

Lignin Coating Promotes Waterproof Paper

Paper is used extensively for communication and for house wares like paper plates and cups. Over the years, researchers have developed coatings to increase the smoothness, ink absorbency, or water-resistance of paper to make it more durable. Paper is usually coated with some substance to impart desired qualities (i.e. weight, surface gloss). Most paper is laminated with wax and/or a plastic film such as polyethylene or polypropylene that makes paper more resistant to water but also unrecyclable. Recycling these coated papers calls for separating the plastic laminate from the paper, adding to recycling costs, and to the cost of disposing or recycling the separated plastic. Because not all paper-recycling facilities are able to separate plastic laminate from paper, a large portion of laminated paper products is not recycled.

Compared to other, more important, issues in a troubled world, waterproof paper may be near the bottom of the international To-Do list. However, environmental damage is a current and growing problem. At present, paper companies are cutting down forests at an alarming rate. Forests store 50% of the world's terrestrial carbon¹. Forests are carbon sinks; they use carbon dioxide in photosynthesis and thereby decrease global warming. Because waterproof paper would last longer, fewer forests would be cut down for paper and less carbon dioxide would be released into the atmosphere.

Researchers at Queensdale University in Australia have developed a lignin coating to replace conventional plastic coating. Lignin is the firm and waterproof material that gives plants structure. In wood processing, lignin is separated from pliable cellulose fibers that are used to make paper. But this separation modifies lignin such that its properties make it unsuitable for a

coating material. Les Edey, an organic chemist, along with colleagues from the Cooperative Research Center for Sugar Innovation through Biotechnology in Brisbane, Australia, have established a new process for separating lignin from sugarcane such that lignin can be used for waterproofing. This process utilizes “green chemistry”ⁱⁱ, defined as the design of chemical processes to reduce or eliminate creation of hazardous substances, that lower waste, and that minimize energy requirements. The Australian process requires extracting cellulose from the cane biomass by absorbing lignin into cellulose fibers to make a type of lignin that can function as a waterproof coating.

Lignin is difficult to break into usable substances because of its complex composition. Processes for breaking down lignin can be divided into three categories: gasification, hydrolysis, and selective thermal processing. Gasification creates a product with the simplest chemical distribution, but this gaseous product must be transformed into liquid fuels and chemicals. Hydrolytic processes, if performed with biocatalysts as in fermentation, create a mixed lignin-sugar product with slightly higher chemical complexity than that from gasification. While selective thermal processing gives a product with a high level of chemical complexity, it is the simplest of the three processes.

Lignin: what it is, how it is separated from sugarcane, and why it is useful

Lignin, cellulose and polysaccharides are the major components of the cell wall in a woody plant. As shown in Figure 1, lignin ($(C_{20}H_{24}CaO_{10}S_2)$) is composed of repeated phenylpropane units linked to each other by ether and carbon-carbon bonds. There are two

categories of lignin: one is sulfur-bearing and the other is sulfur-free. Due to the lack of a suitable industrial process, the sulfur-free lignins (Fig. 1) are as yet non-commercialized.ⁱⁱⁱ

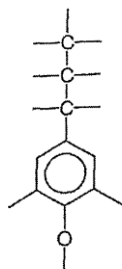


Figure 1: A phenylpropane (C₉) unit

Lignin plays a crucial role in the transport of water in plant stems. The polysaccharide components of plant-cell walls are strongly hydrophilic and thus permeable to water, while lignin is more hydrophobic. Because the cross-linking of polysaccharides in lignin provides an obstacle for water to pass through the cell wall, it is possible for the plant's vascular tissue to transport water efficiently^{iv}. Woody plants synthesize lignin from trans-coniferyl alcohol, trans-p-coumaryl alcohol, and trans-sinapyl alcohol by enzymatic dehydrogenation initiated by a free-radical cross-linking process. All plants, grasses, hardwoods and softwoods produce a lignin rich in a particular type of the repeating phenylpropane unit. Because sugarcane-derived lignin has more available ortho and para sites for reaction in the aromatic groups than softwood and hardwood, it is easier to understand the reactions that affect lignin in sugarcane.

The Australian study focused on finding ways to absorb lignin into cellulose fibers in solution^v. It was observed that paper could exhibit more water resistance by sequentially adding cationic starch^{vi}, and colloidal lignin to the pulp before the paper is formed. The cationic

starch stabilizes the negative charge on the fiber surface that otherwise would prevent lignin from binding to the paper. Results from later studies showed that lignin is in an aqueous solution at a concentration and pH wherein all the lignin is soluble. Paper is contacted with a cationic polymer before it is contacted with the aqueous lignin mixture. On closer inspection, the researchers concluded that colloidal lignin particles are bound to the surface of cellulose fibers such that the non-bound cellulose surface is a charged hydrophilic surface. The oil resistance of the paper's surface is maintained as long as most of the lignin is in soluble form. The soluble lignin is absorbed into the pores of the cellulose fibers.

The Australian process rests on a delicate balance of heat and pH. Raising the temperature increases lignin solubility. The pH needed for complete solubility of lignin depends on the type of lignin, its concentration and temperature. To assess whether lignin is in soluble form, researchers used a scanning-electron microscope to detect possible phase boundaries. Absence of phase boundaries in the lignin indicates that the lignin is soluble. Another method to test lignin's solubility - a simpler one - is to filter the solution to see if there is any remaining residue. As yet, Edye has not provided further details of his process to maintain confidentiality. However, his research has produced a light brown spray-on lignin coating that has been tested on various paper samples. The resulting coating functions as well as wax coatings but is cheaper and more environment-friendly.

Switching to lignin coating could encourage sugarcane growers to work with paper manufacturers to produce waterproof and biodegradable paper products. Costs for replacing billboards ruined by rain would be reduced.

Throughout the world, food and beverage manufacturers need paper-based packaging for storage and transport. At present it is common practice to use cardboards coated with petroleum-based wax, making this packaging non-recyclable. Replacing conventional packing with waterproof paper can reduce the need for landfills, leading to better hygiene for poor populations living near landfills.

It is not yet clear if recyclable paper can increase or decrease the price of paper. Among the US's manufacturing industries, the paper industry is the fourth largest contributor to greenhouse-gas emissions, contributing about 9% of the manufacturing contribution to carbon dioxide emissions^{vii}. Half of the world's original forests have already been cleared or burnt; 80% of the remainder has been seriously degraded^{viii} by pollution. Using recyclable waterproof paper versus non-waterproof paper may allow nature time to recover its resources, promoting environmental stability.

While conventional paper is functionally satisfactory, not all of it is recyclable. Waterproof paper may be cheaper than conventional paper, because waterproof paper is stronger, more durable, and more environment-friendly. Lignin coatings do not interfere with the paper-making process. Their advantage is that they can be put back into the pulping process to make recycled paper.

ⁱ "15 Facts About the Paper Industry, Global Warming and the Environment - thedailygreen.com." Going Green - Environmental Issues and Global Warming News - Green Living Tips. 9 Feb. 2009 <<http://www.thedailygreen.com/environmental-news/latest/7447>>.

ⁱⁱ "Green Chemistry | US EPA." U.S. Environmental Protection Agency. 9 Feb. 2009 <<http://www.epa.gov/greenchemistry/>>.

ⁱⁱⁱ "About Lignin." ILI. 17 Apr. 2009 <<http://www.ili-lignin.com/aboutlignin.php>>.

^{iv} "Lignin -." Wikipedia, the free encyclopedia. 01 Apr. 2009 <<http://en.wikipedia.org/wiki/Lignin>>.

^v Doherty, William, Leslie Edye, Peter Halley, Dylan Cronin, Alan, Orlando, and Sinclair. A Method for Treating a Paper Product. World Intellectual Property Organization International Bureau, assignee. Patent WO 2009/009821 A1. 2009.

^{vi} "Cationic Starch." NC State: WWW4 Server. 17 Apr. 2009 <<http://www4.ncsu.edu/~hubbe/CST.htm>>.

^{vii} "15 Facts About the Paper Industry, Global Warming and the Environment - thedailygreen.com." Going Green - Environmental Issues and Global Warming News - Green Living Tips. 9 Feb. 2009 <<http://www.thedailygreen.com/environmental-news/latest/7447>>.

^{viii} "15 Facts About the Paper Industry, Global Warming and the Environment - thedailygreen.com." Going Green - Environmental Issues and Global Warming News - Green Living Tips. 9 Feb. 2009 <<http://www.thedailygreen.com/environmental-news/latest/7447>>.