overview of the formaldehyde market in the 12 June 2002 issue of *Chemical Week*, an industry publication, noted that

Chris Reuther/EHP; Dave Daniel

the formaldehyde used in wood adhesives make up half of all formaldehyde made.

More than 1.8 million U.S. workers are exposed to formaldehyde on the job, according to the National Institute for Occupational Safety and Health (NIOSH) "current intelligence bulletin" on formaldehyde. Embalmers, laboratory workers, and textile workers making permanent-press fabrics are the most highly exposed, but wood industry workers are also high on the list.

Among the general public, the 2.2 million people who live in mobile homes made with engineered wood products make up the largest formaldehyde-exposed group, according to the *ROC*. That's because these structures are more airtight than conventional homes and thus concentrate whatever fumes occur in them. Further, conventional homes tend to be built with more solid wood compared to manufactured homes (although some residents of conventional homes have also been exposed to high levels of formaldehyde—during the 1970s a urea-formaldehyde foam was used in insulation; use of this foam was discontinued in the early 1980s, however, and most of the foam's formaldehyde has long since dissipated). Many consumer products, including nail polish remover, permanent-press fabrics, and deodorants, also contain formaldehyde.

Formaldehyde from both natural and man-made sources is generally present at about 0.03 parts per million (ppm) in both indoor and outdoor ambient air, according to the Consumer Product Safety Commission document "An Update on Formaldehyde: 1997 Revision." This is much lower than the worker exposure limits of 0.75 ppm over an 8-hour period and 2.0 ppm over a 15-minute period set by the Occupational Safety and Health Administration.

There is wide variation in individuals' sensitivity to formaldehyde. According to a 1995 International Agency for Research on Cancer monograph on wood dust and formaldehyde, concentrations above 0.5–1.0 ppm can cause irritation of the eyes, skin, nose, throat, and lower airways. Acute or long-term exposure may lead to other problems. In rats, ingestion of high doses produces problems such as breathing difficulties and vomiting. In humans, ingestion can also corrode and trigger hemorrhaging in the gastrointestinal tract, as well as cause cardiovascular collapse and convulsions, according to a review in the 19 June 2000 issue of *Human and Experimental Toxicology*.

Rodent studies have established a link between formaldehyde exposure and cancer of the nasal cavity, and human epidemiologic studies have found associations between formaldehyde and nasopharyngeal, nasal, prostate, lung, and pancreatic cancers as well as leukemia, although other studies have not always borne out these associations.

Despite these discrepancies, the potential for human health risks has spurred a number of health organizations to err on the side of caution. In 2004 the *ROC* listed formaldehyde as "reasonably anticipated to be a human carcinogen," and the International Agency for Research on Cancer changed its rating of formaldehyde from a "probable" to a "known" human carcinogen in 2004.

Clued In to a Better Glue

Li's new soy adhesive is an ingenious chemical construct, something of a Holy

Shell game. Mussels stick to rocks, boat hulls, and piers through the strength of a tightly bonding adhesive that adapts to wet and irregular surfaces. A new adhesive inspired by the tenacity of mussels combines those qualities with the affordability and renewability of soy protein.

background: Chris Reuther/EHP, Dave Daniel; mussel photo: Anna Colls/Alamy

Grail in the search to make vegetable proteins that are strong enough and water-resistant enough to hold up in industrial applications. In a report published in the September 2002 issue of *Macromolecular Rapid Communications*, Li noted the fine complementarity between the features of marine adhesive proteins (like those that make clinging mussels such a threat to boat hulls) and soy proteins. Marine adhesive proteins stick to wet and irregular surfaces, bind very strongly, and degrade very little, but are burdensome and costly to synthesize; soy proteins are abundant, renewable, and affordable, but are relatively weak and easily degraded.

Li was able to get the best of both worlds by coaxing soy protein to cross-link with the adhesive's second major ingredient—a proprietary resin known as kymene—in a similar manner to mussel adhesive. Cross-linking organizes large molecules into a mesh-like configuration. In Li's soy adhesive, this occurs after the glue is applied to the wood, during curing (the chemical and physical process by which ingredients are united into a stable form). The cross-links in Li's adhesive are so strong that it can be boiled for hours without degrading, he says.

The commercial formulation now on the market has been patented by Oregon State University and licensed to Wilmington, Delaware–based Hercules Incorporated, the resin manufacturer that produces kymene. Columbia Forest Products, a manufacturer of veneer-core hardwood plywood based in Portland, Oregon, is the first wood products company to convert a manufacturing process to a completely formaldehyde-free soy adhesive. Both companies worked with Oregon State University to develop the commercial formulation.

The soy adhesive is comparable in cost to the urea- and phenol-formaldehyde adhesives, says Charles Grabiel, commercialization manager for the consulting firm Omni Tech International and an adviser to the United Soybean Board. This group of soybean farmers advises the Secretary of Agriculture on ways to increase the utilization of U.S. soybean products.

Optimizing the Innovation

So far, the commercialization of the new adhesive affects only a subset of the very large engineered wood market, since Columbia Forest Products produces decorative hardwood plywood exclusively for interior applications. But work is under way at Oregon State University to commercialize the patented formaldehyde-free wood adhesive for production of particleboard, medium-density fiberboard, exterior-grade oriented strandboard, and plywood.

There is less pressure to convert exterior-grade wood products because they use phenol-formaldehyde resins, which offgas formaldehyde at a much lower rate than the urea-formaldehyde resins. Adhesives in exterior wood products must also meet stricter moisture-proofing standards set for certification by industry organizations such as the Engineered Wood Association, says Grabiel.

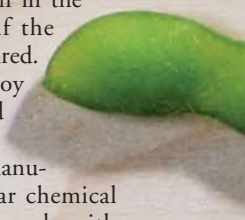
Since Li's soy formulation has demonstrated strength and water-resistance, its certification for use in exterior products is expected to go smoothly. However, the method of applying adhesives differs by product type, Grabiel says. For plywood, glue can be rolled onto the panels before they are pressed, but to form composite products out of small wood pieces and sawdust, the adhesive must be reformulated to a sprayable consistency. Grabiel estimates it will take at least two years to resolve these manufacturing issues so that exterior wood products and other composite types can become formaldehyde-free.

With new products, there is always the chance that "the cure is worse than the disease," but there are no immediate indications that soy adhesives pose as great or greater health threats than their predecessors. One potential concern is allergies. Soy products are known to cause allergic reactions in some people (mostly infants), including digestive, respiratory, and skin reactions. Soy also contains plant estrogens, which are bioactive when ingested. However, owing to extensive processing, these compounds are unlikely to be present in the isolated proteins used in the adhesive.

Before curing, the soy protein used in the wood adhesive is nonvolatile, is not a hazardous air pollutant, and may be handled with basic protective gear such as gloves and safety glasses, according to the United Soybean Board's "Soy-Based Wood Adhesives and the Environment" information sheet. Grabiel adds, "The soy protein in the resin is tightly bound to wood and to itself, so will not degrade readily. The ultimate result of the degradation of the soy resin should be no different than the degradation products of soy flour."

Although many wood products and resin adhesive manufacturers have significantly reduced their use of formaldehyde, and the industry is displaying a lively ingenuity in seeking alternative products, not everyone is on the formaldehyde-free bandwagon. "We're not considering moving to a formaldehyde-free system," says Rob Schmidt, senior vice president for market applications at Dynea North America, a subsidiary of the world's largest producer of formaldehyde resins. "It's not something we consider necessary from a toxicity or cost–benefit point of view," Schmidt says, because of the "minimal hazard associated with using formaldehyde adhesives." Thus, the uneasy tug-of-war between formaldehyde's industrial convenience and its health effects will likely continue until further study can elucidate the physiological fate of the highly functional chemical.

In the meantime, fans of the soy-based approach are finding new ways to employ the bean in wood products. A hybrid adhesive combining soy protein with phenol-resorcinol-formaldehyde is being used by one company to make finger-joined wood products from green (undried) lumber, Grabiel says. Using soy protein in the adhesive mix reduces by half the amount of formaldehyde required. In addition, adhesives using soy protein require less time and use less energy to cure before use. A number of chemical manufacturers are also using similar chemical processes to create adhesives made with other alternative components, including wheat, corn, casein (a dairy protein), and seed gums.



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Suggested Reading

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