

The development of bio-based adhesives for the manufacture of structural-use engineered wood products

by

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Abstract

The increasing demand for sustainable construction has intensified research into bio-based adhesives for engineered wood products (EWPs), aiming to reduce the environmental and health impacts associated with conventional synthetic-based adhesives. Synthetic adhesives such as phenol-formaldehyde, resorcinol-formaldehyde, and polyurethane provide high strength and durability but emit volatile organic compounds (VOCs) and formaldehyde, contributing to poor indoor air quality and hindering end-of-life recyclability. To support green building initiatives and circular economic goals, this report compiles, evaluates, and compares research on lignin-based and soy protein-based bio-adhesives to determine their suitability for structural and exterior applications in EWPs.

This report provides a comprehensive review of existing studies to identify formulation methods, material sources, chemical properties, and performance outcomes of lignin-based and soy protein-based adhesives. Lignin adhesives utilize biorefinery by-products and bio-reactants such as glyoxal to replace petroleum-derived phenol and formaldehyde, while soy protein adhesives, derived from defatted soy flour or soy protein isolate, eliminate formaldehyde and can be modified to improve bond strength and water resistance. The report organizes and synthesizes this information into comparative tables and figures summarizing mechanical performance metrics, such as shear strength, modulus of elasticity, and moisture resistance, under various test conditions.

The findings of this report demonstrate that both lignin and soy-protein-based adhesives show strong potential to meet or approach the performance of current synthetic adhesives while offering significant environmental and health benefits. However, limitations remain in water resistance, curing time, and large-scale manufacturing feasibility. The report serves as a

consolidated reference for researchers and industry professionals seeking to advance the application of bio-adhesives in structural-use EWPs. By presenting a clear comparison of formulation strategies, performance outcomes, and areas for continued development, this report contributes to the progression of safer, recyclable, and low-emission building materials essential to achieving long-term sustainability in the construction industry.

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Chapter 1 - Introduction

This report compiles research on the most promising bio-adhesives and provides recommendations for the next steps in the successful application of bio-adhesives to exterior-use and structural-use engineered wood products, aiming to create a safe, recyclable structural green building material. In Chapter 1, green building practices, the types of engineered wood products discussed, the science and history of wood adhesion, and the product standards governing adhesives and engineered wood products are introduced. Chapter 2 examines the formulations, drawbacks, and benefits of the synthetic adhesives currently used in engineered wood products to provide a point of comparison when discussing the development of bio-adhesives. Chapters 3 and 4 discuss lignin-based natural adhesive and soy protein natural adhesive, respectively. These chapters explore the chemical formulation, development, application methods, areas of improvement, benefits, and key performance factors such as the strength and durability of the natural adhesive. Lastly, Chapter 5 gives the conclusions and recommendations.

1.1 Green Building Practices

According to the United States Environmental Protection Agency, “Green building is the practice of creating structures that are environmentally responsible and resource-efficient through a building’s life cycle. A building’s life cycle includes siting, design, construction, operation, maintenance, renovation, and deconstruction. In addition to environmental benefits, green buildings provide economic and public health benefits for building owners and users” (US EPA, 2014b). Examples of green building practices focused on environmental sustainability during a building’s life cycle include prioritizing energy-efficient design, materials, and systems; water conservation strategies during construction and operation; choosing building materials

with minimal environmental impact during their life cycle; waste reduction strategies; optimum site selection and design; using renewable energy sources; and designing buildings to produce as much energy as they consume. While environmental sustainability is a huge driving factor behind green building practices being utilized, the health of the people occupying the building is imperative. As such, green building practices should include providing good indoor air quality (IAQ) and a healthy and productive environment to their occupants (Tabibi, 2024).

A growing knowledge and awareness of the environmental, economic, social, and health benefits of green building practices has led to their increased utilization as climate change, resource depletion, and the need for healthier buildings become a reality. Green building practices are crucial to “reduce environmental impact, lower energy consumption, and create healthier spaces for occupants” (Gould Construction Institute, 2025). To encourage the use of green building practices, green certifications and standards like LEED, Leadership in Energy and Environmental Design, Energy Star, and the WELL Building Standard have been created to serve as a standard for sustainable buildings (US EPA, 2014b). These green certifications and standards not only help to promote green building practices, but are “profitable, cost-effective, and good for the economy” (*Press: Benefits of Green Building | U.S. Green Building Council*, n.d.). To elaborate, green buildings offer operational cost savings, shorter payback periods, and increased value for their owners. Additionally, they have provided millions of jobs and contributed hundreds of billions of dollars to the United States of America's economy (*Press: Benefits of Green Building | U.S. Green Building Council*, n.d.). Green buildings help to provide an environmental solution to global carbon reduction goals and a public health solution to indoor air quality concerns while providing an economic advantage.

Using green building practices can play a substantial role in reaching global carbon reduction goals because “the built environment is currently responsible for almost 40% of global energy and process-related carbon dioxide emissions” (*Built Environment Decarbonization* | WBCSD, 2023). Buildings are a major source of carbon dioxide (CO₂) emissions due to the combination of operational carbon and embodied carbon. Operational carbon comes from buildings using extensive quantities of energy for heating, cooling, and lighting, which, in most cases, is generated from fossil fuels that release carbon dioxide. Embodied carbon is the carbon dioxide emissions generated from creating, moving, and placing building materials such as steel and cement (*Why Making Buildings Greener Is Crucial to Countering Climate Change*, 2024). Green building practices and the utilization of green building rating systems such as LEED reduce both operational and embodied carbon as well as water usage, energy usage, and waste from buildings. According to the United States Green Building Council, “The Department of Energy reviewed 22 LEED-certified buildings managed by the General Services Administration and saw CO₂ emissions were 34 percent lower, they consumed 25 percent less energy and 11 percent less water, and diverted more than 80 million tons of waste from landfills” (*Press: Benefits of Green Building* | U.S. Green Building Council, n.d.). Green building practices emphasize the use of fewer resources and the minimization of waste compared to traditional building practices. LEED projects will keep 540 million tons of waste out of landfills by 2030 (*Press: Benefits of Green Building* | U.S. Green Building Council, n.d.). Utilizing green building practices can help address the challenges of climate change and resource depletion.

Of equal importance to providing an environmental solution, the health and well-being of the building occupant must be prioritized, which can be achieved through green building practices. People spend approximately 90% of their time indoors, underscoring the importance

of creating comfortable and healthy spaces (*Press: Benefits of Green Building | U.S. Green Building Council*, n.d.). According to the United States Environmental Protection Agency, “Indoor Air Quality (IAQ) refers to the air quality within and around buildings and structures, especially as it relates to the health and comfort of building occupants. Understanding and controlling common pollutants indoors can help reduce your risk of indoor health concerns” (US EPA, 2014a). Indoor air quality considers pollutants originating from both within and outside the building (Yauk et al., 2020). Outdoor sources affecting IAQ include radon, pesticides, outdoor air pollution, bacteria, fungi, and pollen (US EPA, 2014a). Outdoor sources of indoor air pollution mainly enter the building “through infiltration and mechanical ventilation systems” (Yauk et al., 2020). Indoor sources negatively affecting IAQ include fuel-burning combustion appliances such as wood stoves, gas ranges, and furnaces; emissions from building materials and furnishings, including exposed engineered wood products, fresh paint, new flooring or carpet; and household cleaning products (US EPA, 2014a). As design and construction practices continue to improve, making buildings more airtight, the effect of pollutants from within the building becomes a more significant concern (Yauk et al., 2020). The significance of any individual pollutant source depends on how much pollutant it releases, the hazards associated with the emissions, how old the source is, and how long the pollutant stays in the air (US EPA, 2014a). IAQ has recently gained significant attention following the identification of harmful health effects linked to pollutant emissions within buildings. The health effects of poor IAQ can be immediate or long-lasting, such as an increased risk of allergies, respiratory illnesses, chronic disorders, negatively affecting cognition, and cancer (Yauk et al., 2020).

Despite these health problems, IAQ is predominantly unregulated. While few regulations on IAQ exist, several laws and standards focus on reducing emissions from building materials

and products inside buildings. These laws include the 1986 Californian Proposition 65, which warns consumers “about exposure to chemicals that have been found to cause cancer, birth defects, or reproductive harm, allowing citizens to make informed decisions about their exposure to these chemicals” (Yauk et al., 2020). In addition, the Proposition 65 list was created, containing all chemicals, which is updated annually and now includes over 900 chemicals. Of the chemicals on the Proposition 65 list, the indoor air pollutants of the most concern are formaldehyde and carbon monoxide. Formaldehyde is a carcinogen, meaning it causes cancer, and a neurotoxin, meaning it is toxic to the nervous system. Carbon monoxide can cause serious tissue damage and, in some cases, death. In addition to warning consumers, Proposition 65 set a precedent for other countries, states, and governments to tighten their product emission standards regulations, modeling them after the California Air Resources Board (CARB) (Yauk et al., 2020).

Due to tightened product emission standards, certifications based on testing that show compliance for low-emitting products are becoming more common in commercial use. In addition to looking at product emissions, some United States agencies regulate the indoor air concentrations of specific volatile organic compounds (VOCs). For example, the allowed indoor air concentration level for formaldehyde is set by United States agencies and organizations, including the National Institute for Occupational Safety and Health (NIOSH), the Centers for Disease Control and Prevention (CDC), LEED, and the Federal Emergency Management Agency (FEMA) (Yauk et al., 2020). Green building certifications, such as LEED, place emphasis on improving IAQ through two methods: controlling the possible sources of emissions and through ventilation (Wei et al., 2015). To provide good IAQ, a vital step is reducing or

eliminating the toxic chemicals present indoors, such as those in building materials (Yauk et al., 2020).

“The global wood adhesive market is forecasted to reach 6.34 billion USD annually by 2025. The global bio-adhesive market reached a value of 2.2 billion USD in 2021 and is expected to reach nearly 5 billion USD by 2027” (Kumar & Leggate, 2022). The use of engineered wood products (EWPs) as building materials has grown “due to their reliable structural performance, lower weight, renewability, carbon storage, quick on-site installation, and lower levels of construction waste” (Kumar & Leggate, 2022). Using engineered wood products as a building material provides an environmental solution, thanks to the material's reduced construction waste, the renewability of wood, and carbon storage capabilities. Green building practices constitute the building's entire life cycle, which includes deconstruction. Engineered wood products have been made with toxic synthetic adhesives such as urea-formaldehyde resin and phenol-formaldehyde resin since the 1930s due to their low cost and quality adhesion properties. These synthetic adhesives used in engineered wood products can lead to the entirety of the material being unrecyclable at the end of its life. (Fan et al., 2016). Replacing synthetic adhesives with natural adhesives can make the engineered wood product recyclable at the end of its life.

While considering the environmental benefits and drawbacks of EWPs, providing a public health solution is of equal concern for green building practices. As discussed previously, formaldehyde is an indoor air pollutant present on the Proposition 65 list. As such, using formaldehyde-based synthetic adhesives in engineered wood products can lead to harmful emissions during the “preparation, storage, transportation, and use” of the EWPs (Fan et al., 2016). Additionally, these synthetic adhesives use nonrenewable fossil resources. As stated

earlier, one way of providing good IAQ is to remove or reduce the toxic chemicals present in building materials indoors. The considerations of the health of a building's occupants and the recyclability of the material at the end of its life have led to significant research into the development of safe and recyclable biobased adhesives “from abundant renewable biomass resources” (Fan et al., 2016). The successful creation of a bio-based adhesive for use in all engineered wood products could make EWPs the ideal green building material.

1.2 Types of Engineered Wood Products

Engineered wood products are defined as wood-based composite materials consisting of wood elements bonded together with an adhesive. Engineered wood products are made of several wood elements of various sizes and shapes, including fibers, particles, flakes, veneers, and laminates. The invention of engineered wood products aimed to solve multiple problems, including the decrease of old-growth forests with large diameter trees, environmental concerns, and the need for stronger, more efficient building materials. Engineered wood products support responsible forestry practices by allowing small-diameter trees, logging debris, and foreign or invasive species of trees to be utilized. Solid wood properties vary greatly between species, between trees of the same species, and even within the same tree due to the nature of the material and the influence of local deformities such as knots. Engineered wood products were created as a way to effectively use wood containing defects. When wood containing defects is turned into wood elements, the effect of the defects on the properties of the product is reduced. Using wood elements instead of solid lumber allows the properties of the product to be modified and controlled by combining, reorganizing, and separating the elements (Stark & Cai, 2022).

Engineering wood products consist of five main classes: timber or sawn board-based products such as glue-laminated timber (GLT) and cross-laminated timber (CLT), veneer-based products such as plywood and laminated veneer lumber (LVL), strand-based products such as oriented strand board (OSB) and parallel strand lumber (PSL), fiber or particle-based products such as particleboard and hardboard, and composites such as I-joists made of LVL and plywood or mass timber panels made of GLT and LVL (Kumar & Leggate, 2022). This report focuses on glue laminated timber, cross-laminated timber, and plywood to highlight different classes, weather exposures, structural uses, and the products tested in developing bio-adhesives.

1.2.1 Glue Laminated Timber (Glulam)

Glulam belongs to the class of timber or sawn board-based products and is defined as “an engineered, stress-rated product that consists of two or more layers of lumber that are glued together with the grain of all layers, which are referred to as laminations, parallel to the length” (Stark & Cai, 2022). These laminations are typically one or two inches thick, nominal. To meet North American standards, glulam must be made in an approved manufacturing plant. Common species used for making glulam in the United States are Douglas Fir-Larch, Southern Pine, Hem-Fir, and Spruce-Pine-Fir; however, almost any species can be used to make glulam if the mechanical, physical, and gluing properties are met (excluding tropical hardwoods and extremely dense species). Industry standards for both hardwood and softwood species exist, and procedures exist for using non-typical species (*ANSI 405-2023 Standard for Adhesives for Use in Structural Glued Laminated Timber*, 2023). As shown in Figure 1, producing a glulam member consists of four main manufacturing steps: drying and grading the lumber, end jointing the laminations, face bonding the laminations, and finishing and fabricating the product. Most

lumber is visually graded, which consists of inspecting the lumber for imperfections such as “knots, decay, splits, insect holes, surface roughness, number of surface repairs, and other defects” (Stark & Cai, 2022).

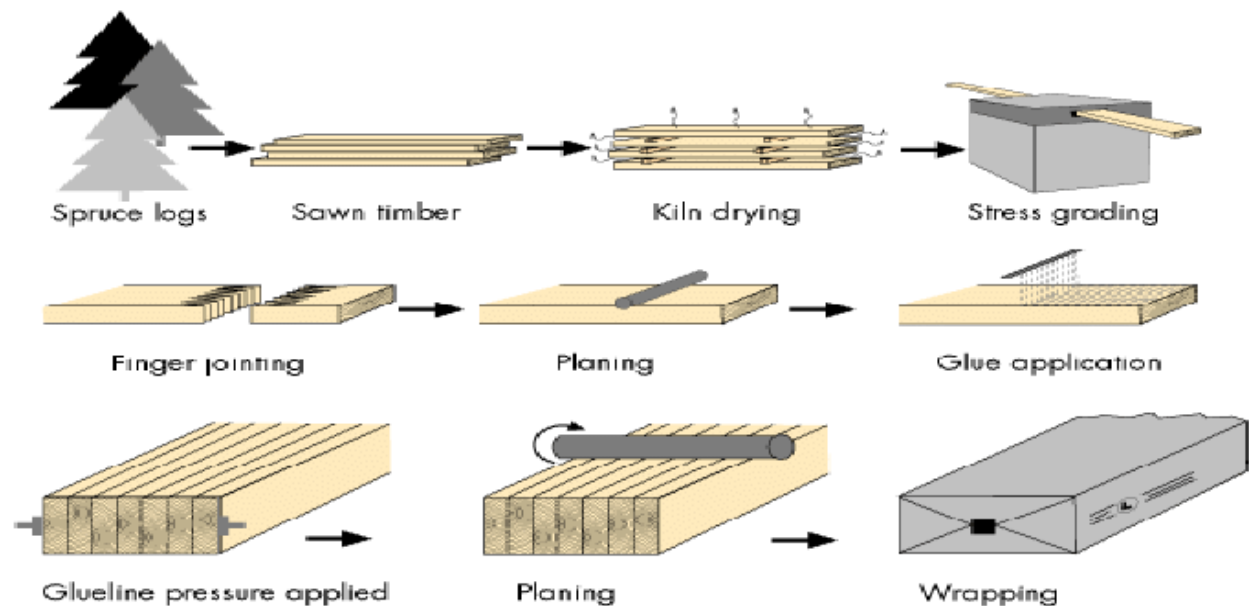


Figure 1: Glulam Manufacturing Process(*Static Analysis of Notched Glulam Beams Reinforced by Fiber Reinforced Polymers, n.d.*)

Glulam is typically used as beams and columns. Glulam has several advantages over sawn lumber, including the size at which it can be produced, the architectural effects that can be achieved, being able to dry the wood before production, and being able to use lower or varying grades of laminations (Stark & Cai, 2022). The size at which glulam members can be produced surpasses the size of the trees from which the timbers are sawn. Previously, the large trees available in the United States provided large sawn timbers, currently smaller diameter trees are harvested more frequently, sawmills are being built to process smaller logs. Making glulam involves joining the smaller lumber into a larger structural member. Since the laminations are joined at the ends, edges, and faces, the size of the final glulam product is only limited by the manufacturing facility being able to produce it, and if it can be transported to the job site.

Straight glulam members up to 100 feet long are typical, and in special cases, up to 140 feet can be made. Glulam sections as deep as seven feet have been produced (Stark & Cai, 2022).

The laminations are joined end-to-end to make the desired length beyond what is typically available in lumber. As illustrated in Figure 1, this is done through end jointing, and the most common end joint is a finger joint, approximately one inch long. Other end joints can be used if they meet the strength and durability requirements. Two reasons finger joints are the most common are: (1) continuous production equipment is available for this type of end joint and (2) use a small length of lumber to make, which reduces waste. The making of the joints is crucial to the sufficient performance of the overall glulam member and “careful control at each stage of the process—determining lumber quality, cutting the joint, applying the adhesive, mating, applying end pressure, and curing—is necessary to produce consistent high-strength joints” (Stark & Cai, 2022). Once the laminations are end joined, they need to be face joined to make the desired size of glulam member.

To make glulam members, the individual laminations must be joined face-to-face to make full-depth members. The individual laminations are planed using stringent tolerances to make parallel and glueable surfaces. Planing occurs directly before the gluing process to ensure the final glulam product is rectangular and pressure can be evenly applied after gluing. After planing, the adhesive is spread across the wide face of the laminations with a glue extruder. The adhesives used must be pre-qualified, which means that the adhesive has been evaluated and has proven to meet the performance and durability requirements. The most common adhesive used for face gluing in glulam is phenol resorcinol. After applying the glue, the laminations are assembled to make the depth of the member. The adhesive requires “proper open assembly time,” and then pressure can be applied (Stark & Cai, 2022). Pressure is applied with clamping

beds, either using a mechanical or hydraulic system, and the adhesive then cures at room temperature for six to twenty-four hours. These steps are illustrated in Figure 1. Radio-frequency can also be used to shorten the curing time by using electromagnetic waves to heat the wood and adhesive uniformly from within, rapidly accelerating the chemical reactions that harden the bond (Gadhav, 2023). After this time, the adhesive will reach approximately 90% of its bond strength. After being removed from the clamping beds, the sides of the glulam member are planed to remove any excess adhesive or dimensional differences between the laminations. Curing of the adhesive continues for the next few days. During the face-to-face bonding process, each step of the process is monitored, including the “lumber planing, adhesive mixing, adhesive spreading, and clamping processes” (Stark & Cai, 2022) to ensure adequacy. The performance of the finished glulam product is tested by conducting shear tests on the end trim pieces that are cut off to produce the final product (Stark & Cai, 2022). Shear tests are performed on the end trim pieces of finished glulam products because those sections are representative of the internal glue-line quality and can be tested without damaging the main member, allowing verification that the adhesive bonds meet strength and durability requirements for certification and quality control (Ross, 2021). During this manufacturing process, several architectural effects can be achieved.

Architectural effects that are difficult to achieve with other materials, such as curved members, can be achieved with glulam. During the manufacturing process, the degree of curvature is determined by the thickness of the laminations. The more curvature desired in the finished glulam member, the thinner the laminations are. Another architectural effect commonly used with glulam beams is tapering the ends of the members by sawing the member on the compression side through the number of laminations needed to make the needed slope. This is

usually done to create sloped roofs, to help with drainage, and to provide a lower wall height at the ends supporting the glulam beam (Stark & Cai, 2022).

In addition to its architectural potential, glulam offers the advantage that its timber is dried before fabrication, thereby limiting dimensional variation in the final product. Seasoning the timber before manufacturing glulam permits the use of higher structural design values relative to those assigned to unseasoned timbers. Kiln-drying is employed to adjust the moisture content of the timber at fabrication to approximate the equilibrium moisture content anticipated under service conditions. The permissible extent of such defects is grade-dependent and established by regional lumber grading standards (Stark & Cai, 2022).

A key advantage of glulam members is the ability to incorporate substantial quantities of lower-grade lumber in the less stressed regions of a beam. When multiple lumber grades are used within a cross-section, the product is referred to as a glulam combination. Combination members designed for flexure optimize both structural efficiency and economy. As illustrated in Figure 2, lower-grade laminations are placed near the neutral axis, where the bending stresses are minimal, while higher-grade laminations are positioned on the beam faces, where the bending stresses are the greatest (Stark & Cai, 2022). In summary, glulam is a timber board-based engineered wood product that has several advantages over sawn lumber, including greater dimensional capacity, enhanced architectural versatility, the use of higher design values associated with seasoned timber, and the efficient incorporation of lower-grade lumber.

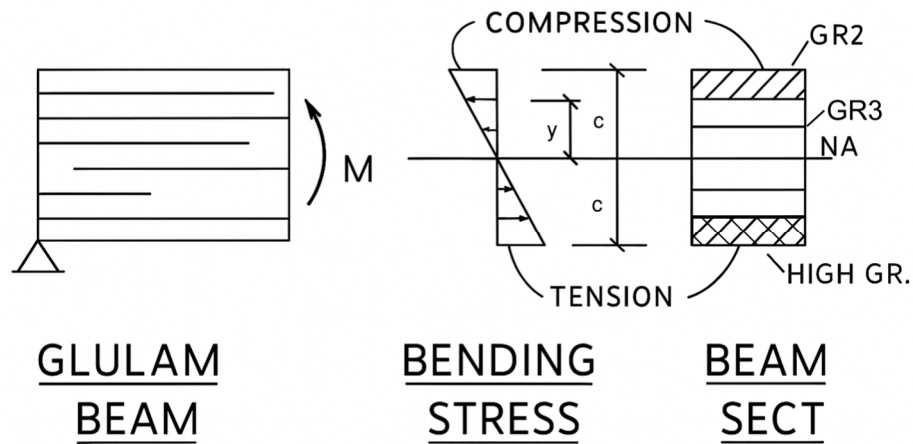


Figure 2: Glulam Beam Stress Diagram

1.2.2 Cross-Laminated Timber (CLT)

Another type of engineered wood product belonging to the timber or sawn board-based products class is cross-laminated timber, or CLT. Similar to glulam, CLT consists of kiln-dried lumber boards bonded with structural adhesive; however, differs in that an odd number of layers are oriented with alternating grain directions, as illustrated in Figure 3.

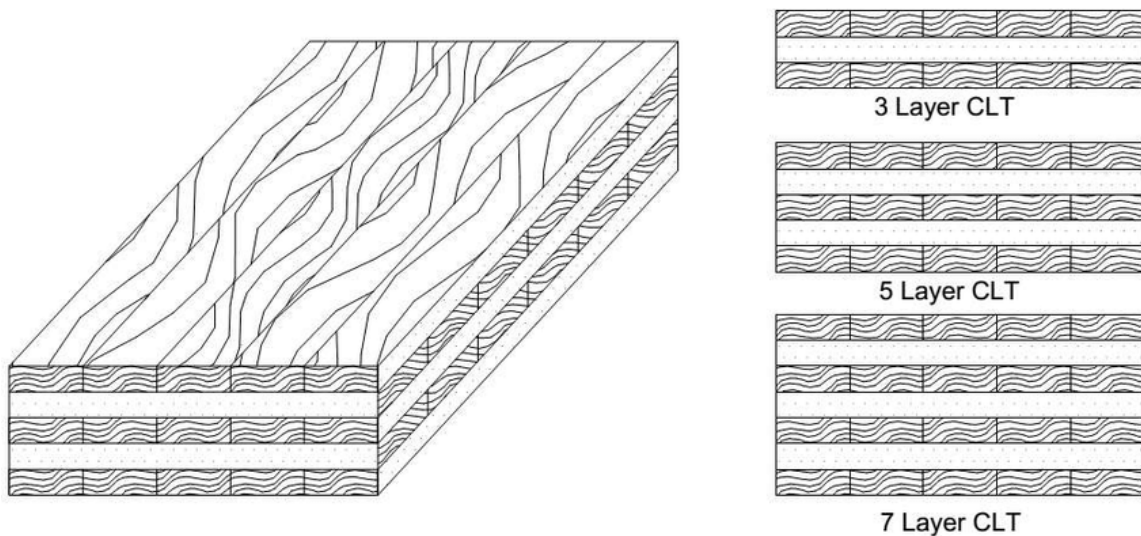


Figure 3: CLT Configuration and Layers (*EXPERIMENTAL AND FINITE ELEMENT ANALYSIS OF CROSS LAMINATED TIMBER (CLT) PANELS*, n.d.)

In North America, CLT is manufactured primarily from softwood species, and all seven stress classes are specified in the *CLT Handbook*. The manufacturing process parallels that of glulam, though the applications differ: glulam is typically used for columns or beams, while CLT is a panelized product employed in walls, floors, and roofs including floor slabs, load-bearing walls, and shear walls (*Cross-Laminated Timber (CLT) - APA – The Engineered Wood Association*, n.d.)(Yadav et al., 2021).

CLT panels generally consist of three to seven layers, though thicknesses up to 20 inches are possible, as shown in Figure 3. The outer layers are oriented to align with gravity loads or the primary span direction. Standard panel dimensions range from two to ten feet wide and up to 60 feet long, though special applications allow widths up to 18 feet and lengths up to 98 feet. Similar to glulam, laminations are joined face-to-face and end-to-end to achieve the desired size (*Cross-Laminated Timber (CLT) - APA – The Engineered Wood Association*, n.d.).

The increasing adoption of CLT in North America is due to its favorable strength-to-weight ratio, environmental advantages, and prefabrication benefits (Yauk et al., 2020). According to APA – The Engineered Wood Association, “cross-laminated timber is proving to be a highly advantageous alternative to conventional materials like concrete, masonry, or steel, especially in multifamily and commercial construction” (*Cross-Laminated Timber (CLT) - APA – The Engineered Wood Association*, n.d.). As mass timber, large-scale engineered wood products continue to gain popularity in the construction industry, the advancement of CLT is driving the expansion of wood use in multi-story building design. CLT panels are stiff and can transfer load on all sides. Because CLT panels are stiff and can transfer loads in multiple directions, they act as a plate-like structural element that efficiently distributes vertical and

lateral forces to supports, improving overall stability and load-sharing in buildings (Cattellino & Jamie, 2020). Another factor that makes CLT an environmentally friendly building material is that it is prefabricated, so the manufacturing process can be customized for the exact measurements needed to reduce waste of the building material (Yadav et al., 2021). CLT panels are quick and easy to install since they are pre-sanded and pre-cut with all necessary openings before being transported to the jobsite. Other advantages of CLT include “superior acoustic, fire, seismic, and thermal performance” (*Cross-Laminated Timber (CLT) - APA – The Engineered Wood Association*, n.d.). In summary, CLT is a board-based engineered wood product with several advantages: it can be manufactured at dimensions far exceeding sawn lumber, serves as an environmentally responsible substitute for conventional material, supports the growth of mass timber construction, and facilitates efficient prefabrication and installation.

1.2.3 Plywood

Plywood is a veneer-based engineered wood product and, like CLT, is manufactured as a panelized material commonly used for sheathing and framing. Unlike CLT, which is made from timber laminations, plywood consists of thin veneers called plies, arranged in an odd number of layers with alternating grain direction as depicted in Figure 4.

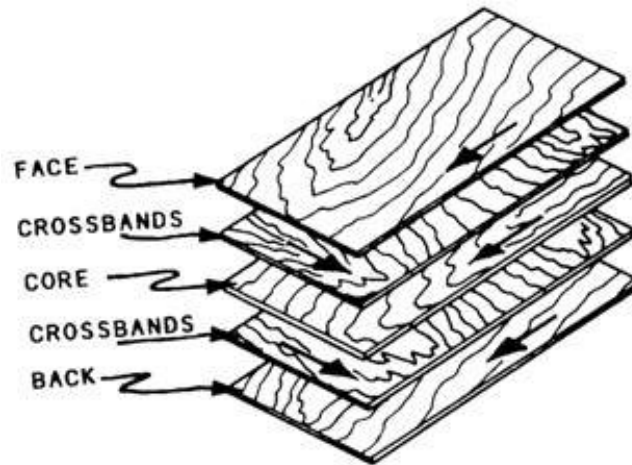


Figure 4: Plywood Layers (*What Is Plywood*, n.d.)

In plywood, each layer may comprise a single ply or multiple plies, with the grains within a layer running parallel. The outer layers, referred to as the face and the back, have their grains oriented along the long dimension of the panel. The inside layers oriented in the same direction as the faces are called centers or cores, while the inside layers with their grain running in the opposite direction are called crossbands, as shown in Figure 4. Plywood panels are described by both the number of plies per layer and the total number of layers (Stark & Cai, 2022).

Construction and industrial plywood are typically manufactured from softwood species, including Douglas-fir and southern yellow pine, though hardwood species are also permitted under standards. Plywood properties depend on veneer grade - particularly of the outer plies, the type of adhesive used, and the quality of bonding during manufacture. Plywood is categorized by veneer grade and exposure rating: *Exposure 1* panels are intended for protected conditions, whereas *Exterior* plywood is suitable for repeated wetting and drying (Stark & Cai, 2022).

The manufacturing process provides several advantages over sawn lumber. Plywood exhibits adequate bending strength in both directions of the panel, with reduced anisotropy compared to solid wood. It also demonstrates high-dimensional stability and limited irreversible

swelling when exposed to moisture, especially relative to particle-based panels. Furthermore, the alternating grain orientation enhances performance with fasteners placed near panel edges. (Stark & Cai, 2022) All three engineered wood products discussed, glulam, CLT, and plywood, are made using wood elements combined with adhesive to create an advantageous product for specific structural uses in building construction.

1.3 How Adhesion Works

The adhesive bond between wood elements is essential to the performance of engineered wood products. Because wood is a heterogeneous material, adhesion is influenced by numerous variables: variations in grain angle, the presence of defects, such as knots, and differences in surface energy, roughness, and chemistry. Adhesives in engineered wood products are responsible for transferring and distributing loads across the bonded joint, thereby providing strength and stiffness. This transfer of loads is dependent “on the strength of the links in an imaginary chain across the adhesive-bonded joint” (Frihart & Hunt, n.d.). Thus, all factors contributing to bond strength should be carefully controlled and monitored during manufacturing. Both mechanical and chemical factors are responsible for the adhesive being able to bond wood elements.

Mechanical interlock is the primary factor responsible for the bond between wood elements and adhesive in engineered wood products, due to wood being permeable. Mechanical interlocking consists of two categories: the adhesive spreading deeply into the microscopic surface features and the adhesive seeping into the cell wall at the nanometer level (Ferdosian et al., 2017). Successful mechanical interlocking occurs when the adhesive infiltrates past the rough surface of the wood, two to six cells deep into the wood. Then, “further penetration into

the cell wall microstructure increases the mechanical interlocking and the surface area for adhesive contact with the wood” (Islam et al., 2022). Chemical factors such as attractive intermolecular forces are also responsible for bond strength. These attractive intermolecular forces include Vander Waal’s forces, dipole-dipole forces, and hydrogen bonding (Islam et al., 2022). For the strongest mechanical and chemical bonds to form, the adhesive needs to be in direct contact with the wood.

The most effective, water-resistant bond occurs when the adhesive flows well and can fill the cell cavities in the wood and penetrate the cell walls. The crevices in wood surfaces can cause air pockets and blockages that prevent the complete coverage, or wetting, of the wood surface. The incomplete wetting of the wood surface can cause stress concentrations after the adhesive has cured. Not only does the adhesive need to completely cover the surface, but it “must be fluid enough to flow into the microscopic holes, or capillary structure, of wood” (Frihart & Hunt, n.d.). The adhesive also cannot be too thin so that the joint becomes compromised when pressure is applied to join the wood. Applying pressure helps to completely cover the wood surfaces with adhesive, get rid of air pockets, and to infiltrate the wood.

Once applied, adhesive stiffens to form a bond; however, full strength may require several hours to days to develop, depending on the adhesive type. Adhesives transition from liquid to solid through three primary mechanisms, which may occur individually or simultaneously. The first involves loss of liquid phase, partly through evaporation into the air and partly by absorption into the wood substrate. The second mechanism occurs when a hot, melted adhesive cools and solidifies. The third mechanism is a chemical reaction that links the molecules in the glue together, known as cross-linking, into a strong, net-like molecular structure resistant to remelting (Frihart & Hunt, n.d.).

Before discussing synthetic and bio-based adhesives in depth, understanding the characteristics of an ideal wood adhesive is important. To prevent bond-line failure, the adhesive must exhibit strength equal to or greater than that of the wood itself. Viscosity and elasticity are vital: insufficient fluidity prevents adequate penetration and mechanical interlocking, while excessive penetration leaves too little material at the bond line to develop cohesive strength between surfaces (Islam et al., 2022). Structural use of engineered wood products must also provide fire resistance, remaining stable up to at least 200 degrees Celsius or 392 degrees Fahrenheit. Moisture resistance is of even greater importance; adhesives must minimize water absorption to maintain long-term performance. Finally, adhesives must accommodate stress variations under repeated loading and unloading (Islam et al., 2022).

1.4 History of Adhesives

Wood adhesives are grouped broadly as either synthetic or natural in nature. The classification and subclassifications of adhesives, as well as examples of each type, are pictured in Figure 5. Synthetic adhesives are then sub-classified by their thermal and mechanical behavior into three categories: thermosetting, thermoplastic, and elastomeric. Thermosetting synthetic adhesives irreversibly harden when they are cured, making them heat resistant. Thermoplastic synthetic adhesives can soften when heated and harden as they cool. Elastomeric adhesives are flexible and remain rubbery after curing. Natural or bio-based adhesives are sub-classified by their source into five categories: lignin, protein, starch, tannins, and PHAs. Lignin comes from the cell walls of vascular plants. Protein can be from animals or plants. Carbohydrate-based adhesives can use starches or sucrose. Tannins also come from plants and are mainly found in bark, leaves, fruits, seeds, and wood (Kumar & Leggate, 2022). PHAs, or

polyhydroxyalkanoates, are produced by microorganisms through bacterial fermentation (*GO!PHA — What Is PHA*, n.d.).

Natural adhesives were first used around 4,000 years ago by Egyptians in the form of collagen-based glues for use in painting and for making wooden furniture. Up until the 20th century, natural sources were used to make wood adhesives. In the 1930s, natural adhesives were mostly replaced by commercially produced synthetic adhesives made from “petroleum or natural gas-derived chemicals” (Kumar & Leggate, 2022). Synthetic adhesives present numerous advantages over natural adhesives, including increased strength, rigidity, durability, and water resistance. Today, a growing concern over the use of synthetic adhesives exists due to the use of non-renewable resources and the environmental hazards they can potentially produce. More recently, environmental legislation has also encouraged the use of bio-based adhesives from natural sources. In modern times, “bio-based product is defined as a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials” (Islam et al., 2022). The use of biomass-based adhesives today makes bio-adhesives more competitive with synthetic adhesives than the traditional natural adhesives that were used in the past.

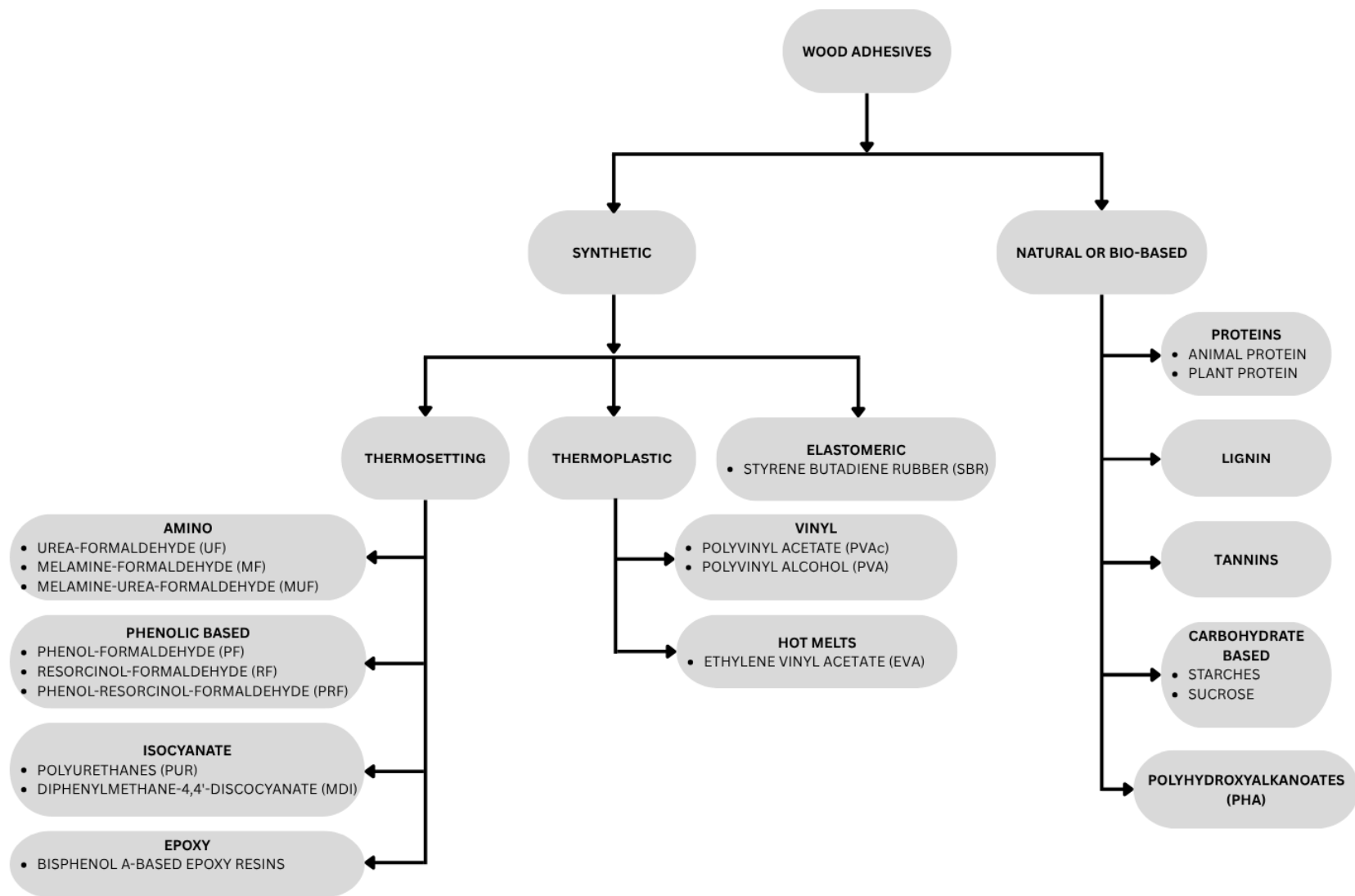


Figure 5: Breakdown of Types of Wood Adhesives (Adapted From Kumar & Leggate, 2022)

1.5 Product Standards

As CLT, glulam, and plywood are manufactured building products, they must pass performance tests and evaluations during the manufacturing and certification process. The performance tests and evaluations are conducted on the adhesive and wood itself used for the production of the engineered wood product. This is dictated by the applicable manufacturing standard, which is referenced in the building code (*Standards and Testing*, n.d.). Both United States and International Standards exist.

1.5.1 Adhesive Standards

The International Standard for adhesives, ISO/CD 20152, states that engineered wood product adhesives must be durable, chemically stable, and non-damaging to the timber. Additionally, the adhesive must be resistant to fungi, creep, rupture, and bond failure under moisture changes and sustained loads (Milner, 2009).

The US standard for engineered wood product adhesives is completely performance-based, meaning any formulation can be used as long as it passes the tests, including various stress and boil tests, and is approved for use. To be approved for use, the adhesive must meet all test standards, including ASTM D2559, and pass the in-plant qualification. “All testing shall be performed or witnessed by a laboratory accredited as a competent testing laboratory in accordance with ISO/IEC 17025 general requirements. Test results shall be submitted by the adhesive manufacturer to the accredited inspection agency” (*ANSI 405-2023 Standard for Adhesives for Use in Structural Glued Laminated Timber*, 2023). The in-plant process for mixing and curing must also match that of the samples provided for testing (*ANSI 405-2023 Standard for Adhesives for Use in Structural Glued Laminated Timber*, 2023).

1.5.2 Glued Laminated Timber (Glulam) Standards

The International Building Code (IBC) Section 2303.1.3 dictates that any glulam product be certified by the ANSI A190.1 standard (*Standards and Testing*, n.d.). The standard for the adhesive used specifically in structural glued laminated timber is ANSI 405, which requires the adhesive to meet several test standards, including moisture and bond durability tests. These test standards are ASTM D2559: Standard Specification for Adhesives for Bonded Structural Wood Products for Use Under Exterior Exposure Conditions, ASTM D1151: Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds, ASTM D7247: Standard Test Method for Evaluating the Shear Strength of Adhesive Bonds in Laminated Wood Products at Elevated Temperatures, and ASTM D1183: Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions (*ANSI 405-2023 Standard for Adhesives for Use in Structural Glued Laminated Timber*, 2023). Some of the items that these test standards check include “shear strengths and percentage wood failure at moisture contents in the range 8–12%, cyclic delamination and resistance to creep at temperatures of up to 71°C, and a lower on pH of 2.5 which is designed to limit acid attack of the wood fiber” (Milner, 2009).

1.5.3 Cross-Laminated Timber (CLT) Standards

The IBC Section 2303.1.4 dictates that any CLT product be certified by the ANSI/APA PRG 320 standard for performance-rated cross-laminated timber (*Standards and Testing*, n.d.). CLT panels should only be used in dry service conditions, moisture content in service of 16% or less, according to Section 1 of PRG 320. The standard for the adhesive used in cross-laminated timber is ANSI 405 with the following exceptions: “Section 2.1.6 of ANSI 405 is not required,

and The CSA 0177 small-scale flame test (Sections 2.1.7 and 3.7 of ANSI 405) shall be conducted using CLT specimens of the same size and geometry as the structural glued laminated timber specimens” (*Standards and Testing*, n.d.).

1.5.4 Plywood Standards

The governing standard for structural plywood is *Voluntary Product Standard 1*, as required by Section 2303.1.5 of the International Building Code (*CHAPTER 23 WOOD - 2018 INTERNATIONAL BUILDING CODE (IBC)*, n.d.). Under PS 1, plywood is classified by both grade and exposure capability. Bond quality between wood and adhesive is evaluated using the same testing procedure for both Exposure 1 and Exterior plywood classifications, with the latter required to demonstrate superior performance. The testing protocol subjects panels to cycles of water saturation, boiling, and elevated temperatures exceeding the boiling point (*Voluntary Product Standard PS 1-22 Structural Plywood*, n.d.).

Chapter 2 – Current Synthetic Adhesives Used

2.1 Formulations Used

The synthetic adhesives currently used for the production of glulam, CLT, and plywood are not the sole focus of this report but are discussed in this chapter to provide a point of comparison when discussing the development of bioadhesives. The most common formulations and bonding methods, along with their benefits and drawbacks, are discussed.

2.1.1 Glued Laminated Timber (Glulam) Adhesive

The bonding of glulam members utilizes cold-set adhesives, which cure at or below room temperature, eliminating the need for external heat and pressure to bond the laminations together. Heat-curing resins are not practical because glulam laminations are too thick for efficient thermal penetration. Pressure is typically applied using hydraulic or vacuum presses (Yauk et al., 2020). The most used synthetic adhesives are phenol-based resins (see Figure 5), specifically resorcinol-formaldehyde and phenol-resorcinol-formaldehyde. These two-part systems consist of a liquid resin and powdered hardener and cure to form a dark red bond line. They have high dry and wet strength, maintain durability under moist conditions, and are suitable for joints exposed to severe service environments (Frihart & Hunt, n.d.). In fact, these synthetic adhesives often outperform the wood itself under high temperatures and in aging conditions (Frihart & Hunt, n.d.).

2.1.2 Cross-Laminated Timber (CLT) Adhesive

The CLT bonding processes are similar to those of glulam, relying on cold-set adhesives and pressure applied with hydraulic or vacuum presses. As with glulam members, heat-curing resins are rarely used because of panel thickness. An exception occurs in some manufacturing

processes that use melamine-urea-formaldehyde, which can be cured with radio frequency presses. The most common CLT synthetic adhesive is polyurethane-based adhesive, classified as an isocyanate thermosetting synthetic adhesive (see Figure 5). Melamine-urea-formaldehyde, an amino thermosetting synthetic adhesive (see Figure 5), is also utilized to make CLT panels (Yauk et al., 2020).

2.1.3 Plywood Adhesive

Two main synthetic adhesives are used in plywood manufacture. The first, melamine-urea-formaldehyde, is an amino thermosetting synthetic adhesive supplied as a white-to-tan powder blended with a catalyst and may be combined with up to 40% urea. Melamine-urea-formaldehyde powder is dissolved in water prior to application and cured in hot presses at 250 to 300 degrees Fahrenheit, with the inside of the layers being at a lower temperature. High-frequency presses allow for accelerated curing. Melamine-urea-formaldehyde produces a colorless bond line, provides high dry and wet strength, and resists moisture. It is widely used in hardwood plywood as well as for end-joint and edge glue lumber (Frihart & Hunt, n.d.)

The second type of synthetic adhesive commonly used in making plywood is phenol-formaldehyde, a phenolic-based thermosetting synthetic adhesive. Phenol-formaldehyde is available in liquid (ready to apply), powder (needs water added), and dry film (pre-applied or manufactured on rolls) forms. All forms of the adhesive are cured in a hot press at 250 to 300 degrees Fahrenheit. When cured, phenol-formaldehyde forms a dark red bondline. Phenol-formaldehyde has high dry and wet strength. It also holds up well in moist and damp conditions. Phenol-formaldehyde performs better in high temperatures and in aging than the wood itself. Phenol-formaldehyde is the primary adhesive for exterior softwood plywood (Frihart & Hunt,

n.d.). Phenol-formaldehyde in resin form is also the main adhesive used in construction and industrial plywood (Stark & Cai, 2022).

2.2 Drawbacks

The current synthetic adhesives used pose risks to both the environment and human health.

2.2.1 Environmental Effects

Building sustainable structures aims to create a circular economy without any waste. In a circular economy, building materials are reused, repaired, or recycled. Products and materials can be kept in circulation in two ways: the technical cycle or the biological cycle.

As shown in Figure 6, the technical cycle, pictured on the right, involves finite materials. These finite materials are made into a product for a user, such as vehicles, electronics, and appliances. In the technical cycle, the goal is to maintain the product as long as possible by starting in the circle's center and working out, only going to the next circle in Figure 6 when needed. For example, when a product can no longer be reused, it should be refurbished or remanufactured before recycling is considered. When recycling is the only option left, the product can be broken down into its components and recycled (Circulate, 2019). The current synthetic adhesives used in engineered wood products fall into the technical cycle. Also shown in Figure 6, the biological cycle, pictured on the left, consists of renewables. Renewable materials include biodegradable materials such as food, wood, and cotton that can be composted and anaerobically digested to feed the soil to in turn create more materials after the consumer is done with them. The figure shows that this is one continuous circle, unlike the multiple circles

involved in the technical cycle (Circulate, 2019). Wood, like what is used in engineered wood products, can be part of both the technical and biological cycle. For example, a wooden board can be maintained and reused, but it can eventually be returned to the biological cycle.

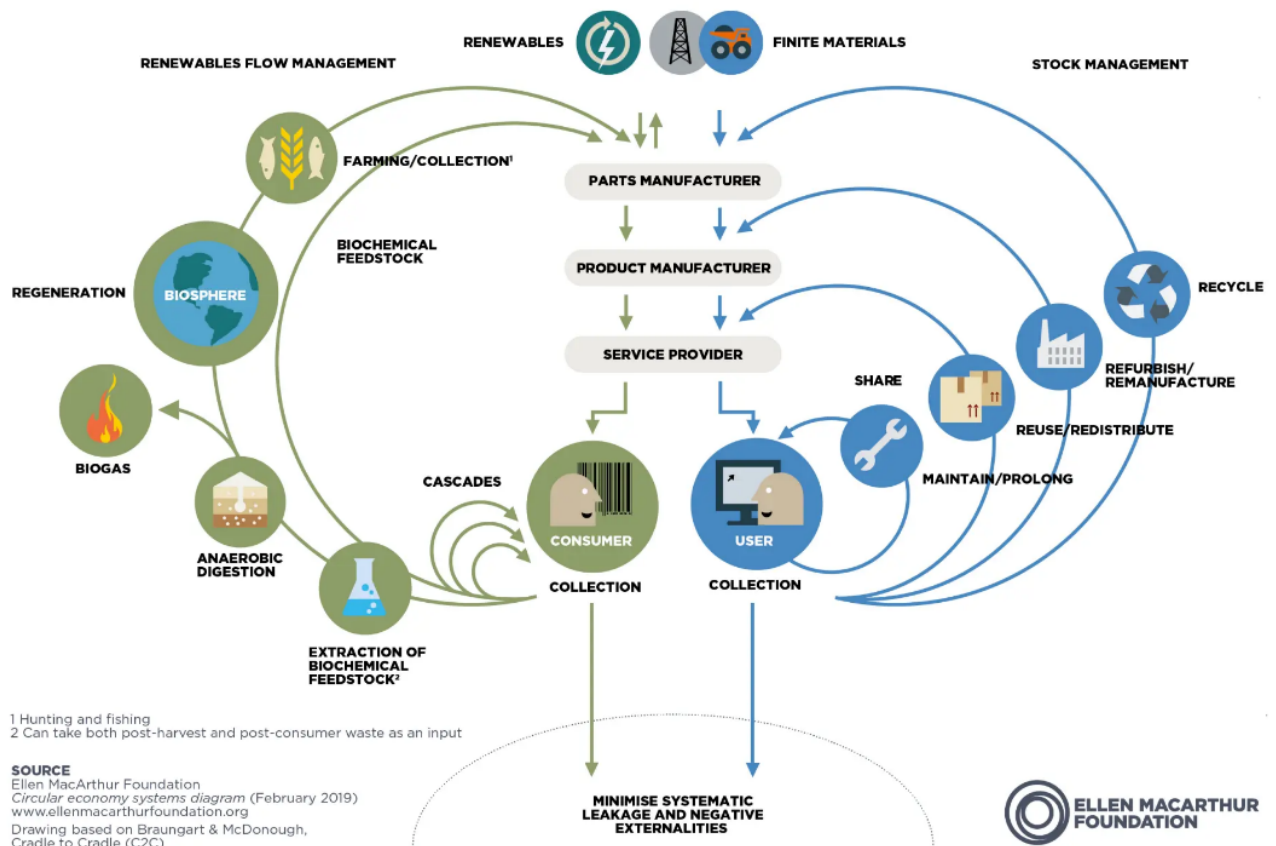


Figure 6: Diagram of the Parts of a Circular Economy (Circulate, 2019)

The technical cycle, pictured on the right in Figure 6, and the biological cycle, pictured on the left, do not overlap. The issue with how engineered wood products is currently made is that they fuse synthetic glue, a technical material, with wood, a biological material. Since these cycles do not overlap, engineered wood products cannot be fully circulated through either cycle and eventually end up as waste (Circulate Products and Materials, 2022). When engineered wood products end up as waste in a landfill, the formaldehyde-based chemicals can contaminate the soil and waterways. According to Naomi Keena, an assistant professor at McGill

University's School of Architecture, "People don't think about 50 years time, but if we keep building the way we're building now ... not thinking about the end of life, then ... we're going to have the same issues in 50 years time," she said. "...As we develop these new products that are being lauded as green ... we have to think about how they can have a long-term, sustainable life cycle" (Logan, 2023). A demand for sustainable products has led to the growth of research and development into bio-adhesives.

2.2.2 Health Effects

Formaldehyde, a key component in the production of many synthetic wood adhesives, is a known human carcinogen. Half of all formaldehyde made is used in wood adhesives. Indoor air concentrations of formaldehyde concentrations are known to cause a range of human health effects from eye irritation to cancer. According to the Consumer Product Safety Commission, ambient levels of formaldehyde from natural and man-made sources average around 0.03 parts per million (ppm) in both indoor and outdoor air. At concentrations above 0.5-1.0 ppm, individuals may experience irritation of the eyes, skin, nose, throat, and lower respiratory tract, with acute or long-term exposure potentially leading to more serious health outcomes (Brown, 2005). Studies conducted on rats showed that high doses of formaldehyde can cause difficulty breathing and vomiting. These studies also revealed that formaldehyde can cause cancer of the nasal cavity. According to a review in *Human and Experimental Toxicology*, "In humans, ingestion (of formaldehyde) can also corrode and trigger hemorrhaging in the gastrointestinal tract, as well as cause cardiovascular collapse and convulsions" (Brown, 2005). Human epidemiologic studies revealed that formaldehyde can cause nasopharyngeal, nasal, prostate, lung, and pancreatic cancers as well as leukemia. The synthetic adhesives commonly used in

engineered wood products release formaldehyde gas during and after the manufacturing of engineered wood products (Kumar & Leggate, 2022).

More than 1.8 million industrial workers in the United States are exposed to formaldehyde. This includes wood industry workers who are exposed to formaldehyde through the gas emitted from the resins used as adhesives in the engineered wood products created in factories. As stated above, people begin experiencing irritation from formaldehyde exposure around 0.5 - 1.0 ppm. 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” (Brown, 2005).

Additionally, the general public can also be exposed to formaldehyde and experience symptoms after moving into buildings constructed with engineered wood materials (Brown, 2005) Over 90% of human exposure to pollutants occurs indoors due to toxic substances present inside buildings, such as the synthetic adhesives used in engineered wood products (Yauk et al., 2020). For example, urea-formaldehyde adhesive is known to release low levels of formaldehyde gas. The level of emission of formaldehyde from urea-formaldehyde adhesive is enhanced by hot or moist environments. If a synthetic adhesive has not been thoroughly tested for its health effects on people, it should be assumed for safety that it is harmful in large amounts or for extended exposure (Frihart & Hunt, n.d.). “Eliminating or minimizing the number and concentration of toxic species present in indoor environments is of key importance and a necessary first step towards preventing their emission” (Yauk et al., 2020).

2.3 Benefits

While synthetic adhesives pose health risks to both people and the environment, they continue to be used due to their benefits over natural adhesives.

2.3.1 Optimized Manufacturing

The synthetic resins used today do not require high curing temperatures, which speeds up the bonding process (Xu et al., 2019). Synthetic adhesives can be easily adapted to the application method needed for the product and to the porosity of the wood being used. Synthetic adhesives have also been formulated to provide adequate penetration into the wood, but not too much for wood species with high porosity (Frihart, 2015).

2.3.2 Desirable Properties

In addition to optimizing manufacturing, synthetic adhesives such as phenol-formaldehyde have many desirable properties, including “strong mechanical properties, high flame retardancy, stable molding processing performance, and low cost” (Xu et al., 2019). Phenol formaldehyde being used to bond wood panels allowed for the creation of durable exterior plywood. The growing knowledge of wood adhesive chemistry is being used to develop these desirable properties. For example, synthetic adhesives can be formulated to have a wide range of desired properties by changing the polymer backbone. Changing the polymer backbone of the synthetic adhesive to increase its strength, for instance, translates to increased product performance. In other words, the increased strength of synthetic adhesive has allowed the amount of wood utilized to grow, as lower-quality wood can be used and strength requirements will still be met. Being able to utilize lower-quality wood has allowed more wood to be utilized,

thus decreasing the waste produced in the manufacturing process (Frihart, 2015). Phenol-formaldehyde resins have remained in widespread use due to their durability and water resistant; however, concerns persist regarding formaldehyde's toxicity and the carbon footprint associated with phenol, a petroleum-derived compound.

Chapter 3 – Lignin-Based Natural Adhesives

Due to the push for using sustainable and green building practices, the use of engineered wood products has soared; however, engineered wood products could be improved further by replacing the current synthetic adhesive that poses concerns to both the health of people and the environment with a bio-based adhesive made of abundant organic materials. Extensive research has been done into bio-based adhesives, and bio-based adhesives have been successfully applied to interior non-structural products, but additional development is needed for exterior and structural use.

3.1 Components: Sources and Properties

A biobased phenolic adhesive was successfully created. Lignin-glyoxal glue simultaneously replaces both petroleum-based phenol and formaldehyde with unfunctionalized lignin and glyoxal. Lignin and its derivatives provide an ecological alternative to petroleum-based adhesives.

3.1.1 Lignin: Source, Structure, and Properties

Lignin accounts for 15-35% of the dry mass of trees and other vascular plants. In plants, lignin strengthens plant cell walls as can be seen in Figure 7. Lignin binds cellulose in plant cell walls and provides flexibility as demonstrated in Figure 7. Lignin is not a single material; it is a family of materials. Lignin is the main renewable source of naturally occurring phenolic compounds (Bekhta, 2023). Phenolic compounds are a large group of natural chemical compounds found in plants. Chemically, phenolic compounds have at least one phenol group, which is “an aromatic or benzene ring with a hydroxyl group –OH” (L. Xu & Wang, 2025). 90% of commercially available lignin is from lignosulfonates (LS), which come as a by-product from the paper pulping process and generally serve as fuel for the recovery boiler of pulp and paper mills (Kumar & Leggate, 2022). To take advantage of this by-product, research has focused on extracting, characterizing, and enhancing the reactivity of LS (Bekhta, 2023).

Due to its phenolic structure, lignin shows promise for replacing phenol in phenolic resins used to make wood adhesives. Lignin is part of the glue that holds plant cell walls together and consists of three basic building blocks, or monomers: coniferyl alcohol, synapyl alcohol, and p-coumaryl alcohol. These monomers are linked together in multiple ways, the main way being linkages or condensed linkages, creating a complex and irregular structure. When these building blocks or monomers combine, they form the structure of lignin, which consists of three units: guaiacyl (G-type), syringyl (S-type), and p-hydroxyl phenol propane (p-H-type), as can be seen in Figure 7. The ratio of these monomers varies, and consequently, the content of the units varies depending on the type of plant (hardwood versus softwood, for example) (Islam et al., 2022). The structure of lignin is also altered during the separation process, so due to the complex and changing structure, lignin is instead described by its size and reactivity.

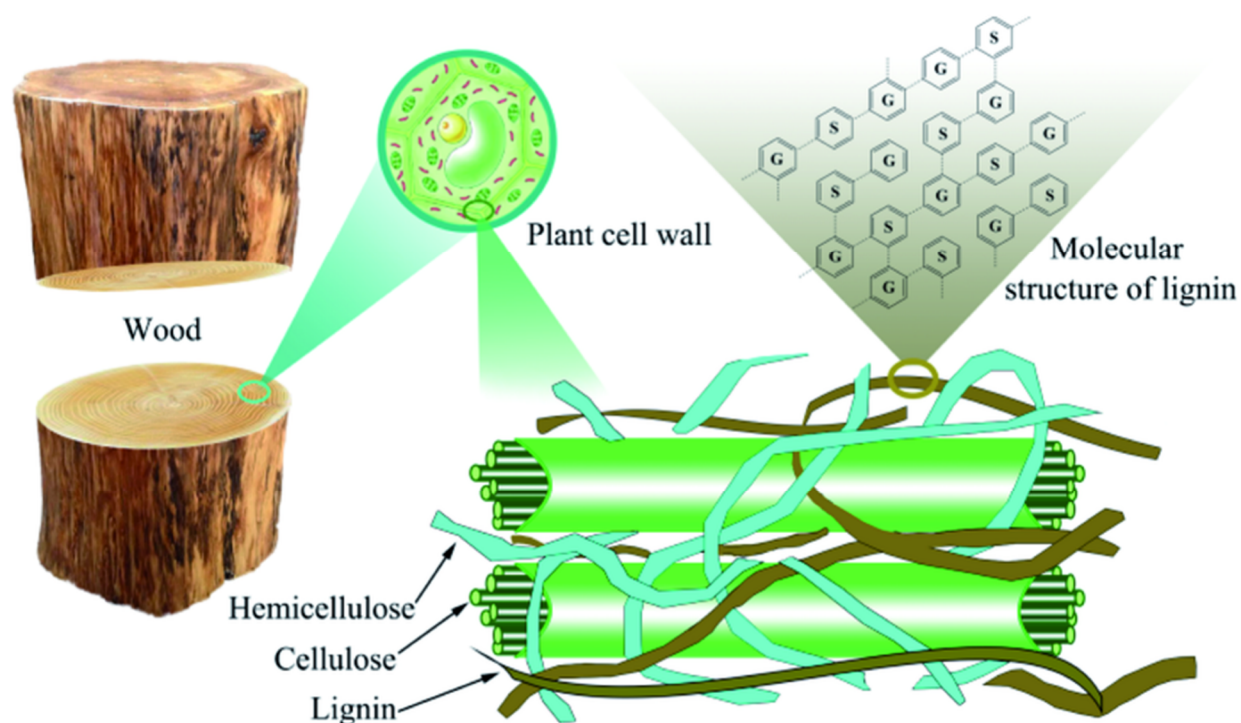


Figure 7: Example of the Origin and Structure of Lignin in Wood (*Lignin Structure of Lignocellulosic Biomass in Wood*, n.d.)

Lignin has multiple properties that make it ideal for use in adhesives. The first ideal property of lignin is high hydrophobicity, meaning it repels water, which can help with water resistance in adhesives. Lignin also has a low glass transition temperature, meaning lignin becomes soft at low temperatures, which can help in bonding. Additionally, lignin has high polydispersity, meaning that the structure of lignin comes in varying sizes as mentioned above, which can give a wide range of properties to be used in the making of adhesives. The abundance and low cost of lignin have led to research focusing on using isolated lignin in wood adhesives (Islam et al., 2022).

3.1.2 Lignin Suitability for Adhesives

The method by which lignin is derived has a big impact on the properties of lignin and the suitability of lignin as a replacement in phenolic adhesives. The methods of extracting lignin are broken down in Figure 8. Whether a type of lignin can work well in a phenolic adhesive depends on the functional groups that are present to take part in polymerization. In other words, certain chemical groups allow the lignin to react and form strong bonds. Sulfur-free processes (see Figure 8) to remove lignin are gentler and thus produce a higher quality lignin. Sulfur processes (shown in Figure 8), such as the one that produces lignosulfonates, often damage the structure, leading to a lower amount of functional groups. Specifically, kraft lignin produced from the paper pulping process “is water-insoluble and mostly solvent-insoluble except in highly alkaline environments ($\text{pH} > 11$)” (Hemmilä et al., 2017). Kraft lignin has been found to be the best option for replacing phenol (Tejado et al., 2007). Other types of lignin, such as lignosulfonates, are water-soluble, and it has been found that they can successfully replace up to 50% of phenol in adhesives (Islam et al., 2022). As the biomass industry continues to grow, more biorefinery lignin will be available and can, in turn, be turned into adhesives instead of being treated as a low-value waste product.

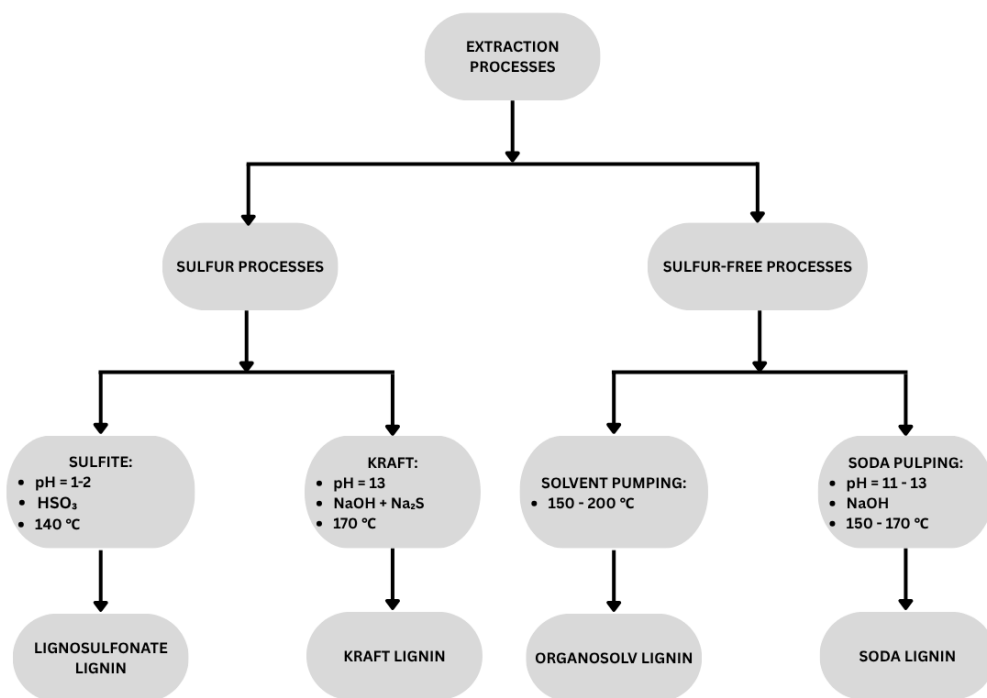


Figure 8: Lignin Extraction Processes (Adapted from Hemmilä et al., 2017)

The properties of lignin can also be improved through chemically modifying the lignin through various methods, including demethylation, which removes methyl groups, opening up more reactive sites for bonding; oxidation, which adds oxygen-containing groups to improve polarity and reactivity; methylation, which improves crosslinking with formaldehyde; and hydrolysis, which breaks up larger molecules to increase solubility. Crosslinkers that are commonly used include polymeric diphenylmethane diisocyanate (pMDI), polyethyleneimine (PEI), hexamine, and tannins. These crosslinkers all co-polymerize with lignin to improve adhesion within the adhesive and to the wood itself in application (Kumar & Leggate, 2022).

3.1.3 Glyoxal: Source, Structure, and Properties

Glyoxal is naturally produced in living cells during the metabolism of fats and sugars, and is also present in the atmosphere from organic compounds breaking down (Ramires et al., 2010). Glyoxal can also be produced in multiple ways, including from biobased feedstocks or intermediates such as sugars,

ethanol, or ethylene glycol. Chemically, glyoxal (OHC-CHO) is “the simplest dialdehyde with two adjacent carbonyl groups” (Siahkamari et al., 2022) as shown in Figure 9. Due to the “two adjacent carbonyl groups”, glyoxal is highly reactive (Siahkamari et al., 2022). Some of the properties that make glyoxal an attractive replacement for formaldehyde in wood adhesives are a low vapor pressure, or non-volatility, low toxicity, biodegradability, and low cost. Glyoxal is already used as a substitute for formaldehyde in adhesives (Ramires et al., 2010).

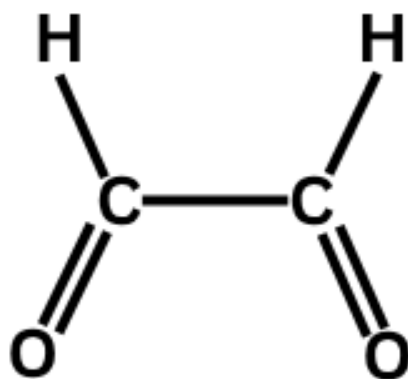


Figure 9: Chemical Structure of Glyoxal

3.2 Formulation: Combining Components

While lignin adhesives exist that offer a partial replacement of phenol and/or formaldehyde, the focus of this report is adhesives with formulations that have replaced both phenol and formaldehyde with alternative biobased components to offer an adhesive with a reduced carbon footprint and lower toxicity. Each of the natural adhesives discussed was developed in unique ways to be able to utilize natural components. This development utilizes the knowledge of adhesion chemistry to produce a natural alternative that has desirable mechanical properties like the current synthetic adhesive.

3.2.1 Biorefinery Lignin and Glyoxal

As shown in Figure 10, two components were added together to create the new biobased glue. The petroleum-based phenol was completely replaced with an unmodified corn stover biorefinery lignin,

pictured on the left in Figure 10. Formaldehyde was completely replaced with glyoxal, a biobased dialdehyde, pictured on the top right in Figure 10. The chemical formulation and the biomaterial that each component is made from are shown in the figure. As shown in Figure 11, to react with glyoxal, lignin with one or two vacant sites in the ortho positions of the aromatic ring had to be used. These ortho positions are next to the phenolic hydroxyl group on the ring, as can be seen in Figure 11. When glyoxal reacts at these sites, it allows crosslinking (shown in Figure 11) and resin formation to occur. The lignin reacts with glyoxal, which links different lignin molecules together, creating a 3D structure. The biorefinery-derived lignin was successful because it contained a higher number of phenolic hydroxyl groups than other lignins tested, including two ortho sites open for reaction. Lignin reacted with glyoxal in a 1:2 ratio under alkaline conditions to produce a lignin-glyoxal resin. The resulting resin had an average molecular weight three times higher than the original lignin, which indicated that the lignin was successfully incorporated into the resin network. This biobased adhesive formulation was applied to interior-grade plywood for testing (Siahkamari et al., 2022)

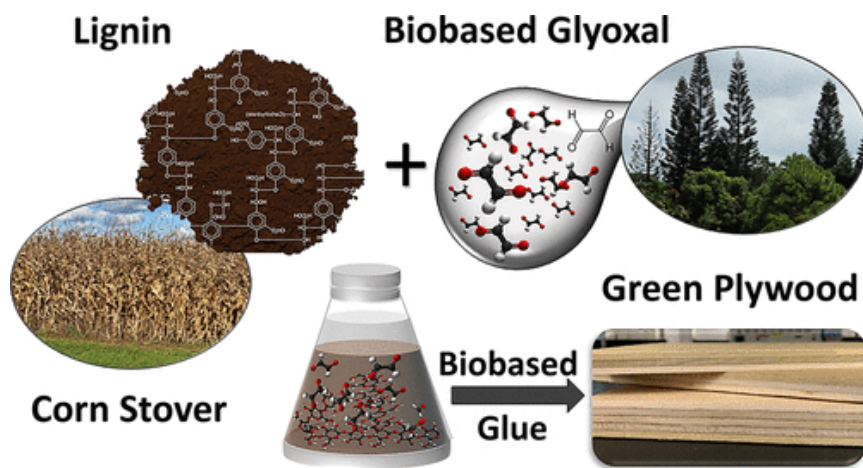


Figure 10: Photograph of the Replacement Components in the Lignin-Glyoxal Adhesive (Siahkamari, 2022)

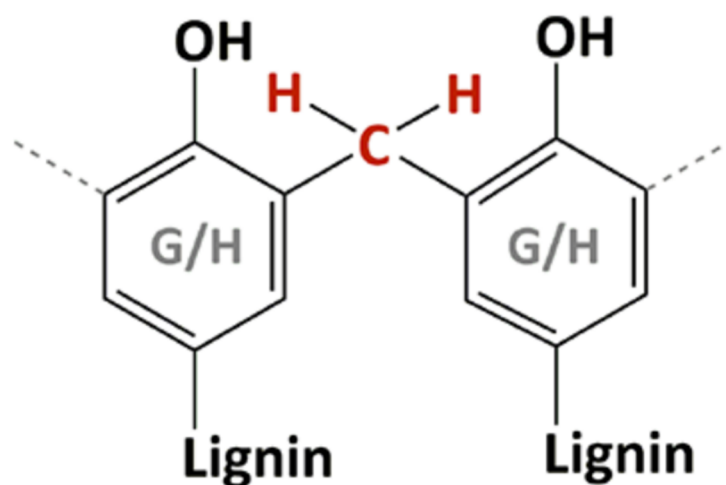


Figure 11: Crosslinking Between Lignin and Glyoxal (Siahkamari et al., 2022)

3.2.2 Calcium Lignosulphonate and Glyoxal

Another lignin-glyoxal adhesive formulation utilized calcium lignosulphonate and glyoxal. The calcium lignosulphonate was modified using pMDI to increase crosslinking and then reacted with glyoxal under alkaline conditions. Calcium lignosulfonate was first treated with pMDI to improve its performance. pMDI reacts with parts of the lignin molecule to make it more hydrophobic, which increases the bonding strength and durability when used on wood. The reaction between calcium lignosulphonate and pMDI also builds a tougher, more interconnected molecular structure. Next, the modified lignin reacts with glyoxal, which links different lignin molecules together, creating a 3D structure. When the adhesive cures, it becomes a solid, crosslinked polymer that sticks strongly to wood. The final result is a hybrid adhesive that has a dense, stable structure that adheres well and can resist moisture and heat. This biobased adhesive formulation was then applied to particleboard for testing. Even though the adhesive was tested using particleboard and not plywood, the results are promising because the adhesive formulation had high enough internal bond strength to meet EN 312 International Standard Specification for exterior-grade panels. The calcium lignosulphonate glyoxal adhesive was also adequately reactive, so that the time the panels had to be pressed was similar to that when commercial

formaldehyde-based adhesives are used (Ferdosian et al., 2017). When creating the lignin-based bio-adhesive with calcium lignosulfonate and glyoxal, it was discovered that using lignin with a lower molecular mass led to a higher hydroxy methylation level, or higher reactivity level, and a better modulus of elasticity (Kumar & Leggate, 2022).

3.2.3 Kraft Lignin and Polyethyleneimine (PEI)

Kraft lignin and polyethyleneimine (PEI) were used to create a formaldehyde-free adhesive to produce plywood. Kraft lignin contains reactive hydroxyl, methoxy, and carboxyl groups that allow it to interact effectively with the amine groups in PEI. When heated under typical hot-pressing conditions (130 – 150 degrees Celsius), the Kraft lignin and PEI formed covalent and hydrogen bonds, producing a crosslinked three-dimensional network. The curing of the adhesive involved both chemical bonding and physical bonding, such as hydrogen bonding with the wood substrate. This results in a thermoset adhesive with adequate mechanical strength, moisture resistance, and thermal stability. Kraft lignin reacted with PEI in a 2:1 ratio produced the highest shear strengths (“including dry shear strength, water-soaking-and-drying strength, boiling water test/dry strength, and boiling water test/wet strength”) and water resistance among the ratios tested (Ferdosian et al., 2017). Various premixing times and molecular weights of PEI were tested, and in the range of greater than 40 minutes of premixing and weights ranging from 70,000 to 150,000, there was no effect on the shear strength of the assembled plywood. The adhesive performed best at a hot-press curing condition of 140 degrees Celsius for nine minutes (Ferdosian et al., 2017).

In a related study, the Kraft lignin was demethylated to increase the number of phenolic sites before being reacted with PEI to promote crosslinking. The demethylated Kraft lignin and PEI adhesive was tested on plywood using lap-shear tests. Various conditions were tested, including premixing time (10 to 120 minutes), press time (three to seven minutes), press temperature (100 to 160 degrees Celsius), solid content (14 to 25 percent), weight ratio (1:4 to 4:1), and PEI molecular weight (10,000 to 750,000) to determine if they affected the shear strength of the adhesive. The premixing time and molecular weight of PEI were again found to have no effect on the shear strength of the assembled plywood. The highest

shear strength of the adhesive occurred when a 1:1 ratio of demethylated Kraft lignin and PEI was used as well as a hot-press curing condition of 120 degrees Celsius for five minutes (Ferdosian et al., 2017).

3.2.4 Lignin, Glyoxal, and Tannin

Lignin has also been combined with glyoxal and tannin, a phenolic compound found in the bark, leaves, and fruit of plants that acts as a plant's natural defense by deterring animals (*Tannins*, n.d.). This bio-based adhesive utilized a lignin with a low molecular mass that was a by-product of wheat pulping. Lignin and tannin are both rich in phenolic hydroxyl groups, which readily react with glyoxal. The wheat pulp lignin was first modified with glyoxal under alkaline conditions. Glyoxal adds reactive groups to lignin molecules, increasing their ability to bond. Then, equal amounts of wheat pulp lignin were mixed with tannin. Hexamine was used to improve the crosslinking between the lignin and tannin. When the adhesive is heated (curing stage), these modified molecules undergo condensation reactions that link them together through methylene and ether bridges. This forms a tightly crosslinked three-dimensional network that gives the adhesive high strength, durability, and water resistance. Because glyoxal replaces formaldehyde as the crosslinker, the system is safer and more environmentally friendly. Overall, this lignin–glyoxal–tannin adhesive offers a renewable, high-performance alternative to traditional petroleum-based or formaldehyde-containing adhesives. The resulting adhesive was tested using bonded panels, and the assembled product met EN 312 International Standard Specification for interior-grade panels (Ferdosian et al., 2017).

3.3 Comparative Assessment of Benefits

3.3.1 Environmental and Health Advantages

Using two biobased materials in place of phenol and formaldehyde provides a non-toxic adhesive, an adhesive that does not emit VOCs at levels known to affect human health or IAQ, that improves the engineered wood products' recyclability. In other words, lignin adhesives are made of abundant

renewable resources and eliminate the economic and environmental issues associated with the current non-renewable petroleum-based adhesive. Replacing phenol in phenol-formaldehyde adhesives with lignin cuts adhesive-related CO₂ emissions by roughly 80%. Since synthetic adhesives account for a majority of the carbon footprint of wood products, around half in plywood, the substitution of a fully bio-based adhesive offers significant environmental benefits, while also reducing formaldehyde usage. Given that six million tons of phenol-formaldehyde adhesive are made each year, the impact could be substantial (VTT Technical Research Centre of Finland, 2017).

3.3.2 Improved Mechanical and Physical Properties

Lignin-based bio-adhesives exhibit several improved mechanical and physical properties that make them comparable to synthetic phenol-formaldehyde adhesives. The naturally high amount of phenol in lignin makes the bio-adhesive fire-retardant. The strong crosslinking that occurs in lignin-based bio-adhesives provides high tensile strength, enhanced thermal stability, and an increased modulus of elasticity. This cross-linked structure also helps to decrease water absorption (Gadhav, 2019). Lignin-glyoxal adhesives further demonstrated high dry adhesion strength (3.9 MPa), with more than 90% wood failure, and showed good stability in room-temperature water, though performance in boiling water remains a limitation for exterior-grade applications. The lignin-glyoxal adhesive required a higher curing temperature (167 degrees Celsius) compared to the phenol-formaldehyde adhesive (142 degrees Celsius), but it cured more quickly and to a greater extent (Siahkamari et al., 2022).

3.3.3 Economic and Production Advantages

Lignin is one of the most abundant natural renewable materials and is the byproduct of many biorefinery processes. As biorefinery lignin is a byproduct, millions of tons of lignin are considered waste and incinerated each year (Gadhav, 2019). Corn stover lignin and other biorefinery lignins show strong potential as a renewable, bio-based raw material for green adhesive production, offering lignin producers

a valuable new opportunity. Instead of burning lignin byproducts at a cost, producers could generate profit by selling them for use in adhesive formulations (Siahkamari et al., 2022). Producing reactive lignin offers pulp mills a high-value product, since the technology can be integrated directly into existing operations and tailored for specific adhesive applications (VTT Technical Research Centre of Finland, 2017).

3.4 Comparative Assessment of Limitations

Lignin-glyoxal adhesives, while promising, are still in development and not yet suitable for all structural applications. Lignin-glyoxal adhesives show adequate strength for interior use but fail under heated water, limiting exterior applications (Siahkamari et al., 2022). Substitution levels are restricted as some studies show up to 50% Kraft lignin replacement improves viscosity, stability, and bonding, but requires longer pressing times (up to 30% longer). Limitations of lignin-glyoxal adhesive include high molecular weight, few reactive sites, poor solubility (depending on the type of lignin), and difficulties isolating lignin from wood. Thus, chemical modifications such as demethylation, methylation, and phenylation are required to improve reactivity and reduce curing time (Ferdosian et al., 2017).

Chapter 4 – Soy Protein-Based Natural Adhesives

4.1 Components: Sources and Properties

4.1.1 Background and Structure

Plant-derived proteins suitable for adhesive applications can be extracted from oilseeds such as soybean, rapeseed, canola, cottonseed, linseed, peanut, safflower, and sunflower, as well as from cereal grains including wheat, maize, oats, rice, and rye. Among these plant-derived proteins suitable for adhesive applications, soybeans are the most protein-rich source at 51% protein. In comparison, cereal grains only have 8-12% protein and are usually utilized instead for their carbohydrate fraction (56-80% starch). Proteins, composed of amino acids and various functional groups, have historically been used as wood adhesives due to their natural chemical reactivity. Despite their long-standing use, conventional protein-based adhesives have limitations in being compatible with modern engineered wood product manufacturing processes and thus require modifications (Islam et al., 2022).

To comprehend the formation of protein-based natural adhesives, understanding the structure of proteins is important. Proteins are large polymers primarily consisting of carbon, hydrogen, oxygen, nitrogen, and sometimes sulfur, with amino acids serving as their fundamental building blocks. As shown in Figure 12, roughly 20 common amino acids combine in various sequences to form polypeptide chains, and the nature and sequence of these amino acids dictate the protein's chemical and physical properties. Each amino acid has a side chain (R-group), as demonstrated in Figure 12, which can be polar, non-polar, acidic, or basic, thus determining if the amino acid is hydrophilic or hydrophobic. These side chains provide reactive functional groups, such as hydroxyl or carboxyl groups, which can participate in hydrogen bonding and cross-linking with wood (Islam et al., 2022).

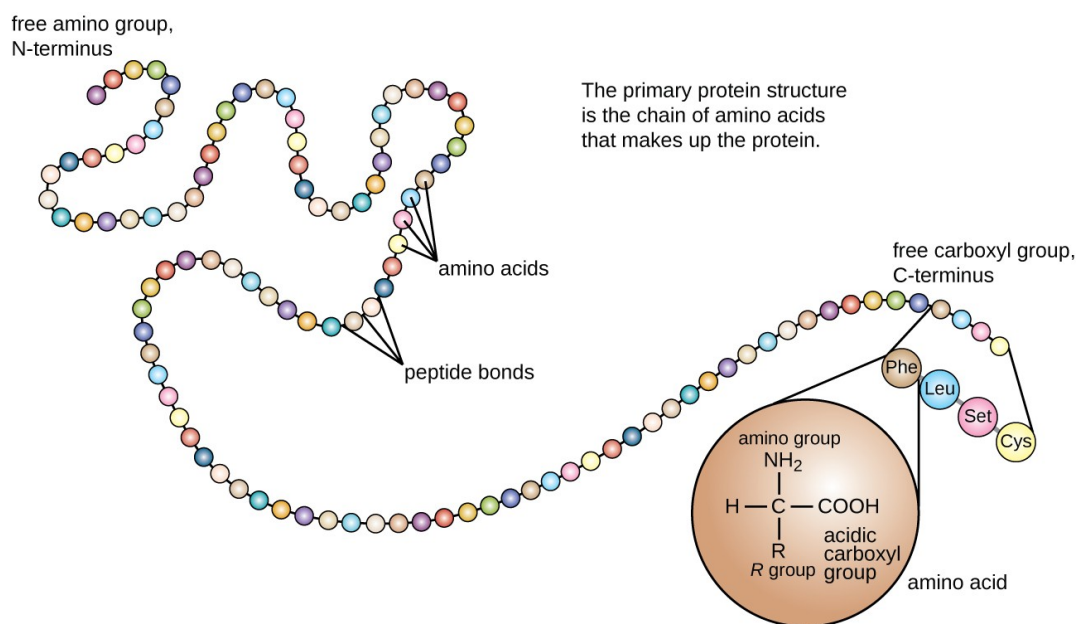


Figure 12: Primary Structure of Proteins (*Proteins* | *Microbiology*, n.d.)

Proteins have a structure consisting of four levels, as illustrated and explained in Figure 13. The primary structure consists of the amino acid sequence. The secondary structure is folded into α -helices and β -sheets. In comparison, the secondary structure of synthetic adhesives is made of crystalline domains. The tertiary structure comes from the three-dimensional folding of the polypeptide chain. The quaternary structure is formed by multiple folded protein subunits that form larger compounds. These levels create rigidity and chemical diversity in proteins, which influences the protein's performance as an adhesive. For example, hydrophobic regions increase water resistance, while polar and charged groups provide binding sites to bind to the wood (Islam et al., 2022).

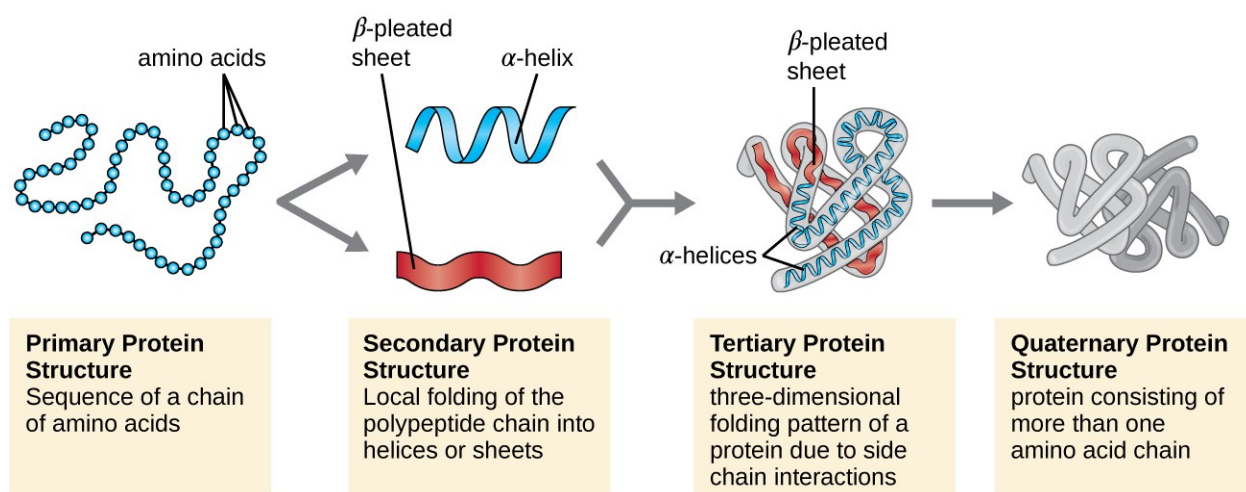


Figure 13: Four Levels of Protein Structure (*Proteins | Microbiology*, n.d.)

Due to the amino acid composition and sequence varying across plant protein sources, the solubility, surface activity, and strength are significantly different between plant protein sources. Compared to synthetic adhesives, where the structure-property relationships are more straightforward, proteins exhibit more complex behaviors due to their higher-order structural organization (Islam et al., 2022). Many plant proteins are considered incomplete because they lack one or more essential amino acids, which makes them relatively easier to modify for use as an adhesive. While soy protein is the most extensively studied, proteins from sources such as canola, whey, cottonseed, and mussel offer distinctive adhesive properties due to their differing amino acid group. For example, mussel proteins are known for high water resistance; however, due to cost constraints, efforts are instead focused on modifying soy proteins to replicate mussel-like moisture resistance instead of using mussel proteins (Hemmilä et al., 2017).

Soy protein specifically is made up of about 18 amino acids that each contain reactive groups that can form bonds with wood. These groups are polar, which makes soy protein water-sensitive but also gives it the ability to crosslink when properly modified. The main protein

fractions are 7S and 11S. A higher proportion of 7S improves hydration and dispersion, while more 11S contributes to the stronger structural integrity of the adhesive. Solubility is highly dependent on pH and reaches a minimum at the isoelectric point (pH of 4.2-4.5), where charges within the protein balance out, causing it to aggregate instead of dissolving. For use as an adhesive, this means that soy protein's performance, including its bonding strength, viscosity, and water resistance, depends strongly on the ratio of 7S to 11S, the pH, and the modification of the reactive groups to reduce water solubility and improve crosslinking with the wood (Islam et al., 2022).

4.1.2 Soy Protein: Sources and Properties

Research on soy protein adhesives has been strongly supported by the United States of America United Soybean Board. Globally, soybeans are grown mainly for oil production and as a source of nutrition for humans and animals. Soybeans make up 52% of oilseed production worldwide, with the majority grown in the United States of America and Brazil. For every ton of crude soybean oil produced, approximately 4.5 tons of soybean meal are generated as a byproduct of oil extraction with a protein content of around 44-50%. Most of this soybean meal is used as animal feed, while a smaller portion is processed into food products for human consumption. These feed products include soymilk, soy flour (SF), soy protein concentrates (SPCs), tofu, and soy protein isolates (SPIs). SPIs have the highest protein content at 80-90%, whereas soy flour has the lowest protein content, making it the cheapest (B.-H. Zhang et al., 2018).

The adhesive properties of soy proteins are influenced by protein content, particle size, molecular structure, viscosity, and pH. Defatted soybean flour (DSF) is an attractive option to produce bio-adhesives due to its availability, low cost, and renewability. DSF is usually used as animal feed and has a low value. As such, DSF has seen an increase in use in China's wood industry. However, widespread usage of DSF adhesives has not taken place due to their poor water resistance and high viscosity. SPIs provide the best adhesive performance due to having a high protein content but are three to five times more expensive than DSF, limiting their economic viability. Efforts are currently focused on taking lower-cost soybean meals and further separating or modifying them to enhance their adhesive properties, thereby increasing the value and providing a sustainable alternative for the engineered wood products industry (B.-H. Zhang et al., 2018).

Soy protein adhesives have very high viscosity due to strong intermolecular interactions from unfolded protein chains. Viscosity can be reduced with salts, reducing agents, or hydrolysis, which improves workability without sacrificing strength. At a high pH, hydrolysis increases adhesive strength and water resistance but reduces the workable time of the adhesive. DSF is approximately 50% protein, 40% carbohydrate, and 10% minor components. The protein in DSF adhesives acts as the primary bonding component, as it contains many reactive groups that allow it to dissolve into the adhesive medium and bond with the wood. The carbohydrate portion is very hydrophilic, which reduces water resistance. Additionally, the large molecular weight of soy protein results in very viscous solutions, which can reduce the spreadability of the adhesive (Islam et al., 2022).

4.2 Formulation

Soy-based adhesives are developed as natural alternatives to synthetic adhesives by applying knowledge from adhesion and protein chemistry. However, natural soy proteins present several challenges, including high viscosity and poor water resistance. Viscosity issues, caused by the uncoiling of protein molecules, can be reduced using salts, reducing agents, and hydrolysis to control the molecular structure and improve flow behavior. Another way to target the challenges of soy adhesives is to increase the pH to increase hydrolysis, which in turn increases the strength of the adhesive and the water resistance, but this can decrease the longevity of the adhesive (Kumar & Leggate, 2022). Poor water resistance, the main limitation of soy protein adhesives, can be addressed through cross-linking, chemical or enzymatic modification, and various additives. Cross-linking with agents such as pMDI can not only significantly improve water resistance but also provide thermal stability. The various additives, including plasticizers and inorganic fillers such as calcium carbonate and clay, improve adhesive strength, flexibility, and moisture tolerance. Some formulations also incorporate mussel-inspired proteins or hydrophilic compounds to improve the adhesive's performance under wet conditions (Kumar & Leggate, 2022). Soy protein adhesives stick to wood first through hydrogen bonds, then become strong and water-resistant when crosslinkers create permanent chemical links between protein molecules. Heat helps the protein unfold and react better, forming a durable adhesive. Through these physical, chemical, and enzymatic modifications, formaldehyde-free soy protein adhesives have been successfully developed for wood panel production, achieving improved strength, durability, and water resistance suitable for both interior and, in some cases, exterior applications.

4.2.1 Defatted Soy Flour (DSF) Based Adhesives

In a study by Zhang et al., 2018, defatted soy flour (DSF) was modified using various methods to create a soy-protein adhesive. To create a DSF adhesive, DSF was initially spread as a thin layer on an open metal plate and then heated in an oven at different temperatures, including 65, 80, 95, 110, and 125 degrees Celsius, for thirty minutes. The thermally treated DSF, T-DSF, was then ground into a fine powder, sieved through a 160-mesh screen, and labeled T-DSF-X, where X indicated the specific temperature. Untreated DSF was also sieved through a 160-mesh screen to be used as the control and then labeled DSF. After being thermally treated, the T-DSF samples were blended with the crosslinker epichlorohydrin-modified polyamide, EMPA, to produce an adhesive. Their bonding performance and water resistance were thoroughly assessed through plywood testing. In this study, EMPA was created by reacting diethylenetriamine with adipic acid to form a polyamide, which was subsequently modified with epichlorohydrin. The epichlorohydrin introduces reactive groups that form bonds with the functional groups in the protein. The EMPA created had a solid content of 13.8%, a pH of 2.6, and a viscosity of 96.4 mPa-s at 25 degrees Celsius.

The adhesives created using the T-DSF-X and DSF were then used to make three-ply plywood. The three-ply plywood was prepared by applying the liquid adhesive onto both sides of the core veneer at 180 grams per square meter per single glue line. The assembled three-ply plywood was then cold pressed at 1.1 MPa at room temperature for 45 minutes, followed by hot pressing at 120 degrees Celsius and 1.3 MPa for four minutes. After pressing was completed, the panels were then allowed to rest at room temperature for 24 hours before testing took place (B.-H. Zhang et al., 2018)

Efforts to modify DSF adhesives to enhance water resistance have mainly focused on modifying the protein component. This is because in its unmodified form, soybean protein has a tightly folded structure, which limits the exposure of reactive groups. This tightly folded structure hinders the protein from properly interacting with or penetrating the wood surface, reducing its ability to form strong adhesive bonds at the interface. Modifying the protein component of DSF is typically done through two main approaches: denaturing the protein to expose reactive groups for better wood adhesion and crosslinking with reactive agents to strengthen the adhesive. Crosslinkers enhance DSF-based adhesives by forming dense, three-dimensional networks that improve cohesion and water resistance, giving them thermal-moisture durability. However, little research has focused on improving water resistance through the modification of the soybean carbohydrate component.

This study, Zhang et al., 2018, examined how thermo-chemical treatment affects DSF and DSF-based adhesives to improve water resistance. The research focused on protein-carbohydrate interactions, including Maillard reactions, a set of reactions that take place between protein and carbonyl compounds. Changes in the functional groups, secondary structure, solubility, reactivity, crystallinity, and thermal stability were evaluated to understand the mechanisms behind enhanced adhesive performance.

In the study by Zhang et al., 2018, the adhesive performance was evaluated using the commercial standard JIS K6806 and forty specimens, 25 mm by 25 mm in size, from the assembled three-ply plywood. Twenty samples were used to measure dry bond strength, and the other twenty samples were used to assess the aged wet strength. To test the strength, a tensile testing machine operated at a crosshead speed of 5 mm min⁻¹ was used. For the aged wet strength test, the specimens were put through a 28-hour boiling-drying-boiling cycle consisting

of four hours boiling, 20 hours of oven drying at 63 degrees Celsius, and then another four hours of boiling, before being cooled in room temperature water. The samples were then tested at room temperature in the wet state. The dry bond strength specimens were tested in dry conditions at room temperature. The results of the strength tests can be seen in Figure 14 for each sample. As shown in Figure 14, the T-DSF-80 + EMPA formulation had the highest dry shear strength, indicating that the moderate thermal treatment at 80 degrees Celsius optimized the unfolding of protein structures and enhanced the molecular reactivity for crosslinking. In contrast, excessive heating at 110 to 125 degrees Celsius led to a reduction in bond strength, likely due to protein over-aggregation and loss of reaction functional groups. The same trend can be observed for the aged or wet bond strength, where T-DSF-80 + EMPA showed the highest strength. This improvement in wet durability is mainly attributed to the Maillard reaction between soybean proteins and carbohydrates during thermal treatment, which transformed soluble carbohydrates into an insoluble three-dimensional network structure. Overall, moderate thermal treatment was the most effective in improving both the dry and aged bond strength, whereas excessive heating reduced performance.

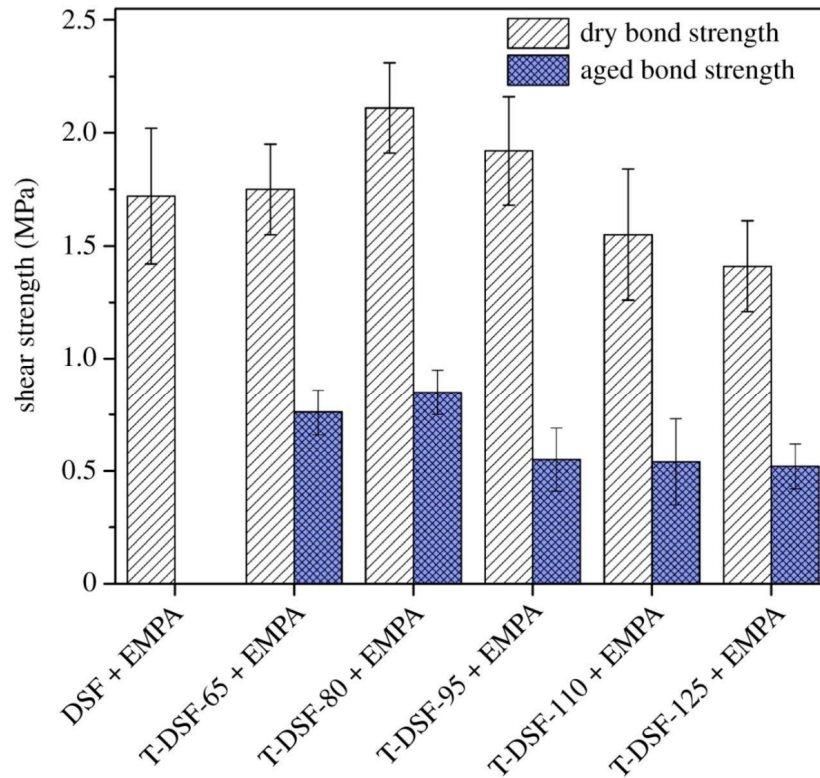


Figure 14: Dry and Aged (Wet) Bond Strength of Plywood Bonded with DSF and T-DSF-Based Adhesives Crosslinked with EMPA (B. Zhang et al., 2018)

Fourier Transform Infrared Spectroscopy (FT-IR) analysis, which is used to identify and study chemical structures and molecular interactions, showed that while thermal treatment did not introduce new chemical bonds in the DSF adhesive, it changed the intensity of peaks associated with protein functional groups. As the temperature increased to 80 degrees Celsius, the protein's tightly folded structure began to unfold, exposing reactive functional groups. These groups are chemically active sites that can participate in reactions with other molecules or form stronger bonds with the wood substrate. At temperatures above 80 degrees Celsius, intermolecular forces became dominant, causing proteins to self-crosslink into larger, less soluble structures. This self-crosslinking reduces the mobility of the protein chains and increases

water resistance. These results were confirmed by doing an acetaldehyde value test, which estimates the amount of active amino groups. The acetaldehyde value test confirmed the exposure of amino groups, as higher values indicated that there were more reactive amino groups. Together, the FT-IR analysis and the acetaldehyde value tests showed that thermal treatment promotes protein self-crosslinking and Maillard reactions between proteins and carbohydrates, forming a network structure that enhances water resistance. Thermal analysis showed that T-DSF-based adhesives had greater thermal stability than untreated DSF adhesives. This improvement resulted from enhanced crosslinking between EMPA and the thermally treated DSF, as well as protein self-crosslinking and Maillard reactions between the soybean proteins and carbohydrates. The Maillard reactions converted soluble carbohydrates into insoluble crosslinked networks. Among all the samples, the T-DSF-80 + EMPA had the highest thermal stability due to its higher concentration of reactive functional groups, as supported by FT-IR and acetaldehyde value tests. The parallel increase in aged bond strength also supports this result (B. Zhang et al., 2018).

4.2.2 Soy Protein Isolate (SPI) Based Adhesives

Thermal treatment of soy protein isolate (SPI) has been extensively studied and shown to cause protein dissociation and unfolding of its quaternary, tertiary, and secondary structures. Recent research by Chen et al., 2021, developed a water-resistant SPI-based adhesive through a two-step modification process combining thermo-chemical activation and chemical crosslinking. During activation, SPI was treated at 120 degrees Celsius for 30 minutes with denaturing agents, which disrupted hydrogen and disulfide bonds, unfolded the compact protein structure, and exposed reactive groups. This structural change then enhanced the crosslinking with EMPA,

forming a dense three-dimensional network that converted hydrophilic to hydrophobic groups. As a result, the adhesive showed greatly improved water resistance, maintaining a wet bond strength of 1.22 MPa after 28 hours of boiling–dry–boiling treatment—surpassing the 0.98 MPa requirement for structural use. Despite this, the high production cost limits the application of SPI as a wood adhesive (Chen et al., 2021).

In another study by Xi et al., 2020, a stronger soy protein adhesive called SPIPA was created by reacting SPI with maleic anhydride and hexamethylenediamine. Normally, soy protein has a compact structure and does not stick well when wet because its reactive sites are hidden inside the protein. To fix this, researchers added maleic anhydride, a chemical that can easily react with the reactive sites inside the protein. When it reacts, the ring structure of maleic anhydride opens up and connects to the soy protein chains, creating new chemical bridges between them. Next, hexamethylenediamine reacts with the opened maleic anhydride. This links several soy protein molecules together, turning the loose protein molecules into a more tightly connected network. This network makes the adhesive stronger and much less likely to soften or break apart in water. A silane coupling agent (KH560), which works like “molecular glue” between the soy protein and the wood, was also added. Finally, citric acid and more maleic anhydride were added before hot pressing to further increase the dry and wet bonding strength of the plywood. The plywood bonded with SPIPA adhesive met and exceeded the China National Standard GB/T 9846/2015 for plywood bonding strength and water resistance. Overall, the chemical modification transformed the inherently hydrophilic and weakly bonded SPI into a crosslinked, water-resistant polyamide network, suitable for structural wood adhesive applications (Xi et al., 2020).

The rest of this section is on the study by Fan et al., 2016. In this study, a soy protein-based wood adhesive exhibiting high bond strength, superior water resistance, and favorable processing properties was developed through a combination of thermal-alkaline degradation, thermal-acid treatment, and crosslinking modification. Thermal-alkaline degradation breaks down the long chains of soybean protein into smaller molecules through hydrolysis of the bonds, producing a low-viscosity high high-protein solution, defatted soybean protein (DSP), that improves processability. In contrast, thermal acid treatment enhances water resistance by promoting the formation of a water-resistant intermolecular network among protein molecules to produce thermally denatured soybean protein (TSP). Since limited research existed on this combined modification approach, this study investigated how the type of crosslinker, its optimal concentration, and the ratio of DSP to TSP affect the water resistance of soybean protein adhesives, with the goal of developing an optimized formulation suitable for structural applications (Fan et al., 2016).

In the study by Fan et al.,2016, soybean protein adhesives were prepared by mixing DSP solution with varying amounts of TSP powder to obtain DSP/TSP ratios of 1:1, 1:2, 1:3, and 1:4 (based on solid protein). To study how different crosslinkers affect soybean protein-based adhesives, the 1:2 DSP/TSP mixture was combined with four different crosslinkers separately: glyoxal, epoxy latex, polyisocyanate, and modified polyamide. The crosslinkers were each added to the DSP/TSP mixture at 20% of the total weight level based on the total solid protein. The four crosslinkers are compared and explained in Table 1.

Crosslinker	Main Reactive Groups	Reaction with Soy Protein	Type of Bonds Formed	Main Effects on Adhesive	Advantages	Drawbacks
Glyoxal	–CHO (dialdehyde)	Reacts with amino groups (–NH ₂) on soy protein chains	Schiff base (C=N) and hydrogen bonds	Creates moderate crosslinked network	Improves dry strength; inexpensive	Limited water resistance due to reversible bonds
Epoxy Latex	Epoxide rings (–C–O–C–)	Epoxide ring opens and reacts with –NH ₂ , –OH, –COOH groups	Strong covalent ether or ester linkages	Forms tight 3D network	Good balance of strength, flexibility, and water resistance	More complex synthesis; can increase viscosity
Polyisocyanate	Isocyanate (–N=C=O)	Reacts with –NH ₂ and –OH groups on soy protein	Urea (–NH–C–O–NH–) and urethane (–NH–C–O–O–) linkages	Highly crosslinked, hydrophobic network	Excellent water resistance and bond strength	Expensive; moisture-sensitive before curing
Modified Polyamide	Amide (–CONH–), possibly epoxy or imide groups	Reacts with –NH ₂ and –COOH groups of protein	Amide and covalent crosslinks	Forms flexible, dense polymer network	Strong wet/dry strength, durable, thermally stable	Slightly higher cost; requires controlled curing

Table 1: Comparison of Crosslinkers Added to DSP/TSP Adhesive

Then, each crosslinked mixture was mixed with water at room temperature to produce modified soybean protein adhesives. Two control adhesives were also prepared: one without any crosslinkers (pure soybean protein adhesive) and a commercial urea formaldehyde (UF) adhesive. Additionally, to determine the optimal crosslinker content, varying amounts from 0% to 40% in 10% increments of the modified polyamide crosslinker (best performing crosslinker) were incorporated into the DSP/TSP mixture with a 1:2 ratio. To evaluate the effect of the DSP/TSP ratio, adhesives were also prepared with ratios of 1:0, 1:1, 1:2, 1:3, 1:4, and 0:1, each containing 20% modified polyamide and water. All adhesive formulations were adjusted to a

solid content of 35% using an appropriate amount of water before being applied to the wood veneers (Fan et al., 2016).

To test the adhesives discussed above, three-ply plywood panels were made using birch veneers measuring 420 mm x 420 mm x 1.6 mm. The prepared adhesives were applied to the veneers in a single bond line at a thickness of 140 grams per square meter. The assembled three-ply plywood was cold pressed at 0.80 MPa for five minutes to ensure proper adhesive penetration and pre-bonding, followed by hot-pressing at 120 degrees Celsius and 1.3 MPa for four and a half minutes to cure the adhesive. Both the DSP and SPI adhesives without crosslinkers required longer hot-pressing times, eight and eight and a half minutes respectively, to prevent delamination. Two plywood panels were made for each adhesive and allowed to rest at room temperature for 24 hours. 40 test specimens, 25 mm x 25 mm in size, were cut from each panel to measure the bond strength and water resistance per JIS K6806-2003 standard (Fan et al., 2016).

The soybean protein adhesives were tested to measure viscosity using a viscometer and work life by timing how long the adhesive stayed usable before thickening. The molecular size of the DSP solution was analyzed using a GPC instrument. The surface structure of the adhesives, both before and after being boiled in water, was observed under a scanning electron microscope (SEM). Finally, FTIR analysis was used to study the chemical bonds and functional groups in the cured adhesive film. Bond strength (dry strength) and water resistance (cycled wet strength) were tested using a tensile machine operating at 5 millimeters per minute. For the wet test, the samples went through a 28-hour cycle of boiling, drying, and boiling before being cooled and tested in their wet state (Fan et al., 2016).

The results of the testing comparing DSP/TSP can be seen in Table 2. Soybean protein solutions have very large molecules, which makes them thick and hard to spread, even at low concentrations. Due to this high viscosity, plywood made with the SPI 10% protein adhesive already had a high viscosity of 58,000 mPa s, as can be seen in Table 2. This SPI 10% protein adhesive also required a nine-and-a-half-minute hot-press cycle, which, as can be noted in Table 2, is much longer than that required with the commercial UF adhesive. Therefore, it was discovered that the protein content of the protein adhesive must be increased to shorten the hot-press cycle. Reducing the hot press cycle reduces energy consumption and increases plywood productivity. The NA in Table 2 indicates that the samples delaminated after the first four hours of boiling. The DSP adhesive had a higher protein content at 35% and the plywood bonded with it required a shorter hot-press time at eight minutes, but this was still not comparable to the UF adhesive, as shown in Table 2. To improve this, a polyisocyanate crosslinker was added to the DSP solution. This modification reduced the hot-press time to make it comparable to the UF adhesive's performance (see Table 2). Table 2 shows that without adding the polyisocyanate crosslinker, the DSP/TSP adhesive with 35% protein required a longer hot-press time of eight minutes. When 20% weight of the crosslinker was added, the press time dropped to four and a half minutes. Additionally, the DSP/TSP/polyisocyanate adhesive showed much better durability than the DSP/polyisocyanate adhesive, as demonstrated by the cycled bond strengths shown in Table 2. This portion of the study suggested that combining thermal alkali degradation, thermal acid treatment, and crosslinking was a promising way to enhance the strength, water resistance, and usability of soybean protein adhesives. Thus, the best crosslinker type, amount, and DSP/TSP ratio was then investigated to develop a commercial-grade adhesive

meeting JIS K6806-2003. To meet this standard, the adhesive must maintain a bond strength of 0.98 MPa after 28 hours of boiling-dry-boiling aging (Fan et al., 2016).

Adhesive Formulation	Solid Content (wt%)	Viscosity (mPa-s, 25°C)	Hot-Press Cycle (min)	Dry Bond Strength (MPa)	Cycled Bond Strength (MPa)
SPI Solution Only	10	58,000	9.5	1.19 ± 0.15	NA
DSP Solution Only	35	1,162	8	1.28 ± 0.21	NA
DSP Solution and Crosslinker	35	1,219	4.5	2.11 ± 0.28	0.31 ± 0.09
DSP/TSP Mixture	35	1,335	8	1.31 ± 0.24	NA
DSP/TSP Mixture and Crosslinker	35	1,367	4.5	2.15 ± 0.30	1.02 ± 0.19
UF Adhesive (Control)	52.4	107.3	4.5	1.51 ± 0.12	NA

Table 2: Properties of Soybean Protein Adhesives with Various Formulations (Adapted

From Fan et al., 2016)

Four common crosslinkers: glyoxal, epoxy latex, polyisocyanate, and modified polyamide were tested by Fan et al., 2016 for their effects on soybean protein adhesives. As shown in Table 3, the type of crosslinker greatly influenced the adhesive's bond strength, water resistance, and overall performance due to their different chemical bonding mechanisms. The DSP/TSP adhesive mixture with glyoxal crosslinker in Table 3 had poor water resistance and weak bonding despite faster curing, making it not suitable for structural use. The DSP/TSP adhesive mixture with epoxy latex crosslinker had similar results to those of the glyoxal

crosslinker, as illustrated in Table 3. The DSP/TSP adhesive mixture with polyisocyanate (pMDI) crosslinker had good dry and cycled bond strength but had poor workability with a work life of only half an hour, making it not ideal for practical use. The DSP/TSP adhesive mixture with polyamide crosslinker was the best overall crosslinker with high strength, excellent water resistance, and good usability, as shown in Table 3 (Fan et al., 2016).

Adhesive Formulation	Viscosity (mPa-s, 25°C)	Work Life (h)	Hot- Press Cycle (min)	Dry Bond Strength (MPa)	Cycled Bond Strength (MPa)
DSP/TSP Mixture Only	1,335	>>20	8	1.31 ± 0.24	NA
DSP/TSP/Glyoxal	1,255	>20	4.5	1.25 ± 0.22	NA
DSP/TSP/Epoxy	3,470	>4	4.5	1.30 ± 0.20	NA
DSP/TSP/Polyisocyanate	1,367	0.5	4.5	2.15 ± 0.30	1.02 ± 0.19
DSP/TSP/polyamide	1,234	>16	4.5	2.71 ± 0.23	1.12 ± 0.13

Table 3: Properties of Soybean Protein Adhesives that were Modified with Various Crosslinkers (Adapted From Fan et al., 2016)

Once the best crosslinker was determined to be polyamide, the amount of crosslinker was then varied to find the ideal level. For all of the crosslinker levels, the DSP/TSP ratio was 1:2, and the solid content was 35%. Although increasing the amount of crosslinker theoretically improves bond strength and water resistance, the results shown in Figure 15 showed that these properties first increased and then decreased when the polyamide level rose from 0 to 40%. This decline was caused by excessive crosslinker, reducing the adhesive's viscosity, allowing too much liquid to penetrate the wood instead of remaining at the bond line. As illustrated in Figure 15, the highest dry strength occurred at 20% crosslinker, while the best water resistance was achieved at 30%. Therefore, 20% crosslinker was identified as the optimal level, as it provided

strong, water-resistant bonds that met the JIS K6806-2003 structural standard (>0.98 MPa) using less crosslinker (Fan et al., 2016).

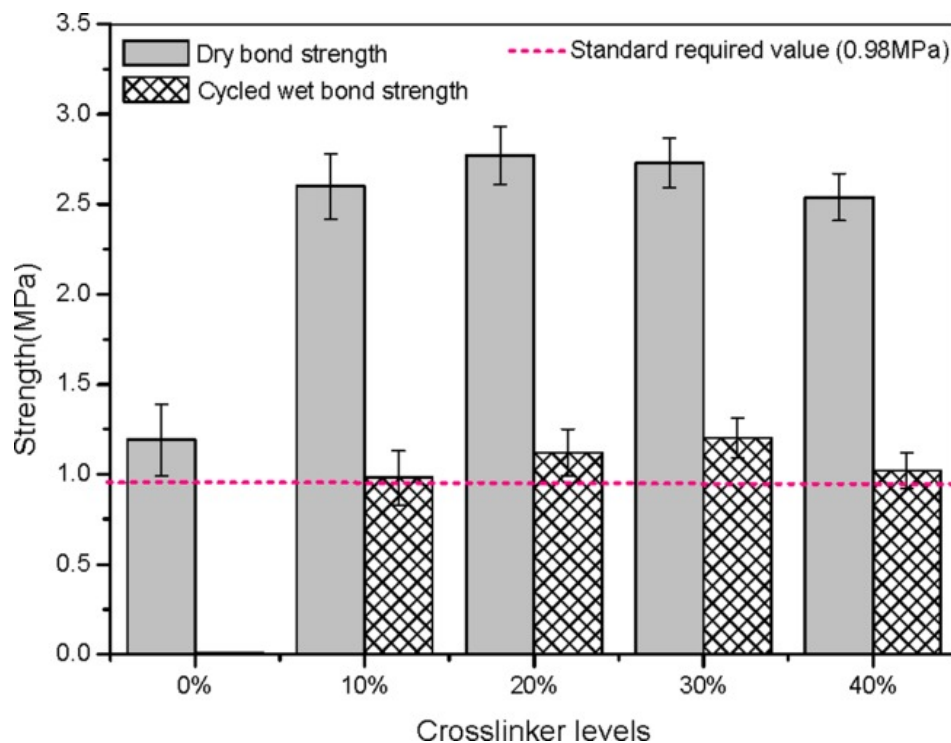


Figure 15: Strength of Varied Crosslinker Levels (DSP/TSP/polyamide mixture)(Fan et al., 2016)

Once the ideal crosslinker (polyamide) and crosslinker level (20%) were determined, the DSP/TSP ratio was then varied to find the ideal ratio. Figure 16 shows that the adhesive with a DSP/TSP ratio of 1:3 achieved the highest dry bond strength at 2.94 MPa and the highest cycled wet bond strength at 1.29 MPa. Both values exceed the JIS K6806-2003 standard requirement of 0.98 MPa, demonstrating the strong potential of this formulation for structural plywood applications. The DSP/TSP/polyamide adhesive formed a stable, uniform solution with a long work life of 16 hours, an appropriate viscosity for plywood manufacturing (500 to 2000 mPa s at 25 degrees Celsius), and showed no powdering when it was applied to the veneer surface. “The optimal DSP/TSP/polyamide adhesive that was prepared with 20 wt % modified polyamide and

a DSP/TSP ratio of 1:3” showed performance comparable to conventional UF and PF wood adhesives, making it suitable for various engineered wood products (Fan et al., 2016).

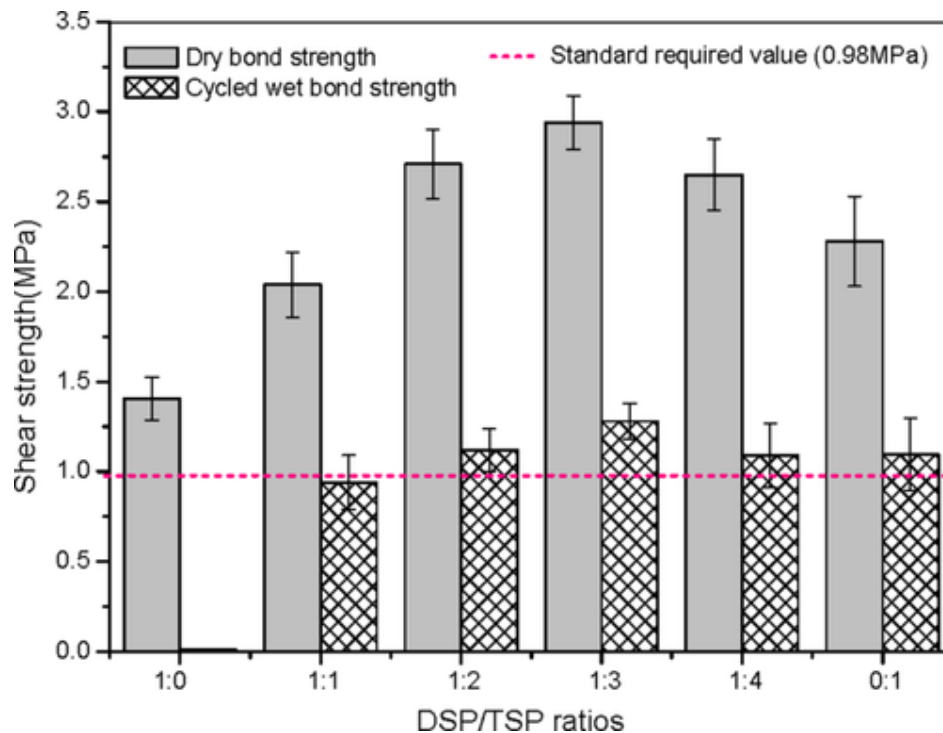


Figure 16: Strength of Varied DSP/TSP Ratios (20% polyamide crosslinker)(Fan et al., 2016)

4.3 Comparative Assessment of Benefits

4.3.1 Environmental and Health Advantages

Soy protein adhesives are considered safe and environmentally friendly alternatives to conventional synthetic adhesives, as they are nonvolatile, nonhazardous, and formaldehyde-free, posing no greater health risks than traditional options (Brown, 2005). Taking lower-cost soybean meals and further separating or modifying them to enhance their adhesive properties,

increases the value and provides a sustainable alternative for the engineered wood products industry.

A study evaluated volatile organic compound (VOC) emissions from cross-laminated timber (CLT) panels bonded with different adhesives to assess their effects on indoor air quality (IAQ). Four samples were tested: a soy-based cold-set adhesive, a polyurethane (PUR) adhesive, a dowel-joined panel without adhesive, and a commercially produced panel using melamine formaldehyde (MF) adhesive. All panels were made from Douglas-fir. The results showed that the soy, PUR, and dowel samples had very low formaldehyde emissions ($\leq 2.5 \mu\text{g}/\text{m}^3$), well below the reference limit of $\leq 9.0 \mu\text{g}/\text{m}^3$. In contrast, the MF-bonded sample emitted $54.4 \mu\text{g}/\text{m}^3$, which far exceeded both the standard limit and LEED v4/v4.1 indoor air quality criteria. These findings demonstrate that soy-based protein adhesives provide a safer, low-emission alternative suitable for interior applications of CLT, supporting healthier indoor environments and compliance with green building standards (Yauk et al., 2020).

4.3.2 Improved Properties and Economic Advantages

Soy protein adhesive has been successfully used in making interior plywood. The cross-links allow the adhesive to be boiled for hours without degrading. Though the adhesive has not yet been certified to be used in exterior products, the current formulation has demonstrated strength and water resistance meeting standards. Soy protein adhesives also require less time and energy to cure.

Physical modification provides a quick, inexpensive, and non-toxic way to increase the bonding and water resistance of soy-protein adhesive. For comparison, the wet shear strength of the plywood created using the modified SM adhesive was 212% greater than the wet shear

strength of plywood made using the unmodified SM adhesive. Compared to the current synthetic adhesive, the dry shear strength of this double cross-link modified soybean protein adhesive increased by 22.3% and the wet shear strength increased by 69.6% (Xu, 2022). Soy proteins are cost-effective, simple to work with, and allow bonding at relatively high wood moisture levels while requiring low pressing temperatures (Kumar & Leggate, 2022).

Many natural adhesives face issues of inconsistency or high cost, making them less viable for industrial wood bonding compared to synthetic adhesives, which are easier to produce and more durable. However, soy-based adhesives have re-emerged as a sustainable alternative to urea-formaldehyde (UF) resins due to health and environmental concerns and the discovery of effective soy co-reactants. Soy flour is particularly promising because it is inexpensive, abundant, and consistent in quality, offering good adhesion strength and thermal stability while being environmentally friendly (Islam et al., 2022). Soy protein adhesives create a valuable market for United State of America grown soybeans, especially for portions of the crop not suitable for human consumption. The widespread cultivation of soybeans could, in turn, support the increased production and adoption of soy-based wood adhesives (Yauk et al., 2020).

Thermal treatment of defatted soy flour (DSF) significantly enhances adhesive water resistance by unfolding the protein's globular structure, exposing reactive groups, and promoting self-crosslinking and Maillard reactions between proteins and carbohydrates. When combined with the EMPA crosslinker, thermally treated DSF (especially at 80°C) produced plywood with strong, water-resistant bonds achieving aged bond strengths up to 0.85 MPa after a 28-hour boiling–dry–boiling cycle, nearing structural standards (0.98 MPa, JIS K6806-2003). This demonstrates that thermal treatment is a simple, low-cost, and effective method for improving

soy-based adhesives without the need for harsh chemicals or complex processing equipment (B. Zhang et al., 2018).

4.4 Comparative Assessment of Limitations

While soy-based adhesives offer major environmental and safety advantages over traditional formaldehyde-based adhesives, several limitations still need to be addressed before they can be widely adopted for structural and exterior applications. One potential health concern is the risk of allergic reactions, as soy is a known allergen. However, aside from this, soy adhesives are considered safe, non-toxic, and non-volatile (Yauk et al., 2020).

From a manufacturing perspective, the consistency of soy protein adhesives presents a challenge. While the current formulation works well for plywood, where the glue can be rolled onto panels, it is not yet suitable for applications such as glulam or cross-laminated timber (CLT) that require sprayable adhesives. The formulation must therefore be adjusted to achieve a lower, sprayable viscosity, and manufacturing systems would need to be adapted accordingly. In addition, most soy-based adhesives are thermoset, requiring heat and pressure to cure. For greater versatility in applications such as CLT, a cold-set formulation would need to be developed (Yauk et al., 2020).

Another drawback is that current soy adhesive formulations are not certified for exterior use, even though they have demonstrated significant bond strength and water resistance in testing. Their performance can be improved through chemical modification and crosslinking, but a more detailed investigation into how these treatments alter protein structure is needed to optimize adhesive properties. Recent research, including studies on commercial products like Soyad®, which uses a polyamidoamine-epichlorohydrin (PAE) crosslinker, has shown that

factors such as wood type and moisture content can cause inconsistent bonding performance. Industry trials reported uniformly low wood failure percentages, indicating that the adhesive's reliability still falls short of commercial expectations (Kumar & Leggate, 2022).

Overall, while soy protein adhesives are promising due to their safety, renewability, and bonding potential, they still face technical challenges. These include improving water resistance, achieving consistent performance across different wood species and moisture levels, and developing formulations suitable for exterior and cold-set applications. Continued research and optimization are essential to advance technology for efficient and safe industrial use.

Chapter 5 - Discussion

5.1 Summary

To summarize the introduction provided in Chapter 1, green building emphasizes sustainability through energy efficiency, resource conservation, and the use of environmentally responsible materials (US EPA, 2014b; Tabibi, 2024). Adhesives are a critical but often overlooked component of sustainable construction because they influence both the recyclability and toxicity of composite wood products (Fan et al., 2016). Traditional petrochemical adhesives, while effective, release volatile organic compounds (VOCs) and formaldehyde, which pose health and environmental concerns (Yauk et al., 2020). The development of bio-based adhesives aligns with green building standards such as LEED, WELL, and Energy Star, aiming to reduce carbon footprints while maintaining structural integrity and durability in engineered wood products (Press: Benefits of Green Building | U.S. Green Building Council, n.d.; Built Environment Decarbonization | WBCSD, 2023).

Engineered wood products (EWPs) such as plywood, oriented strand board (OSB), laminated veneer lumber (LVL), glulam, and cross-laminated timber (CLT) have become vital in sustainable construction due to their efficient use of wood resources and favorable strength-to-weight ratios (Kumar & Leggate, 2022; Stark & Cai, 2022). Adhesives are essential in bonding these products, determining their mechanical performance, dimensional stability, and water resistance (Frihart & Hunt, n.d.; Ferdosian et al., 2017). The current reliance on synthetic adhesives limits recyclability and environmental performance, creating a need for bio-adhesives that meet or exceed the performance requirements outlined in ASTM, ANSI, and ISO standards for structural and exterior applications (ANSI 405-2023; ISO/CD 20152).

Wood adhesion relies on both mechanical interlocking and chemical bonding between the adhesive and the wood's cellular structure (Islam et al., 2022; Frihart & Hunt, n.d.). Historically, natural adhesives such as casein, animal glue, and starch were used before the dominance of synthetic resins in the mid-20th century (Kumar & Leggate, 2022). Synthetic adhesives like phenol-formaldehyde (PF), urea-formaldehyde (UF), and melamine-formaldehyde (MF) revolutionized engineered wood manufacturing due to their strength and water resistance (Fan et al., 2016). However, environmental and health concerns, combined with legislative pressure, have revived research into bio-based adhesives derived from proteins, lignin, starches, and tannins, offering renewable alternatives for sustainable wood bonding (Islam et al., 2022; GO!PHA — What Is PHA, n.d.).

Performance standards for engineered wood products ensure structural reliability, durability, and safety (Standards and Testing, n.d.; Milner, 2009). Organizations such as ASTM International, the American National Standards Institute (ANSI), and the APA – The Engineered Wood Association establish testing protocols for shear strength, moisture resistance, creep, and bond durability (ANSI 405-2023; ASTM D2559; PRG 320). Adhesives used in structural applications must meet these standards to comply with building codes and ensure long-term performance under varying environmental conditions (Voluntary Product Standard PS 1-22, n.d.). Consequently, bio-adhesive development requires rigorous evaluation to match or exceed the mechanical, chemical, and durability standards of established synthetic adhesives (Milner, 2009; Stark & Cai, 2022).

To review Chapter 2 on the synthetic adhesives currently used, synthetic adhesives are the standard in manufacturing glulam, CLT, and plywood, serving as a benchmark for developing bio-adhesives. Glulam primarily uses cold-set phenol-based resins such as

resorcinol-formaldehyde and phenol-resorcinol-formaldehyde, which provide high dry and wet strength, durability under moist conditions, and resistance to high temperatures and aging (Frihart & Hunt, n.d.; Yauk et al., 2020). CLT production similarly relies on cold-set adhesives, mainly polyurethane-based isocyanate adhesives and melamine-urea-formaldehyde, with heat curing limited to specific radio-frequency processes due to panel thickness constraints (Yauk et al., 2020). Plywood adhesives include melamine-urea-formaldehyde, which cures in hot presses and delivers colorless, moisture-resistant bond lines, and phenol-formaldehyde, which produces dark red, highly durable bonds suitable for exterior and industrial plywood (Frihart & Hunt, n.d.; Stark & Cai, 2022). These adhesives demonstrate superior mechanical performance and water resistance compared with natural alternatives.

Despite their performance, synthetic adhesives pose environmental and health risks. From an environmental perspective, engineered wood products combine renewable wood with non-biodegradable synthetic adhesives, preventing full recycling or composting and contributing to landfill waste (Circulate, 2019; Logan, 2023). Formaldehyde-based adhesives such as urea-formaldehyde and phenol-formaldehyde release formaldehyde gas during manufacturing and over product lifespans, which can contaminate soil and waterways (Kumar & Leggate, 2022). Human exposure to formaldehyde, even at low concentrations, can cause irritation, respiratory issues, and long-term carcinogenic effects, particularly in indoor environments where engineered wood products are widely used (Brown; Yauk et al., 2020). Over 1.8 million U.S. industrial workers are exposed to formaldehyde, highlighting the occupational and public health implications of synthetic adhesives in wood products.

Synthetic adhesives continue to be widely used due to their manufacturing advantages and desirable performance properties. They allow rapid curing at moderate temperatures,

ensuring efficient bonding while adapting to wood porosity and application methods (Xu et al., 2019; Frihart, 2015). Additionally, adhesives like phenol-formaldehyde provide strong mechanical properties, moisture resistance, flame retardancy, and consistent molding performance, enabling the use of lower-quality wood while maintaining structural performance and minimizing manufacturing waste (Frihart, 2015; Xu et al., 2019). These benefits underscore why synthetic adhesives remain dominant in engineered wood production, even as research increasingly seeks safer and more sustainable bio-based alternatives.

The growing demand for sustainable building practices, as introduced in Chapter 1, has highlighted the need to replace conventional synthetic adhesives in engineered wood products, which, as discussed in Chapter 2, pose significant environmental and health risks. Lignin-based adhesives discussed in Chapter 3 have emerged as a promising bio-based alternative due to lignin's abundance, phenolic structure, and natural role in providing strength and flexibility to plant cell walls. Lignin, particularly Kraft lignin or modified lignosulfonates, can replace petroleum-based phenol in phenolic adhesives, while glyoxal, a biobased dialdehyde, can substitute formaldehyde, producing adhesives with reduced toxicity and environmental impact.

Various formulations have been explored, including lignin-glyoxal, lignin-glyoxal-tannin, and Kraft lignin-polyethyleneimine (PEI), each demonstrating strong internal bonding, good water resistance, and mechanical properties comparable to phenol-formaldehyde adhesives. The lignin adhesives discussed in Chapter 3 are summarized and compared in Table 4. The adhesives' performance is influenced by lignin source, molecular weight, functional groups, and chemical modifications, which can enhance reactivity and crosslinking. Testing on interior-grade plywood and particleboard has shown that lignin-based adhesives can achieve high dry

adhesion strength and modulus of elasticity, though limitations remain for exterior applications due to reduced performance under boiling water conditions.

Feature	Biorefinery Lignin–Glyoxal Adhesive	Calcium Lignosulphonate–Glyoxal Adhesive	Kraft Lignin–Polyethyleneimine (PEI) Adhesive	Lignin–Glyoxal–Tannin Adhesive
Raw Material	Unmodified corn stover biorefinery lignin (rich in phenolic hydroxyl groups) + biobased glyoxal	Calcium lignosulphonate (modified lignin) + glyoxal + pMDI crosslinker	Kraft lignin (unmodified or demethylated) + polyethyleneimine (PEI)	Wheat pulp lignin (low molecular mass) + glyoxal + tannin + hexamine
Replacement Type	Complete replacement of phenol and formaldehyde	Complete replacement of phenol and formaldehyde	Complete replacement of formaldehyde and phenol	Complete replacement of phenol and formaldehyde
Preparation / Reaction Conditions	Lignin reacted with glyoxal (1:2 ratio) under alkaline conditions; crosslinking occurs at ortho positions	Calcium lignosulphonate modified with pMDI, then reacted with glyoxal under alkaline conditions	Kraft lignin reacted with PEI (2:1 or 1:1 ratio); hot-press cured at 120–140 °C for 5–9 min	Wheat pulp lignin modified with glyoxal (alkaline); mixed with tannin and hexamine to enhance crosslinking
Key Chemical Features	Lignin with two open ortho sites enables glyoxal crosslinking; resin MW ~3× higher than lignin	Low molecular mass lignin increases hydroxymethylation and elasticity	PEI provides strong amine–phenol crosslinking; demethylation increases reactive phenolic sites	Tannin contributes reactive phenolic hydroxyls; hexamine improves condensation and crosslinking
Tested Substrate	Interior-grade plywood	Particleboard (EN 312 standard)	Plywood	Interior-grade panels (EN 312 standard)
Bond Strength	Good bonding; high molecular weight resin indicates strong network formation	High internal bond strength meeting EN 312 exterior-grade requirement	High shear strength (dry, wet, boiling-water conditions); best at 120 °C, 5 min cure	Sufficient to meet EN 312 interior-grade standard
Water Resistance	Not explicitly stated; improved due to crosslinked structure	Adequate for exterior-grade use	Excellent; maintained after boiling-water test	Adequate for interior-grade use
Pressing / Processing Conditions	Standard hot pressing (for plywood)	Press time comparable to commercial formaldehyde adhesives	Optimal at 120–140 °C, 5–9 min	Standard hot pressing for panel bonding
Advantages	Fully biobased; low-cost feedstocks; high crosslinking efficiency	Short curing time; strong bonds; exterior-grade performance	Excellent shear and water resistance; tunable curing	Uses natural tannin; meets strength standards; simple preparation
Limitations	Still experimental; may need curing optimization	Requires pMDI for optimal crosslinking; cost of modification	PEI cost; sensitivity to ratio and curing conditions	Strength suitable for interior use only; not yet commercialized
Commercialization Status	Laboratory scale; promising for interior plywood	Laboratory scale; meets industrial strength standards	Laboratory scale; good plywood performance	Research scale; proof-of-concept stage

Table 4: Summary and Comparison of Lignin Adhesives Discussed in Chapter 3

From an environmental and economic perspective, lignin-based adhesives offer significant advantages over synthetic adhesives. By using abundant, renewable lignin, often a byproduct of biorefinery processes, these adhesives reduce CO₂ emissions, minimize formaldehyde exposure, and provide an opportunity for producers to create value from previously wasted material. While lignin-glyoxal adhesives are not yet fully suitable for all structural applications, ongoing chemical modifications and process optimizations show strong potential for replacing formaldehyde and phenol-based adhesives in a greener, safer, and more circular wood products industry.

Building on the discussion in Chapters 1 and 2 regarding the environmental and health impacts of conventional synthetic adhesives and the potential of natural bio-adhesives, Chapter 4 examines soy protein as a renewable and safe alternative. Soy protein is derived primarily from defatted soybean meal, a byproduct of oil production, making it abundant, low-cost, and protein-rich compared to other plant sources (Islam et al., 2022; B.-H. Zhang et al., 2018). Proteins are composed of amino acids with reactive functional groups, and their higher-order structures (primary, secondary, tertiary, and quaternary) dictate their chemical reactivity, water resistance, and bonding performance (Islam et al., 2022). These properties are analogous to the chemical considerations in lignin-based adhesives discussed in Chapter 3, where functional groups and polymer networks determine performance (Islam et al., 2022; Siahkamari et al., 2022).

Soy protein adhesives face inherent challenges, including high viscosity and poor water resistance due to their globular protein structure and hydrophilic carbohydrate content. To overcome these limitations, various physical, chemical, and enzymatic modifications are employed. Thermal treatment unfolds protein structures and exposes reactive groups, while chemical crosslinkers such as epichlorohydrin-modified polyamide (EMPA), polyisocyanate

(pMDI), and others create dense three-dimensional networks that enhance bond strength, water resistance, and thermal stability (B. Zhang et al., 2018; Fan et al., 2016; Kumar & Leggate, 2022).

Defatted soybean flour (DSF) and soy protein isolate (SPI) adhesives have been optimized through thermal, alkaline, and acid treatments to improve both dry and wet bonding properties. The soy-protein adhesives discussed in Chapter 4 are summarized and compared in Table 5. DSF-based adhesives combined with crosslinkers and moderate thermal treatment (80°C) demonstrated improved water resistance and mechanical strength, approaching structural standards for plywood (B. Zhang et al., 2018). SPI-based adhesives, while offering superior performance, are limited by higher cost, though chemical modifications like SPIPA have yielded adhesives suitable for structural applications (Kumar & Leggate, 2022).

Soy protein adhesives are formaldehyde-free, non-toxic, and low-emission, supporting healthier indoor air quality and compliance with green building standards, paralleling the environmental benefits of lignin-based adhesives discussed in Chapter 3 (Brown; Yauk et al., 2020). Soy protein adhesives utilize abundant byproducts, providing economic value and sustainability. DSF is particularly promising due to low cost, availability, and potential for modification to meet structural requirements (Islam et al., 2022). Challenges remain in achieving consistent performance, especially for sprayable formulations needed in glulam or CLT, and in developing adhesives suitable for exterior use. Allergic potential is a minor health concern, and manufacturing processes must be optimized for broader industrial application (Yauk et al., 2020; Kumar & Leggate, 2022).

Feature	Defatted Soy Flour (DSF) Adhesives	Soy Protein (SPI / Soy Meal / Soy Flour) Adhesives
Raw Material	Byproduct of soybean oil industry; contains protein + carbohydrates	More refined protein source (SPI), or less refined soy meal/flour with higher protein content
Cost	1/4 – 1/5 the cost of SPI adhesives → very economical	Higher cost, especially SPI; soy meal/flour is cheaper but less consistent
Preparation	DSF thermally treated (65–125 °C), ground, sieved; applied to veneers and hot-pressed	SPI dissolved/denatured in water; soy meal/flour mixed and modified via chemical/physical treatments
Main Weakness (Native Form)	Very poor water resistance; poor bond strength without modification	Poor water resistance, high viscosity, lower bond strength than PF/UF resins
Modification Methods	- Physical/chemical denaturation (heat, alkali, acid, salts, urea, SDS) - Self-crosslinking via Maillard reactions (protein–carbohydrate) - Crosslinkers: EMPA, glyoxal, glutaraldehyde, polyisocyanates, epoxy, PF, MUF	- Thermal-alkali degradation (low MW proteins, lower viscosity) - Thermal-acid treatment (network formation) - Enzymatic hydrolysis - High-pressure homogenization (smaller particles, more reactive groups) - Crosslinkers: glyoxal, epoxy latex, polyisocyanates, modified polyamides, PEI, tannins, melamine-formaldehyde
Special Variants	EMPA-crosslinked DSF (good boiling-water resistance)	- DSP/TSP system (alkali + acid treated soy proteins) - Mussel-inspired SPI adhesives - SPI with daidzein-epichlorohydrin (DDE) double crosslinking
Additives & Blends	Limited but effective: EMPA, PF/MUF blends, epoxy resins	Wide range: polysaccharide fillers (cottonseed, soy replacement), tannins, blood meal, nanoparticles, plasticizers
Bond Strength	Improved DSF + EMPA: passes hydrothermal durability tests	Optimized SPI adhesives: dry strength up to 2.94 MPa; wet strength up to 1.29 MPa (structural grade)
Water Resistance	Poor in native form; good with EMPA/strong crosslinkers	Poor in native form; significantly improved with chemical crosslinking and DSP/TSP systems
Applications	Promising for low-cost plywood and structural adhesives with crosslinkers	Potential replacement for UF and PF resins in structural wood products (when crosslinked); eco-friendly adhesives
Commercialization Status	Still largely at research stage; strong cost advantage	Some SPI + resin systems commercialized, but adoption limited by cost and wet strength issues

Table 5: Summary and Comparison of Soy Protein Adhesives Discussed in Chapter 4

5.2 Conclusions

Table 6 provides a side-by-side summary and comparison of lignin-based adhesives and soy protein-based adhesives.

Category	Criteria / Observations	Lignin-Based Adhesives	Soy Protein-Based Adhesives
Environmental & Health Benefits	Renewable, biobased raw materials	☒ Derived from lignocellulosic biomass and paper/biorefinery byproducts	☒ Derived from soybeans (renewable agricultural feedstock)
	Formaldehyde-free formulation	☒ Typically formaldehyde free (uses glyoxal, PEI, etc.)	☒ Formaldehyde-free; uses natural or mild crosslinkers
	Low VOC emissions and non-toxic	☒ Low toxicity; reduced VOCs compared to phenolic resins	☒ Very low VOC emissions; improves indoor air quality
	Contribution to sustainable building standards	☒ Supports green building practices through waste valorization	☒ Recognized as eco-friendly binder in low-emission panels
Performance Potential	Mechanical strength suitable for wood composites	☒ High dry and wet bond strength after chemical modification	☒ Comparable dry/wet strength when crosslinked (SPI, DSF)
	Water resistance for structural use	☒ Excellent after crosslinking (e.g., glyoxal, PEI systems)	☒ Improved with EMPA, glyoxal, or tannin modification
	Thermal and chemical modification enhances properties	☒ Crosslinking, methylation, and glyoxalation improve performance	☒ Denaturation and chemical crosslinking (glyoxal, epoxy) improve bonding
	Meets or exceeds industrial standards (e.g., EN 312, plywood)	☒ Laboratory and pilot tests meet plywood/particleboard standards	☒ Optimized SPI systems meet structural-grade performance
Economic & Resource Advantages	Uses waste or low-cost byproducts	☒ Utilizes lignin from pulp/biorefinery waste streams	☒ Uses defatted soybean meal (inexpensive byproduct)
	Cost-effectiveness compared to petrochemical resins	☒ Cost-competitive due to lignin availability	☒ DSF offers strong cost advantage; SPI is costlier but greener
	Supports circular economy and resource efficiency	☒ Converts biomass waste into value-added products	☒ Promotes agricultural waste valorization and sustainability
Current Limitations	Consistency across wood types and process conditions	☐ Performance variability; needs optimization by species and curing method	☐ Sensitive to wood species, pH, and moisture conditions
	High viscosity and limited sprayability	☐ Often viscous; difficult to handle at high solids	☐ High viscosity; may require dilution or special application methods
	Exterior-use certification or weather durability	☐ Some systems lack certification for exterior-grade applications	☐ Still limited for structural/exterior use despite lab success
	Industrial scalability and curing control	☐ PEI/pMDI systems increase cost and complexity	☐ Protein denaturation and curing control remain challenges

Table 6: Summary and Comparison of Lignin and Soy Protein Adhesives

Legend:

☑ = Advantage / Strong characteristic

☐ = Limitation / Area needing improvement

The key conclusions of this report are outlined below:

1. Environmental and Health Benefits: Both soy protein-based and lignin-based adhesives offer renewable, non-toxic, and formaldehyde-free alternatives to conventional synthetic adhesives. Soy protein adhesives reduce VOC emissions and support healthier indoor air quality, while lignin-based adhesives, derived from abundant biomass byproducts, lower formaldehyde exposure and contribute to greener building practices.
2. Performance Potential: Modified soy protein adhesives (DSF and SPI) and chemically optimized lignin adhesives can achieve mechanical strength and water resistance approaching or exceeding standards for engineered wood products. Thermal, chemical, and crosslinking modifications in both adhesive types enhance dry and wet bond strength, creating bio-based alternatives suitable for structural applications.
3. Economic and Resource Advantages: Soy protein adhesives utilize defatted soybean meal, while lignin adhesives leverage biomass byproducts from the paper and biorefinery industries. Both approaches convert low-value or waste materials into high-value adhesives, providing cost-effective, sustainable alternatives to petrochemical-based adhesives and supporting circular economy goals.
4. Current Limitations: Challenges remain in achieving consistent adhesive performance across different wood species, moisture levels, and manufacturing processes. High viscosity, limited spray ability, and lack of exterior-use certification restrict broader adoption for glulam, CLT, and other structural applications.

5.3 Recommendations

The key recommendations of this report are outlined below:

1. **Optimize Formulations:** Focus on DSP/TSP ratios, moderate thermal treatment, and polyamide crosslinker levels to balance viscosity, work life, and bond strength for industrial-scale plywood, glulam, and CLT production.
2. **Expand Application Research:** Develop sprayable and cold-set soy protein adhesives to extend use to structural EWPs requiring high-volume, automated manufacturing processes.
3. **Exterior-Use Development:** Conduct targeted research on moisture resistance and long-term durability under outdoor conditions to meet exterior-use standards.
4. **Health and Safety Monitoring:** Continue to monitor allergenic potential and provide labeling guidance while promoting soy adhesives as low-emission alternatives to formaldehyde-based adhesives.
5. **Industrial Integration:** Collaborate with engineered wood manufacturers to pilot large-scale production, focusing on process adaptation, energy efficiency, and product consistency.
6. **Complementary Bio-Adhesives:** Explore hybrid approaches combining soy protein with lignin-based or other natural adhesives to optimize mechanical performance, water resistance, and sustainability metrics.

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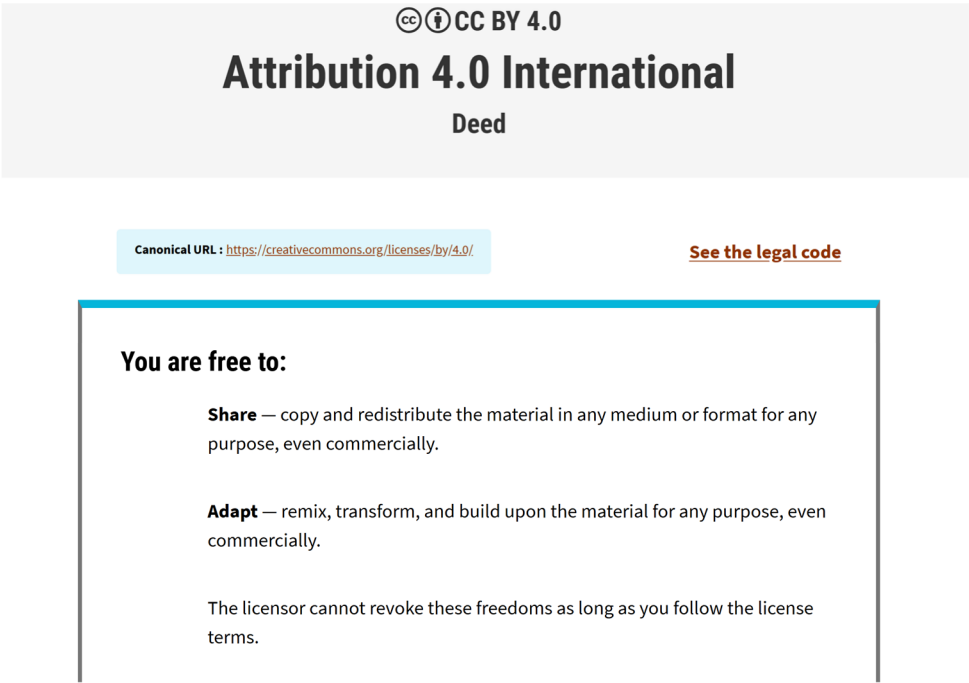


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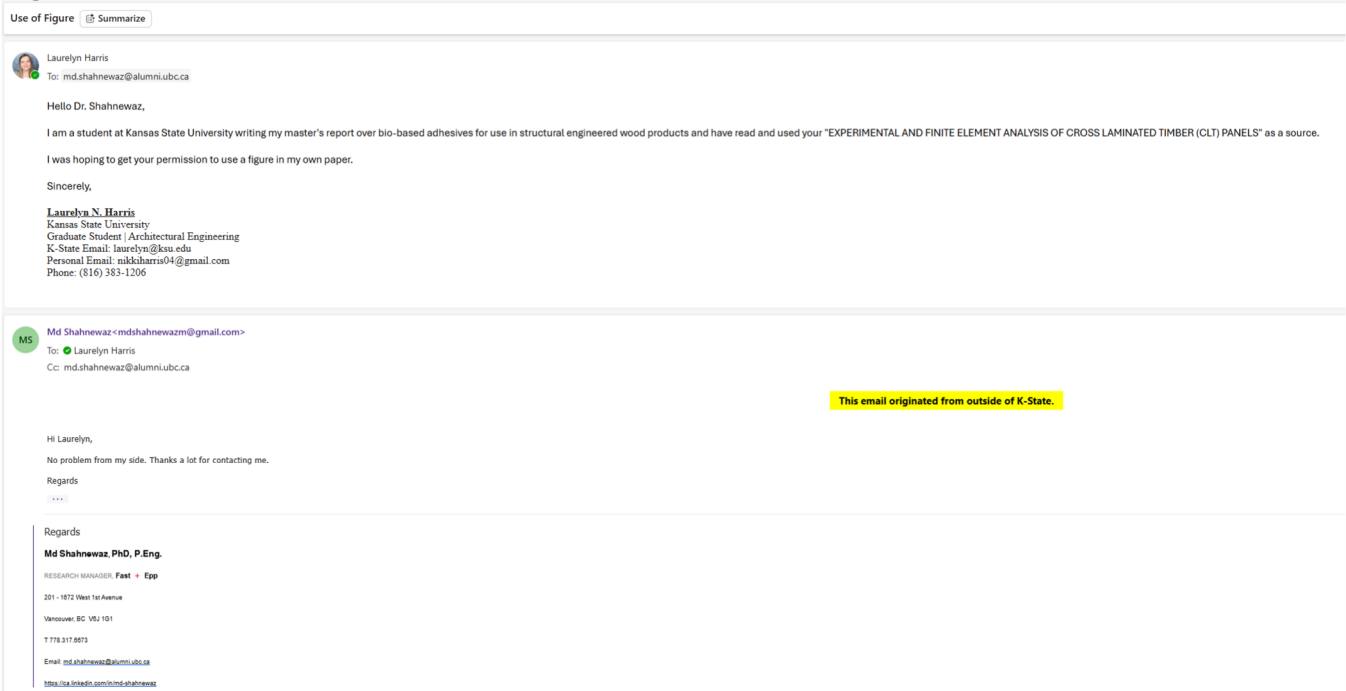


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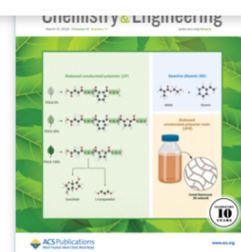
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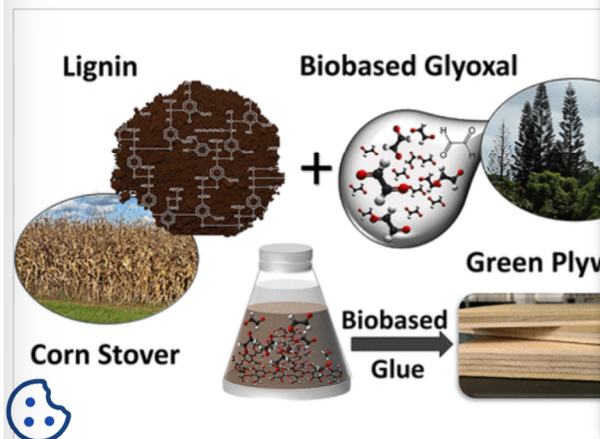
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