Developing soybean-based adhesives for heat-treated plywood

by

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B.S., Donghua University, P.R. China, 2014
M.S., University of Akron, 2016

AN ABSTRACT OF A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

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Manhattan, Kansas

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Abstract

Heat treatment on wood in the absence of oxygen is commonly practiced in industry to improve raw wood properties. However, heat treatment is not widely applied to engineered wood such as plywood because most synthetic adhesives such as urea formaldehyde (UF) adhesives fail in high temperature. In addition, synthetic adhesives, upon heat treatment, would release toxic substances to pollute the environment. In this study, inspired by the high-temperature, controlled, (non-)oxygen condition used in baking, we explored the idea of using plant-protein-based adhesives for heat-treated plywood. Soybean protein (SP) is a proven material for making biobased adhesives for plywood; however, soy flour (SF) is a more affordable candidate. In this study, soy flour was used as the base material for wood adhesives and further modified and formulated with low-value lignin to improve adhesion properties and reduce cost. Glucose was then added in the formula to reveal the effect of the Maillard reaction. Yellow pine plywood samples were prepared and heat treated at different temperatures (190-200 °C) for varied times from 1 to 4 h. The key results were that heat treatment improved the wet adhesion strength of plywood made with SF-based adhesives. Even with unmodified, SF-only adhesives, plywood exhibited robust adhesion and strong water resistance after heat treatment. For example, after 200 °C treatment for 2 h, the wet strength of SF plywood improved from 0 MPa to 1.28 MPa, while plywood made with UF adhesives became delaminated after heat treatment. A content ratio of 50% was the most lignin that can be added into the formula, and it achieved a wet strength of 1.31 MPa. Lignin25%-SF75% was the most practical application, achieving a wet stregnth of 1.43 MPa after heat treatment. Changing the pH of the lignin-SF slurry changed the adhesion of plywood. At a higher pH, more lignin content can be added to the adhesive formula. Heat-treated plywood prepared using soy flour and glucose (SFG) adhesives exhibited a better water resistance of 1.51MPa. The treatment

temperature range overlapped with that of the Maillard reaction. The Maillard reaction forms crosslink structures and plays an important role in the water resistance of heat-treated soybean adhesives. It was proposed that hydrophilic functional group loss, protein denaturation, and crosslinking after denaturation helped heat treatment to improve wet adhesion. This study points to new applications of protein-based adhesives and ways to improve plywood properties at a considerably lower cost.

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Chapter 1 - Introduction

1.1 General background

Engineered wood including plywood has seen increasing production and is used for construction, furniture, and decoration. In 2017, the annual global production of plywood reached 157 million m^3 (FAO). The wood adhesive consumption of the industry is estimated to reach 6.24 billion by 2025, and soybean-based adhesives are predicted to experience the fastest growth due to their abundance and environmental friendliness. The cost and lack of water resistance of soybean adhesives are main problems that restrict their application.

Heat-treated wood studies were initiated in the early 1920s and received much attention in Europe (Yan-jun, Yi-xing, et al., 2002). The annual production of heat-treated wood in Europe reached 280,000 m^3 in 2013 (UNECE/FAO, 2014). Compared to the entire market of wood materials, the heat-treated wood market is still relatively small. The limited size, higher cost, and unavailability of treated engineered wood hindered the development of the heat-treated wood market (Espinoza, Buehlmann, et al., 2015).

1.1.1 Heat treatment on wood: benefits and restrictions

Given the unsatisfactory properties of raw wood materials, different wood modification methods were developed (Homan and Jorissen, 2004). These modifications mostly aim to improve durability, mechanical properties, and resistance to termites and fungi (Esteves and Pereira, 2009, Homan and Jorissen, 2004). Human use of heat treatment on wood has a long history. For example, fire hardening the spear end was applied by ancient humans (Ennos and Chan, 2016). Modern heat-treated wood has been developed since the 1920s (Rapp, 2001). It is also referred to as thermal modified wood or carbonized wood (Byrne and Nagle, 1997, Sandberg and Kutnar, 2016). Modern wood heat treatment is usually conducted in a non-oxygen or low oxygen environment to prevent

wood from burning at a high temperature (CEN, 2007, Esteves and Pereira, 2009, Rapp, 2001). Heat treatment can realize some significant improvements in raw wood properties at a relatively low cost (Esteves and Pereira, 2009, Homan and Jorissen, 2004). Nonetheless, heat treatment is almost only applied to raw wood pieces. Most engineered wood products are not able to be heat treated because urea formaldehyde resin, the wood adhesive most commonly applied in these wood products, is not resistant to heat at high temperature (Girods, Dufour, et al., 2008).

1.1.2 Plywood and other engineered wood

Engineered wood is made of composite materials derived from wood usually bonded or fixed by adhesives. It is a family of manufactured boards including medium density fiberboards, oriented strand boards, and particle boards. Plywood consists of odd numbers of layers of wood veneers bonded by adhesives and manufactured by hot pressing machines (SELLERS JR, 1977). Engineered wood, including plywood, is usually manufactured using wood from economic trees, which grow fast but have biodegradability and low dimension stability (Bekhta, Salca, et al., 2020, Hsu, Hung, et al., 2021). Because trees grow radially in nature, there are density differences in different parts of the wood log. Wood pieces cut from natural lumber logs have inner stress when temperature and moisture change, showing poor stability (Wimmer, Downes, et al., 2002). Plywood, by perpendicularly stacking odd numbers of layers of rotary cut veneers, also known as cross-graining structures, has many benefits. The cross-graining structures balance stress and reduce expansion and shrinkage, making plywood less likely to deform and have better mechanical properties than raw wood. Raw wood only has strong strength along the grain direction, while plywood has consistent strength across all directions. The wood veneers nailed at the edges have a lower tendency to split on the surface. The odd numbers of layers prevent the warping of the

products. Plywood and other engineered wood also utilize wood materials at a higher rate than raw wood and produce less waste.

Most wood adhesives applied in the industry are susceptible to water and moisture, except for some formulas with higher costs. Plywood intended for outdoor use is usually produced using phenol formaldehyde adhesives, which are more expensive than the most applied urea formaldehyde adhesives. Creating water-resistant, durable, and economical plywood and other engineered wood products for long term and outdoor use is an important, unmet need.

1.2 Objective

The overall goal of this research is to investigate the technique of producing plywood products and protein-based adhesives specially designed for heat treatment applications. With a deeper understanding of protein-based adhesives and heat treatment on wood, we can develop protein-based adhesives that withstand heat treatment with low cost. The specific objectives are:

1. Develop soy flour adhesives for heat-treated plywood. The mechanical properties of the product will be tested, evaluated, and compared with those of plywood made using the commercial polyamide epichlorohydrin (PAE) adhesives. Results will also be compared with those of previous research regarding the influence of heat treatment on plywood and raw wood. The laboratory heat treatment method will be compared with existing techniques.
2. Develop low-cost soybean-based adhesives, formulated with lignin, for heat-treated plywood. The adhesive will be characterized before and after heat treatment.
3. Investigate the mechanism through which heat treatment enhances wet strength and use glucose, a reducing sugar, as a model system. The mechanism through which protein-based adhesives endure high temperature during heat treatment will be proposed.

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Chapter 2 - Literature Review

2.1 Soybean and soybean-based adhesives

Soybean is the one of the most abundant sources of protein and oil. Soybean flour is a major product of the plant oil industry. It contains around 45% protein, 2% fat, and 40% carbohydrate. Most soybean flour goes to the animal feed industry and has a relatively low added value. Therefore, seeking applications of higher added value for soybean flour has been a research interest for years.

In ancient times, gelatin, the effective functional content of which is protein, has been applied as an adhesive (Lee, Martín-Rey, et al., 2018). In 1930s, the early plywood products were prepared by the soybean based adhesive (Lambuth, 2003). As petroleum industry developed, synthetic adhesives with lower cost and better properties gradually replaced soybean adhesive. However, the synthetic adhesive such as urea formaldehyde, the currently most widely applied wood adhesive, is derived from the nonrenewable source and emits carcinogen (Cancer, 2007). In the last two decades, protein-based adhesives have received more attention due to their sustainability and non-formaldehyde emission.

Proteins containing various functional groups such as carboxylic, amide, and hydroxyl groups can interact with wood surface to form adhesion. Soybean flour slurry directly applied on veneers can produce plywood with sufficient dry strength but has weak water resistance (Frihart and Satori, 2013, Lorenz, Birkeland, et al., 2015). The adhesion mechanism of the protein-based adhesives has been investigated, and theories have been developed. According to Wool and Sun, protein-based adhesives work by flowing into the pores of wood and forming root-like structures to grasp the wood surface (Wool and Sun, 2011). The cohesion of protein-based adhesives has significant influence on the adhesion strength of the adhesive. Soybean proteins have a globular

structure with hydrophobic groups buried inside the protein, making the slurry not too viscous when applied on the wood surface (Wool and Sun, 2011). After hot pressing, the denatured protein chains exhibit hydrophobic properties and help improve water resistance. Consequently, the idea of maximizing denaturation and unfolding protein chains have been promoted to improve soybean-based adhesives. Unfolding agents such as alkali(NaOH), urea, guanidine hydrochloride, and sodium dodecyl sulfate (SDS) have been explored (Hettiarachchy, Kalapathy, et al., 1995, Huang and Sun, 2000, Huang and Sun, 2000, Sun and Bian, 1999).

The entanglement and crosslink between proteins plays an important role in cohesion and water resistance. The covalent bonds between proteins help form a compact protein complex with entangled and cohesive networks, which can resist water soaking. Thus, the idea of enhancing crosslinks by inducing crosslinkers has been proposed. Different crosslinkers such as urea formaldehyde (UF), phenol formaldehyde (PF), and polyamide epichlorohydrin (PAE) have been investigated and show improved adhesion strength (Li, Peshkova, et al., 2004, Wu, Xi, et al., 2019). Among these modifiers, PAE was found to be one of the most effective crosslinkers, with acceptable price and practical parameters for industrial applications (link). PAE-modified soybean adhesives are the most common soybean adhesives on the market today. Crosslinking induced by the Maillard reaction of proteins was also studied in food science, and it decreases water sensitivity (Gerrard, 2006). Using ascorbic acid as a reducing sugar to enhance the Maillard reaction during hot press has been demonstrated to achieve a higher dry strength (Román and Wilker, 2018).

Temperature, pressure, and time are main parameters of the hot press process and can affect the performance of adhesives. A higher temperature and pressure and a longer time are usually advantageous for increasing adhesion strength (Wool and Sun, 2011). With a high temperature and enough time, soybean adhesives can gain sufficient wet strength even without modifiers. Previous

studies also showed that post heat treatment after hot pressing using temperature of only 90 °C-120 °C can improve the wet shear strength of plywood bonded by protein-based adhesives (Luo, Luo, et al., 2015). However, in practical applications, an extremely high temperature is not acceptable and a longer pressing time is also unfavorable due to lower production efficiency. In addition, although crosslinking in adhesive helps increase adhesion strength, over crosslinking is not desirable because high viscosity makes it difficult to brush adhesives onto the wood surface. High concentrations of glutaraldehyde as crosslinkers showed poor flowability making the adhesive difficult to be brushed (Kim, 2015). Effective, practical adhesive formulas should thus satisfy the following requirements: relatively mild hot press temperature, press pressure, short press time, and good flowability or proper viscosity. These parameters should be comparable to those of synthetic adhesives such as urea formaldehyde adhesives. Especially, successful modifiers of soybean adhesive should be effective without requesting higher hot press temperature.

Soybean protein has much better thermal stability than synthetic adhesive such as UF glue. According to the weight loss of protein in thermogravimetric analysis, soybean protein has a high degradation temperature. Thermogravimetric analysis (TGA) curve showed that soybean flour backbone won't degrade until the temperature has reached 230 °C (Figure 2.2). This durability against heat gives soybean protein the potential of being used as an adhesive for heat treatment.

2.2 Methods of heat treatment on wood and the resultant properties

The earliest articles about wood heat treatment date back to the 1920s (Esteves and Pereira, 2009); however, heat-treated wood has not been commercialized until recently. The main reason for this lack of commercial application is the complicated process involved in large-scale production at high temperatures. Another problem is that wood often gets burned before the shielding gas technique is applied. The treatment also decreases wood's strength and makes it too

brittle for many applications (Yan-jun, Yi-xing, et al., 2002). To clarify, heat treatment in this research doesn't refer to the term used in the wood industry, which means 30 mins of 56 °C treatment for export and import as governed by the global standard HT ISPM 15 (IPPC, 2002).

Several heat treatment technologies have been developed such as the Westwood process, Plato process, ThermoWood process, and Perdure process (Homan and Jorissen, 2004, Rapp, 2001, Sandberg and Kutnar, 2016). Products manufactured using these methods are mainly commercialized in European countries including the Netherlands, Germany, France, and Finland (Yan-jun, Yi-xing, et al., 2002). The common feature of these heat treatment methods is realizing high temperatures in a non-oxygen or low-oxygen environment.

The ThermoWood method from Finland uses steam generators to produce water steam to shield timber from burning (Syrjanen, 2001). The process includes the following steps:

1) The temperature rise period (warm up to 100°C and keep drying for up to 48 hours).
2) Heat treatment (constant temperature of 150-240 °C) for 0.5-4 hours.
3) Cooling and stabilizing for up to 24 hours.

During these three steps, water vapor fills the oven to uniformly transfer heat and prevent wood from burning (Rapp, 2001, Yan-jun, Yi-xing, et al., 2002).

The Plato process was developed in the Netherlands. It uses water steam or hot air as the shielding gas to apply treatment at 170-190 °C (Militz and Tjeerdsma, 2000). Since the temperature is lower than that of other methods, Plato wood requires 14-16 hours of treatment time depending on the application of the end product (Militz and Tjeerdsma, 2000).

Retification (Retified wood), developed in France, processes timber at 210-240 °C and uses nitrogen as the shielding gas (Bourgois and Guyonnet, 1988). The concentration of oxygen in the system is less than 2%. Due to the high temperature applied in the process, wood durability is

much improved despite severe loss of 40% of the modulus of rupture (Bourgois and Guyonnet, 1988, Yan-jun, Yi-xing, et al., 2002).

Instead of shielding gases, Germans circulate wood with hot oil at 180- 220 °C (Rapp and Sailer, 2000). Wood treated by hot oil exhibits much less hygroscopicity and better stability, owing to the water repellent effect of oil (Yan-jun, Yi-xing, et al., 2002).

Temperature and time are the main factors affecting the intensity of heat treatment (Candelier, Thevenon, et al., 2016). For any heat treatment method, temperature and time can vary based on raw wood species and the requirements for end products (Esteves and Pereira, 2008). The microstructure of wood changes during heat treatment, including chemical and physical changes such as the removal of hydroxyl groups, degradation of hemicellulose, and increased crystallinity of cellulose (Tjeerdsma and Militz, 2005, Weiland and Guyonnet, 2003, Wikberg and Maunu, 2004). With these chemical and physical changes, heat treatment improves the properties of wood in several aspects, such as better size stability, resistance to moisture, improved durability against decay, and resistance to bugs and fungi (Esteves and Pereira, 2008, Hakkou, Pétrissans, et al., 2006). The loss of hydroxyl groups induces lower balanced moisture content and reduced hygroscopicity in heat-treated wood (Borrega and Kärenlampi, 2010, Rautkari, Hill, et al., 2013). The increased durability of heat-treated wood leads to an extended product life, so heat treatment is also considered a wood preservation method (Richardson, 2002). Heat treatment also modifies the surface of the wood physically and chemically (Hakkou, Pétrissans, et al., 2005). With certain time and temperature settings, heat-treated wood can exhibit an antique dark color (Patzelt, Emsenhuber, et al., 2003, Robert Welzbacher, Brischke, et al., 2007, Sundqvist, Karlsson, et al., 2006).

At the same time, heat treatment can lower the modulus of rupture and cause brittleness, unwanted color change, and reduced density, which are usually undesirable in industry applications (Boonstra, Van Acker, et al., 2007, Srinivas and Pandey, 2012). Another restriction for the application of heat-treated wood is size, as the size of the product is limited by that of the raw wood logs. The brittleness induced by heat treatment would make wood veneers easier to crack (Shida and Saito, 2007). The wood density loss due to heat treatment will cause the veneers to shrink in thickness when being hot pressed (Guller, 2012). Meanwhile, surface chemical changes including the loss of functional groups and the change in wettability will make adhesives perform worse (Hakkou, Pétrissans, et al., 2005, Šernek, Humar, et al., 2007). UF applied on heat-treated veneers showed a decreased shear strength of adhesion (Šernek, Humar, et al., 2007).

Still, given the advantages of heat treatment and its low cost, heat treatment is usually a desirable method (Kamdem, Pizzi, et al., 2002), and the changes of wood properties can be controlled by adjusting treatment time and temperature (Candelier, Thevenon, et al., 2016). In most cases, the declines of mechanical properties are relatively small and even negligible compared to the improvement in other properties (Srinivas and Pandey, 2012).

2.3 The structural changes of protein related to heat treatment

Heat-induced protein structural changes are common in everyday life. For example, cooking eggs causes phase changes due to protein denaturation. Protein denaturation involves secondary, tertiary, and quaternary structure changes but less primary structure changes, which means that the sequence of amino acids remains stable. This is the fundamental reason why soybean protein can withstand high temperatures. During denaturation, the structure and conformation of amino acid will change, and new properties such as hydrophobicity will appear.

Soybean protein mainly contains 11S and 7S. The 11S contain more disulfide bonds and are more stable than 7S, and they denature at higher temperatures (Wool and Sun, 2011). Soybean protein denaturation caused by heat is usually irreversible. The denaturation can be observed in differential scanning calorimetry (DSC) scans. In the first DSC scan of pristine soybean protein samples, there are two peaks, however in the second scan, the peaks disappear due to the thermoset property of soy protein (Wool and Sun, 2011). The thermoset property stabilizes the structure of soybean protein after hot pressing, giving soybean protein the potential to undergo heat treatment after hot pressing. By contrast, for thermoplastic adhesives, which have reversible thermal properties, heat treatment of wood assemblies will be impossible because the adhesive resin will flow upon heating. Soybean protein denaturation temperature is affected by a few factors. Water content has a significant influence on the denaturation temperature of soybean protein (Kitabatake, Tahara, et al., 1990, Oates, Ledward, et al., 1987). Normally, the denaturation temperature decreases with increased water content (Sheard, Fellows, et al., 1986, Wool and Sun, 2011). Though adding water can significantly decrease the denaturation temperature, changing water content is restricted in practice because the pressing time and energy cost to evaporate water is unacceptable in the industry. Therefore, other modification methods need to be applied to lower the denaturation temperature of protein adhesives if a wood assembly is not heat treated after hot press. For example, hydrogen bonds are important for maintaining the secondary, tertiary, and quaternary structures of proteins. Disrupting hydrogen bonds can reduce the structural stability of polymers, decreasing the glass transition temperature and denaturation temperature of soybean protein (Marqusee and Sauer, 1994, Tominaka, Kawakami, et al., 2017).

Because the primary structure of soybean protein is relatively stable, it is difficult to induce peptide bond breaks or hydrolysis without proper enzymes or acids (Damodaran, 1997). The

thermogravimetry graph of soybean protein with 90% protein content is shown in Figure 2.2. The first weight loss starts from room temperature to around 100 °C, which is mainly attributed to water content evaporation. The first weight loss doesn't correspond to primary structure change or other conformation change. From 100 °C to about 200 °C, the soybean protein sample maintains its weight. Starting from approximately 230 °C, soybean protein starts to lose weight, mainly due to the decomposition of protein backbone chains, peptide bonds, and other carbon-carbon bonds. The decomposition mostly finishes after 500 °C. The final leftover solids are ashes.

Davis et al. reviewed the structural change of protein at high water content under 125 °C and determined the levels of structural change in different temperature ranges (Davis and Williams, 1998). Though dependent on many factors, the tertiary structure, which is stabilized mainly by the hydrophobic effect and Van der Waals force, is lost earlier than secondary structure when protein is heated (Davis and Williams, 1998). During heating, the protein gains energy and the side groups start to move and rotate. The buried hydrophobic groups in the "raw" protein start to orient outward being exposed to water. The degree of unfolding increases as temperature rises with the total loss of tertiary and secondary structures. At this point, the protein is fully unfolded and becomes random coils. Meanwhile, disulfide bonds start to break and due to the free movement of side chains, the previously unmet thiol groups interact with each other and form new disulfide bonds. These reactions partially lead to the thermoset property of soybean protein. New hydrophobic interactions and ionic interactions also start to form. Multiple reactions occur during the heating, such as deamination of asparagine, the Maillard reaction, and other side group reactions. Induced by water evaporation, the soybean protein starts to aggregate and coagulate.

Due to hydrophobic interactions, protein molecules form aggregates, leading to precipitation, coagulation, or gelation (Damodaran, 1997). The formation of gel matrices or

coagula happens in sequential stages including denaturation, aggregation, and crosslinking. Crosslinking, during denaturation, is important to "lock" the denaturation and lead to the thermoset property.

The dissociation of quaternary structures of soybean protein is often reversible, which means the subunits still interact with each other and stay close. However, the dissociation of secondary and tertiary structures can be irreversible. The heating of protein can affect the α-helix and β-sheet and their ratio in protein (Yu, 2011). Yu et al found that the α-helix was transferred to the β-sheet by dry heating (Yu, McKinnon, et al., 2005). Temperature has significant influences on the process, both on the reaction product and reaction speed. If temperature is not high enough, unfolding generally remains partial (Cherry, 1981).

Privalov et al. reviewed the stability of small globular proteins and provided a two-state model for denaturation (Privalov, 1979). The model assumes that the native and the denatured states are the only states of the protein macromolecule. Though the model is not perfect as a polymer can fold into distinct compact structures, it helps us to understand the change in heating and provides some predictions of structural change (Privalov, 1979). The thermodynamic calculations correspond well with results such as temperature change.

2.4 Studies of heat-treated plywood and other engineered wood

Theoretically, there are two basic technology pathways to make heat-treated plywood. The first pathway is using heat treatment to prepare treated veneers and then gluing the treated veneers together and applying hot press. It is shown in Figure 2.1 as the pathway 1. In this pathway, only the wood veneers go through the heat treatment, and the adhesive in the glue line is applied after the treatment and avoids being exposed to high temperature. Numerous studies have been done

using this pathway to prepare heat-treated plywood or other engineered wood (Goli, Cremonini, et al., 2014, Hsu, Hung, et al., 2021, Lovrić, Zdravković, et al., 2017). Though this pathway avoids the most important factor that causes adhesive failure after heating and previous studies managed to prepare plywood products, in practical application it has many defects. The heat treatment on wood surface will induce brittleness and finally make the veneers easy to crack (Shida and Saito, 2007). The wood density loss due to heat treatment will cause the veneers shrink at thickness when being hot pressed (Guller, 2012). Meanwhile the surface chemistry change on wood due to heat treatment including functional groups loss and changes in wettability will worsen adhesive performance (Hakkou, Pétrissans, et al., 2005, Šernek, Humar, et al., 2007). UF applied on heat-treated veneers showed a decreased shear strength of adhesion (Šernek, Humar, et al., 2007). The key to this technology is to avoid the decomposition and failure of synthetic adhesives during heat treatment.. However, those defects make it not feasible in practical production considering cost, efficiency, and qualified product ratios.

Melamine-urea-formaldehyde (MUF) was used to bind treated poplar veneers by Lovrić et al., and the plywood products showed reduced thickness swelling and water absorption (Lovrić, Zdravković, et al., 2017). It was also observed that due to pre-treatment, the wet adhesion strength of the MUF adhesive was not robust enough for application in humid circumstances. With higher treatment temperatures, the product exhibits less thickness swelling and water absorption and a weaker modulus of rupture (Lovrić, Zdravković, et al., 2017). Aro et al studied the mechanical and physical properties of heat-treated plywood and oriented strand board (OSB), which were bonded by phenolic and methylene diphenyl diisocyanate (MDI) resins. The heat-treated plywood exhibited decreased moduli of rupture (MOR) and elasticity (MOE) and internal bond strength,

and the thickness swell performance of both products were substantially improved (Aro, Brashaw, et al., 2014).

The other possible technology pathway to produce heat-treated plywood is to bind the untreated veneers, hot press the wood assembly, and then apply heat treatment to the prepared plywood to produce heat-treated plywood products. It is shown in Figure 2.1 as the pathway 2-(1). Traditional plywood and engineered wood are manufactured with petroleum-based adhesives such as urea formaldehyde (UF) (Sellers Jr, 2001). These synthetic adhesives would decompose at high temperatures during heat treatment (Kadowaki, 1936). Therefore, after the treatment, the plywood will dissemble into wood veneers because of adhesion failure (Goli, Cremonini, et al., 2014). This problem of synthetic adhesives is what confined the application of heat treatment to raw wood. Without application on engineered wood, heat treated wood product size is limited.

In the research of this paper, protein-based adhesive is proposed to replace the UF glue in the pathway 2-(1). This modified pathway is shown in Figure 2.1 as pathway 2-(2).

2.5 Lignin and its application in wood adhesives

A byproduct of the paper pulping and biofuel industry, lignin is the most abundant and underutilized biopolymer and a possible modifier or additive for soybean-based adhesives (Mankar, Chaudhari, et al., 2012, Pye, 2005, Stewart, 2008). In the paper pulping industry alone, 70 million tons of lignin are produced annually, most of which is of low value (Mankar, Chaudhari, et al., 2012, Stewart, 2008). Lignin usually contains three major subunit groups or three monolignols: paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Christopher, Yao, et al., 2014). Lignin contains functional groups such as carbonyl, methoxyl, phenolic hydroxyl, and alcoholic hydroxyl groups. The subunits are mostly linked by ether and ester bonds, and the

molecular weight of lignin molecules usually ranges from 1000 to 20000 g/mol (Doherty, Mousavioun, et al., 2011). Lignin derived from different sources have slightly differnent strucutres and molelualr weight distributions. Among them, kraft lignin has a low molecular weight containing abundant phenolic hydroxyl groups (El Mansouri and Salvadó, 2006).

Lignin contains basic aromatic subunits and phenolic hydroxyls, which can react with protein to form a protein-lignin complex or network (Le Bourvellec and Renard, 2012, Pradyawong, Qi, et al., 2017). The aldehyde group in lignin (Liu, Wang, et al., 2015) is especially active under the high temperature of heat treatment. These properties make lignin an efficient and promising modifier for soy protein adhesives (Pradyawong, Qi, et al., 2019, Wei, Zhu, et al., 2019). Kraft lignin has been developed as a modifier to improve the water resistance of soy meal adhesives (Luo, Luo, et al., 2015). Sorghum lignin was added into soy protein adhesives and improved their wet strength (Xiao, Li, et al., 2013). Soy protein adhesives modified by sorghum lignin present better water resistance in an alkaline solution than in the neutral condition (Xiao, Li, et al., 2013).

Chemical modification has been applied to lignin to derive more reactive functional groups such as aldehyde, which can function as a crosslinking agent in future processing. Among these chemical modifications, fragmentation and depolymerization methods such as pyrolysis, oxidation, and hydrogenolysis are widely applied (Xu, Arancon, et al., 2014). Lignin has relatively better thermal stability compared to synthetic glues such as urea formaldehyde resin, which means its weight loss to heat decomposition during wood heat treatment will be acceptable (Zhang, Resende, et al., 2012). Heat may induce depolymerization of lignin, while molecule chains maintain their backbone structure.

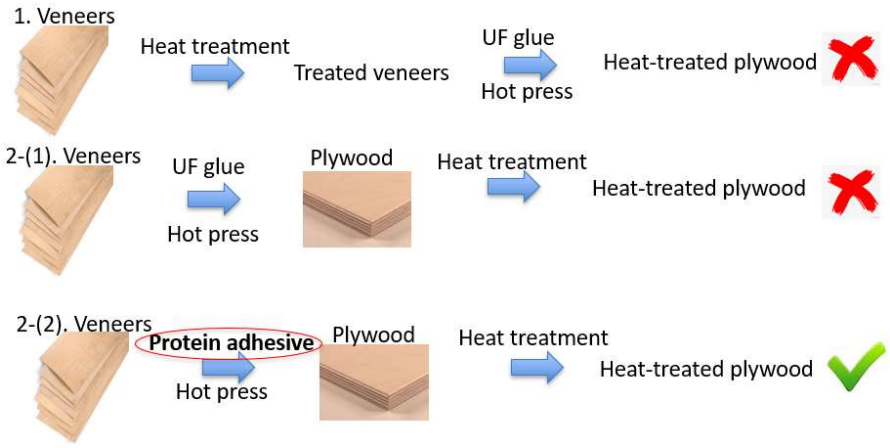

Figure 2.1 Two basic theoretical technology pathways to prepare heat-treated plywood

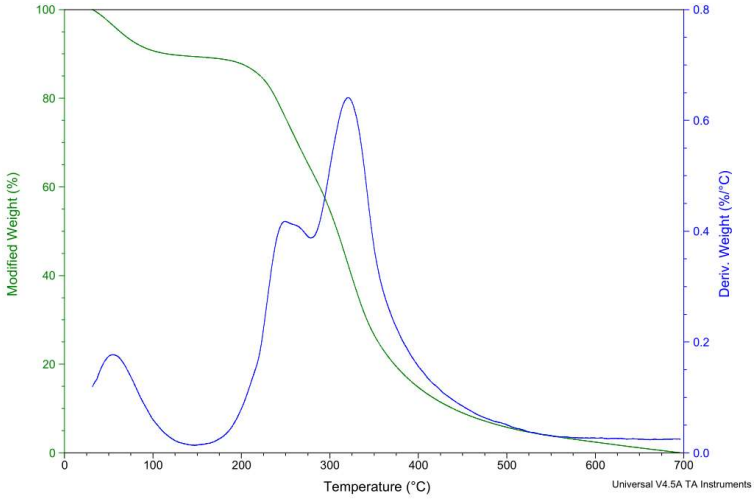

Figure 2.2 TGA graph of soy flour

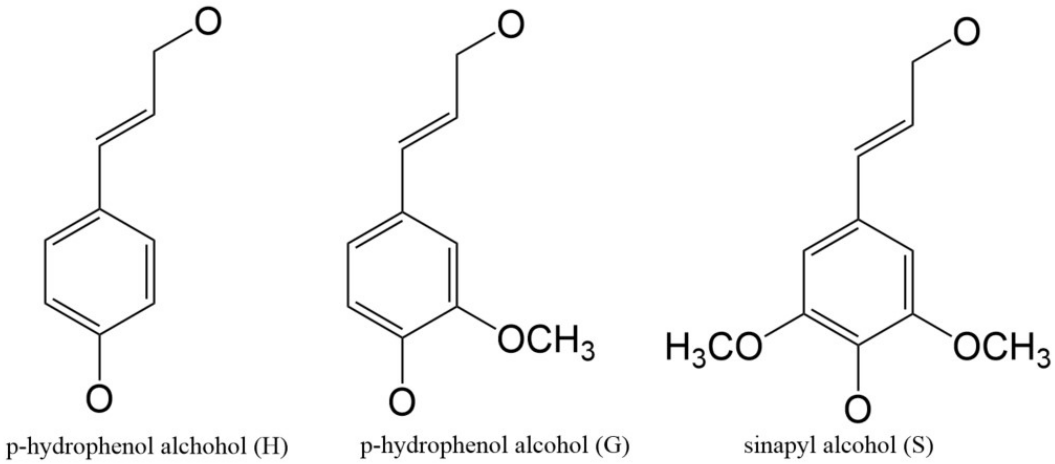

Figure 2.3 Major subunits of lignin

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Chapter 3 - Soy flour and PAE Modified Soy flour Applied on Heat Treated Plywood

3.1 Abstract

Heat treatment on wood in the absence of oxygen is commonly practiced in industry to improve raw wood properties. However, heat treatment is not widely applied to engineered wood such as plywood because most synthetic adhesives (i.e., urea formaldehyde based adhesives) fail in high temperature process. In addition, these synthetic adhesives, upon heat treatment, would release toxic substances to pollute our environment. In this study, inspired by the high-temperature, controlled (non-)oxygen condition used in baking, we conceived the idea of using protein-based adhesives for heat-treated plywood. Three adhesive formulas, soy flour (SF), polyamide-epichlorohydrin modified soy flour (PAE/SF) were used to prepare plywood samples with yellow pine wood. These samples were then heat treated at different temperatures (190-200 °C) for varied time length from 1 to 4 h. Urea formaldehyde (UF) adhesive was used as comparison. Plywood made with protein-based adhesives, including the unmodified SF adhesive, exhibited strong adhesion and high water resistance after heat treatment while the plywood made with UF adhesive become delaminated during heat treatment. For example, after treatment of 200 ° C for 2 h, the wet strength of the SF plywood was improved from 0 MPa to 1.28 MPa. This study points to new applications of protein-based adhesives and ways to improve plywood properties at a considerably low cost.

3.2 Introduction

Dating back to ancient humans burning the wood spear end to harden it, heat treatment on wood has a long history and is widely applied in today's industry (Ennos and Chan, 2016, Esteves and Pereira, 2008). Heat-treated wood, also known as thermal modified wood and carbonized wood, undergoes high-temperature (usually higher than 150 °C) treatment usually under non-oxygen or low-oxygen conditions (Esteves and Pereira, 2008). The exact temperature and time of heat treatment can vary based on raw wood species and product requirements (Esteves and Pereira, 2008). During the treatment, wood experiences microstructure reconstruction, including chemical and physical changes such as hydroxyl groups reduction, hemicellulose degradation, and crystallinity increase in cellulose (Tjeerdsma and Militz, 2005, Weiland and Guyonnet, 2003, Wikberg and Maunu, 2004). Due to these chemical and physical changes, treated wood exhibits improved properties including size stability, resistance to moisture, and resistance to bugs and fungus (Boonstra, Van Acker, et al., 2007, Esteves and Pereira, 2008, Guller, 2012, Hakkou, Pétrissans, et al., 2006, Srinivas and Pandey, 2012). Heat treatment also changes the surface appearance of wood (Hakkou, Pétrissans, et al., 2005). Depending on treatment time and temperature, heat-treated wood presents a hydrophobic surface with an antique, dark-color look (Patzelt, Emsenhuber, et al., 2003, Robert Welzbacher, Brischke, et al., 2007). Heat treatment does weaken some properties, causing, for example, increased brittleness and diminished bending strength (Boonstra, Van Acker, et al., 2007, Srinivas and Pandey, 2012). However, in most cases, the negative effect is relatively small and acceptable compared with the improvements in other properties, especially given the low cost of heat treatment (Kamdem, Pizzi, et al., 2002). Besides, the negative effects can also be minimized by using optimal heat treatment conditions. To date, heat treatment is only limited to raw wood due to the lack of affordable and durable adhesives,

thus, not only the variety of end products are limited by the natural size of the wood, but also the benefits of plywood and heat treatment are severely restricted.

Plywood and other engineered wood represent great milestones in wood manufacturing, allowing us to fully utilize natural wood regardless of size or low grade wood (Sarin, Kent, et al., 1981). Conventional plywood and engineered wood are manufactured with hot press using petroleum-based adhesives such as urea formaldehyde (UF). UF is the most commonly applied synthetic adhesive in wood industry due to its low cost and high usability. However, UF adhesive would decompose when exposed to the high temperature used in heat treatment (Girods, Dufour, et al., 2008). This has restricted the application of heat treatment on engineered wood. UF and other formaldehyde based resins also pose pollution causing health issues and are increasingly rejected by customers and abandoned in industry (Cancer, 2007).

To sum up, if heat treatment can be applied on plywood, two existed products will be improved and have new applications. For plywood, it will gain similar features as heat treated wood with low cost and will have chance to be applied to new circumstances such as wet conditions. For heat treated wood, the end product will no longer be restricted by raw wood size.

A theoretical alternative to producing heat-treated plywood is to heat treat the wood veneers first and then bond the treated veneers using hot press (Song, Wei, et al., 2017). However, several issues make this approach infeasible in actual manufacturing. To start, the brittleness induced by heat treatment would make the veneers easy to crack. Secondly, wood density loss due to heat treatment will cause the veneer shrinking in thickness when hot pressed. Thirdly, wood surface chemistry changes due to heat treatment, including functional group loss and wettability change, will compromise glue performance (Hakkou, Pétrissans, et al., 2005).

Similar to heat treatment, baking happens in high temperature. In baking, proteins and reducing sugar engage in the Maillard reaction, which causes some degradation but increases protein crosslinks and strength (Román and Wilker, 2018, Zghal, Scanlon, et al., 2001). Proteins also have high degradation temperatures, for example, soy protein will not become decomposed until the temperature reaches 230 °C, which is beyond commonly heat treatment temperature (~200 ºC) used by industries (Wool and Sun, 2011). Since main obstacle for preparing heat treated plywood is the failure of adhesive, the qualified adhesive must have resistance to degradation and stable adhesion when heated. Bakery inspired us to apply protein based adhesive to prepare heat treated plywood.

Protein-based adhesives have been studied for decades, especially soy-based adhesives given the abundance and low cost of soy (Wool and Sun, 2011). These studies were initially motivated by the health concern of UF (Cancer, 2007). The main challenge facing the application of protein-based adhesives is water resistance (Sun and Bian, 1999) . Pristine grounded soybean flour mixed with water without any modification is able to bond wood with enough dry strength after hot press, but the plywood would delaminate when submerged in water due to weak water resistance that results in low wet adhesion strength (Frihart and Satori, 2013). Multiple modification methods have been investigated to improve protein adhesive wet strength. Among them, polyamide-epichlorohydrin (PAE), a wet strength agent used in paper industry, has been found to achieve good adhesion with relatively low cost and is already applied in the plywood industry (Li, Peshkova, et al., 2004). Previous study also showed that prolonged hot pressing can improve the wet shear strength of plywood bonded by protein-based adhesives.(Luo, Luo, et al., 2015)

In this study, we investigated the possibility of applying heat treatment to plywood made with protein-based adhesives. Three formulas of adhesives were used: PAE modified soy flour adhesive (PAE/SF) was used to represent commercial soybean adhesives; unmodified soy flour adhesive (SF) was used to represent reference and show the treatment effect without modification; and UF adhesive was used to represent traditional synthetic adhesives for comparison purpose.

3.3 Material and methods

3.3.1 Materials

PAE solution (12%wt) was purchased from Wuhu Hangchen Trading Co. Ltd (WuHu, China). UF powder adhesive was provided by Quality woodworking Co. Ltd (CT, USA). Soy flour was provided by Zhengzhou BIO Biological Co. Ltd (Zhengzhou China). Yellow pine wood veneers with dimensions of 300 mm × 300 mm × 1 mm (width × length × thickness) were provided by Veneer One (Oceanside, NY).

3.3.2 Preparation of adhesives

UF wood adhesive: 50g UF powder was mixed with 50g tap water using hand stirring at room temperature for 5 min to prepare the UF glue solution. The adhesive was used within 1 h.
PAE/SF adhesive: 100g of PAE solution (8%wt) was uniformly mixed with 50g soybean flour using hand stirring at room temperature for 5 min. The adhesive was used within 1 h.
SF adhesive: 81g water was uniformly mixed with 50g soybean flour using hand stirring at room temperature for 5 min. The content was made to achieve a similar solid content as the PAE/SF adhesive and with applicable viscosity and flowability. The adhesive was used within 1 h.

3.3.3 Preparation of three-layer plywood

Yellow pine wood veneers (300 mm × 300 mm × 1 mm) were preconditioned in a 23 °C, 30% RH chamber for one week. Three veneers were layered in such a way that the grain line

of the middle panel was perpendicular to the grain lines of the top and bottom panels. 20-21g/ft2 (wet basis) adhesives were brushed on the two faces of the middle veneer panel. The assembled wood specimen stood for 15 min before hot press. The hot press conditions were 110 °C for12 min at 1.03 MPa. Then the bonded three-layer wood specimens were conditioned in a chamber at 23 °C and 50% RH for two days. They were then cut into 10 small pieces (82.6 × 25.6 mm) for adhesion test (ASTMD906-98, 2017).

3.3.4 Heat treatment

Raw wood samples and plywood samples were dried at 105 °C for 5 h to remove moisture. The samples were then placed in an oven set to 190 °C or 200 °C. The oven, connected to a vacuum pump and nitrogen gas source, was vacuumed first and then filled with nitrogen gas. The samples were treated for 1 h, 1.5 h, 2 h, 4h, and 120 h. After heat treatment was completed, the samples were cooled in air and then stored in the chamber at 23 °C and 50% RH.

3.3.5 Mechanical strength and water resistance

Five small three-layer wood specimens were soaked in water at 23 °C for 24 h to test wet adhesion strength, and another five specimens were used to test dry adhesion strength. Both wet strength and dry strength were tested with an Instron Tester (Model 4465, Canton, MA) according to ASTM Standard Method D906-98 at a crosshead speed of 1.6 mm/min. Adhesion strength was recorded as stress at the maximum load.

The bending strength of wood samples was tested following ASTM D4761 using the Instron Tester. Plywood was cut into pieces of 150 mm × 30 mm × 4 mm, and raw wood was cut into 150 mm × 30 mm × 1 mm.

3.3.6 Thickness swelling and water absorption

The wood samples under each heat treatment condition underwent the process as regulated by ASTM 3503. Raw wood was cut into pieces of 10 cm × 4 cm × 1 mm and conditioned at 23 °C, 50 RH for 3 days until size stabilized according to the sizes being monitored. Samples were then soaked in water for 24 h and sizes were measured. They were then dried at 80 °C for 24 hours and measured again.

3.3.7 Scanning electron microscopy (SEM)

The surface morphology of the soy flour, adhesive films and rupture were observed with SEM (Hitachi S-3500N). The accelerating voltage was 10 kV. Prior to SEM, samples were dried and coated with gold/palladium in an argon atmosphere using a Balzers evaporator (model SCD 050, Baltec Lichtenstein, Austria). The film samples were prepared by hot pressing and drying adhesive slurries into films. And then film samples were heat treated and soaked by water respectively. The rupture samples were prepared by the breaking the films, and the cross section of the rupture images were observed on the rupture area.

3.3.8 Fourier-transform infrared spectroscopy (FTIR)

Heat treated soy protein isolates (200 °C for 2h) and untreated soy protein isolates were characterized by FTIR. Samples were dried at 90 °C for 1 h prior to FTIR. FTIR spectra were acquired using a PerkinElmer Spectrum 400 FT-IR/FT-NIR Spectrometer (Waltham, MA) over the 4000–400 cm^{-1} region at a resolution of 4 cm^{-1}.

3.3.9 Thermogravimetric analysis – mass spectrometry (TGA-MS)

The thermogravimetric analysis was carried out by TGA test (PerkinElmer, Norwalk, CT) in a nitrogen environment, provided an inert atmosphere during pyrolysis. The 5 mg samples were heated from 50 to 400 °C at a heating rate of 10 °C /min. Weight loss was detected and the

evolved gas was analyzed by tandem mass spectrometry (Discovery TGA-MS, TA instrument, Schaumburg, IL).

3.3.10 Differential scanning calorimetry (DSC)

The DSC thermal curves were characterized via differential scanning calorimeter (Q200, TA instrument, Schaumburg, IL). Samples (10 mg) of untreated and treated (200 °C for 2 h) SF were hermetically sealed in aluminum pans. Temperature was held at 20 °C for 1 min and then increased to 250 °C with a heating rate of 10 °C/min.

3.3.11 Ninhydrin test – Qualitative analysis of amino groups

Ninhydrin reagent reacts with amino groups and produces a blue color. The concentration of amino groups can be determined by changes in absorbance at 570 nm. Soy protein was heat treated for 5 min at 200 °C and then dissolved and diluted in water to make 600 μg/mL sample solution. 1 mL ninhydrin reagent solution was mixed with 2 mL sample solution and placed in a boiling water bath for 10 min. The sample was then cooled down and mixed with 5 ml 95% ethanol. Absorbance was read at 570 nm. The same process was repeated using 2 mL water to replace the soy protein sample as a reference. Compared with the standard curve (glycine solution was used to make the standard curve c=0.17708abs-0.00046, R2=0.9927, c: concentration of amino groups, abs: absorbance), the concentration of amino groups was determined.(Moore, Spackman, et al., 1958),(Sarin, Kent, et al., 1981)

3.3.12 Water soaking test

Two different adhesives (SF and PAE/SF) were used to make films in pans. Two grams of adhesive slurry was placed in the pan and cured at 110 °C for 30 mins. Curing time was longer than that used in hot press because there was no pressing and the samples were much thicker than

actual adhesive layers between veneers. The samples then went through different heat treatments. After cooling down, the pans were soaked in water for 1 h and dried in oven at 100 °C for 24 h.

Weight loss in water soaking can be calculated as

$$\text{Weight loss}=\frac{W_i-W_f}{W_i-W_g}$$

where Wg is the weight of the pan, Wi is the weight of the pan and cured adhesive film, and Wf is the weight of the pan and adhesive film after soaking and drying.

3.3.13 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was performed with a DMA (Q800 New Castle, DE) using a tension mode at a frequency of 1 Hz and an amplitude of 5μm. The dynamic mechanical properties, moduli and glass transition of the adhesive films were obtained by heating from room temperature to 250 °C at 3°C/min in the atmosphere of nitrogen gas. The measurements were within the linear viscoelastic region of the films.

3.4 Results and discussion

3.4.1 Adhesion strength

PAE/SF and SF adhesives were selected to make three-layer plywood to compare how chemical modification of soy flour affects plywood performance in heat treatment. UF adhesive was used to show to what extent heat treatment can delaminate traditional plywood. To investigate protein-based adhesive durability under heat treatment, different treatment times and temperatures were used. As shown in Figure 3.1(a), the dry and wet strength of untreated UF plywood were 2.22 MPa and 2.0 MPa, respectively. While, after heat treatment at 190 °C for 1 h, dry strength of UF adhesive reduced to 1.86 MPa and wet strength to 1.85 MPa, and further, the dry strength of

UF adhesive reduced to 1.30 MPa and wet strength to 0.82 MPa when heat treatment lasted for another 0.5 h. It was also noticed that UF plywood bended considerably when coming out of the oven, making the plywood unacceptable as a product. This bending should be caused by the UF resin melting and then curing after cooling down. In addition, once the UF plywood was treated at 190 °C for 2 h or 200 °C for 1.5 h, 2 h, and 4 h, the plywood samples became completely delaminated as 3 layers of separated veneers, demonstrating complete loss of adhesion and cohesion.

The PAE/SF formula showed good dry and wet strength under all heat treatment conditions (Figure 3.12, Figure 3.1 (b)). Particularly, the wet strength of PAE/SF plywood was improved from 1.33 MPa to 1.74 Mpa after heat treatment at 190 °C for 1 h (Figure 3.1(b)), and then reduced to 1.2 MPa when treatment temperature increased to 200 °C for 4 h. Among the tested samples, wood failure was observed for most of the fractures, and wood failure become dominated as treatment time and temperature increased. The only trade-off of the heat treatment is that the dry strength of PAE/SF plywood was reduced from 1.93 MPa (untreated sample) to 1.36 MPa (treated sample) at 200 °C for 2 h (Figure 3.12) but this is still relatively high for plywood to meet industry requirements.

Untreated SF adhesives have shown acceptable dry strength but unacceptable wet strength (Lorenz, Birkeland, et al., 2015). Accordingly, in our study, SF plywood had 1.75 MPa dry strength but no wet strength as all samples delaminated after being submerged in water (Figure 3.1(b), Figure 3.12). However, after heat treatment, SF plywood showed surprisingly increased wet strength up to 1.05 MPa at 190 °C for 1 h and 1.31 MPa at 190 °C for 2 h (Figure 3.1(b), Figure 3.12). As treatment continued, wet strength decreased, as did dry strength. Thus, contrary to its effect on synthetic adhesives, heat treatment did not decrease but could actually increase the

adhesion strength of protein-based adhesives, especially their wet strength. According to Figure 3.1(b), whether the treatment temperature is 190 °C or 200 °C, PAE/SF plywood had highest wet adhesion strength after 1 h treatment. However, SF plywood reached highest wet strength of 1.31 MPa at 190 °C for 2 h and 1.48 MPa at 200 °C for 1.5 h. PAE already modified SF by crosslinking before treatment, so short time of heat treatment improved PAE/SF adhesion but longer treatment didn't make further increase. For unmodified SF, it took longer treatment to crosslink and reach the highest wet adhesion strength. To examine how samples endure extreme conditions in heat treatment, SF plywood was treated at 200 °C for 120 h, and it was still strong with a dry strength of 1.46 MPa and wet strength of 0.98 MPa (Figure 3.12), though it has a very dark color. By contrast, there was considerable wood failure in extremely treated samples. This result shows that SF can withstand extreme heat treatment with acceptable decrease in adhesion.

3.4.2 Bending strength and tensile strength

Previous study has shown that heat treatment can make wood more rigid and brittle (Ennos and Chan, 2016) To evaluate this effect, we tested heat-treated raw wood and plywood for bending and tensile strength in parallel comparison. The raw wood samples went through the same heat treatment process as used for PAE/SF plywood. Bending strength of the raw wood decreased as heat treatment time and temperature (Figure 3.2), from 120 MPa without heat treatment to 104 MPa treated at 200°C for 4 h. The tensile strength of untreated raw wood perpendicular to the wood grain was 7.15 MPa, and reduced to 6.0 MPa treated at 200 °C for 4 h, however, there is no significant change of wet tensile strength after 24 h submerged in water (Figure 3.3). This 13% loss in bending strength and 8.4% loss in dry tensile strength are considered not significantly to affect the quality of plywood products undergoing heat treatment at 200 °C for 4 h, however, in this study, the optimal heat treatment conditions for plywood is found at 200 °C for 2 h.

3.4.3 Wood swelling and color

Swelling property, enhanced by heat treatment, is an obvious quantitative quality property of the heat treated plywood.. As heat treatment temperature and time increased, thickness swelling decreased from 8% for untreated wood to 5.75% after treated at 200 °C for 2 h (Figure 3.4). As plywood thickness swelling restricts its application in some cases (e.g., furniture, floor), heat treatment can be an advantageous modification method. In addition, when wood samples were submerged in water for 1 h, the swelling of heat treated wood samples was not significant among the samples with treatment intensity from at 190 for 1.5 h to at 200 for 2 h (FIGURE 4(b)) compared with the original dimension of the raw wood before soaking. (redo the experiments and add the original length)

According to literature, heat treatment changed wood color (Guller, 2012) . The colors of untreated and treated raw wood are shown in Figure 3.6 In accordance with previous studies, wood samples became darker as treatment time and temperature increased (Patzelt, Emsenhuber, et al., 2003) . Therefore, color darkness induced by heat treatment can be controlled by tuning treatment time and temperature.

3.4.4 Adhesive film soaking test

Water resistance was further examined by using film weight loss in water soaking test. Heat-treated samples showed smaller weight loss indicating stronger water resistance (Figure 3.7). After 1 h of water soaking, the weight loss of SF film was significantly reduced from 25% weight loss (untreated) to about 10% and 5% treated at 190 °C and 200 °C, respectively, regardless treatment time tested in this study. These results indicated that heat treatment temperature has a significant effect on water resistance. The untreated PAE/SF film had 7.3% weight loss, which is

much lower than that of the untreated SF, showing the effect of PAE in improving water resistance (Figure 3.7). As for water resistance, heat treatment effects on SF plywood is in the similar way to how PAE modification did, which corresponds with the wet strength data presented above.

3.4.5 Dynamic mechanical analysis (DMA)

DMA tests were conducted on SF and PAE/SF films. Crosslink degree was calculated based on the relative calculation method used by Li et al (Li, Li, et al., 2016). The results are shown in Table 3.1. With longer treatment time and higher temperature, SF and PAE/SF films exhibited increased glass transition temperatures from 182 ºC to 202 ºC and 156 ºC to 184 ºC respectively (Bengoechea, Arrachid, et al., 2007), which indicates more crosslinked amorphous structures. Untreated SF had a crosslink density of 1.85 and untreated PAE/SF had a crosslink density of 2.77, correlating with our understanding that PAE improves crosslinking the proteins presented in SF. These findings suggest that heat treatment had a similar effect as PAE in crosslinking proteins. Chemical changes that happen during heat treatment may crosslink protein chains and improve water resistance.

3.4.6 TGA and TGA-MS

TGA gives information about thermal properties and the derivative thermogravimetry (DTG) curves of untreated and treated SF are shown in Figure 3.8. Untreated SF had two peaks at around 250 °C and 310 °C (Figure 3.8(a)), respectively, and treated SF at 200 °C for 2 h had only one peak at 310 °C (Figure 3.8(b)). The disappearance of the peak at 250 °C of the treated SF indicates that the SF became partially decomposed during heat treatment at 200 °C for 2 h. As shown in Figure 3.8(a), such decomposition started from around 190 °C, therefore, some chemical compositions of SF should be decomposed undergoing heat treatment at 200 °C for 2 h. This may explain that the adhesion strength decreased as heat treatment duration increased (Figure 3.8(b)).

Based on Figure 3.8(a), about 80% mass content of SF remained intact until temperature reached 250 ºC, which suggesting SF has enough thermal resistance to decomposition at 190°C and 200°C ensuring the strength of protein-based adhesives after heat treatment.

The evolved gas of heated soy protein isolates detected by MS in Figure 3.8(c) depicted the lost mass composition of protein during heat treatment. Evolved water (18 AMU) had two peaks: the originally existed moisture evaporated before 120 °C, and a vapor peak appeared again around 160 °C, which should be water created by heat treatment reactions. The evolved CO_2 (44 AMU) increased around 220 °C, corresponding with the weight loss peak in TGA graph (Figure 3.8(c)) and indicating the degradation. Therefore, temperature from 160 °C to 220 °C should be the theoretical range of heat treatment for protein based adhesive so as to induce the crosslinking and functional groups changes without degradation.

3.4.7 DSC

DSC was used to characterize the thermal transitions of SF and treated SF. Dry SF powder was heat treated at 200°C for 2h and then conditioned. Untreated and treated SF were scanned using DSC at temperatures ranging from room temperate to 300 °C. The thermographs are shown in Figure 3.9 Untreated SF showed denaturation peaks of 7S at around 145 °C and 11S at 197 °C. Treated SF exhibited denaturation peaks of 7S at 130 °C and 11S at 190 °C. Treated SF had a broader peak for 11S. Covalent bond crosslinking and other permanent structural changes induced by heat treatment may lead to the lower denaturation temperature and broader peaks. At 170 °C and 200 °C, the untreated and treated protein had glass transition curve, respectively. Which correspond to the glass transition temperature observed in DMA test (Table 3.1)

3.4.8 SEM

SEM imaging were used to observe the morphology of untreated and treated SF powder (200 °C 2h) as shown in Figure 3.10. Untreated SF powder exhibited a rough and porous surface (Figure 3.10(a)), while treated SF powder had a more globular shape and smooth surface (Figure 3.10(a)), indicating that heat treatment changed the surface morphology of SF powder. Denaturation, decomposition, and recrystallization of proteins and polysaccharides would happen in the heat process and hence may induce these changes in surface morphology. Once the SF was made into film by hot press at 110°C for 10 min for untreated SF, and at 200°C for 2h for heat treated SF, the cross section of the untreated SF film had a smooth rupture surface (Figure 3.10(b)) indicating a brittle material, while the cross section of the treated SF film had a rough surface with porous structures (Figure 3.10(b)), indicating a tough material resulted from possible crosslinking and entanglement between proteins or polysaccharides during heat treatment. However, after soaking in water for 1 h, the cross section of the untreated SF film exhibited a porous and rough surface due to water uptakes (Figure 3.10(c)) while the treated SF film remained relatively smooth (Figure 3.10(c)), indicating heat treatment improved water resistance.

3.4.9 FTIR

The FTIR was used to examine the chemical changes in soy protein during heat treatment (Figure 3.11). Since soy flour has other contents such as lipids and polysaccharides, soy protein isolate was used for FTIR characterization. For untreated soy protein, the characteristic absorption peaks were at 3000–3500 cm^{-1} (O–H stretching and N–H bending), 2925 cm-1 (C–H stretching), and 1640 cm^{-1} (secondary amide) (González, Strumia, et al., 2011). Compared with treated soy protein, untreated soy protein exhibited an extra peak at 1060 cm^{-1}. This could be the stretching vibration of C-N of amino groups or C-O of hydroxyl groups (Roeges and Baas, 1994).

The disappearance of this peak in treated SF may indicate loss of hydroxyl groups and amino groups. In treated SF, a new peak appeared at 1165 cm^{-1}, which could be the stretching of C-O-C, indicating newly created ether structures (Tarantilis, Beljebbar, et al., 1998). After treatment, the peak at 1615 cm^{-1} to 1710 cm^{-1} became higher, which could be caused by the loss of hydroxyl groups or new C=C stretching vibration. According to previous study, the stretching vibration of S-S is weak and appearing around 400-500 cm^{-1}, but the at around 2600 cm^{-1}, the untreated sample showed more stretching vibration of S-H, indicating the heat treatment may transfer some S-H bonds to S-S and forming crosslink (Mittler, Yamada, et al., 1994). The evolved water detected in TGA-MS could have come from the vapor provided by forming new amide groups, ether groups, and hydroxyl group loss.

3.4.10 Qualitative analysis of amino groups

Concentrations of amino groups in untreated and treated soy protein were determined using ninhydrin tests. Compared with untreated soy protein, soy protein treated at 200 °C for 5 min lost 14.6% amino groups. This supports our FTIR analysis (Figure 3.11) of amino group loss after heat treatment, which corresponds with Jessica K. Román et al's finding that lysine may be important in protein crosslinking (Román and Wilker, 2018).

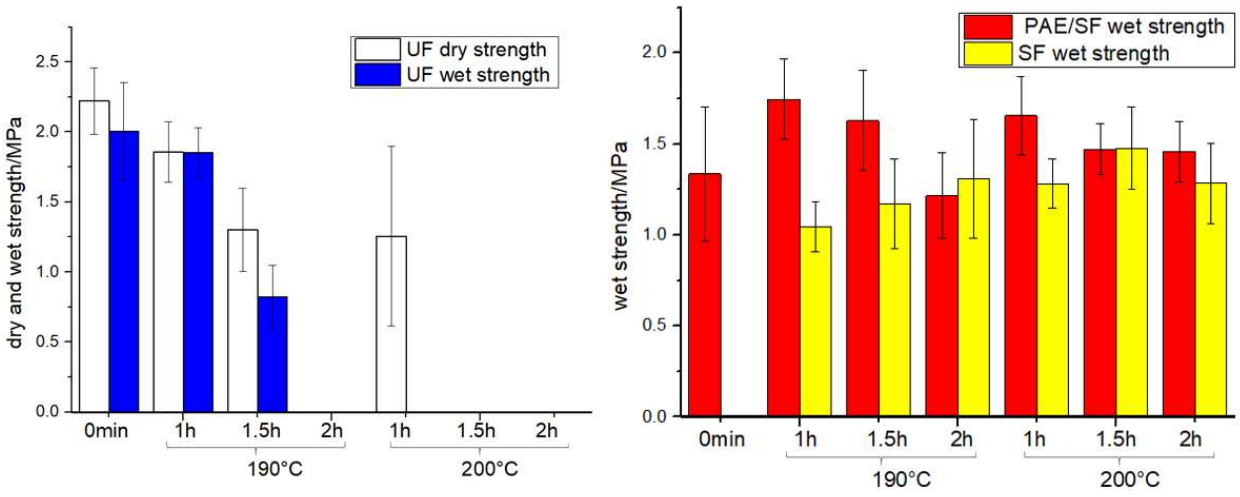
3.4.11 Discussions

We suspected that soy protein might be the key contributor to the wet adhesion strength of SF after heat treatment, we examined the wet adhesion strength of soy protein isolates (SPI) for plywood and treated at 200 °C for 2 h. As Figure 3.12 shows, SPI plywood had low wet adhesion strength of almost zero wet strength before heat treatment and then high wet adhesion strength of 1.23 MPa after heat treatment.

According to the results, the protein denaturation, some functional group change, crosslinking and newly formed water-resistant structure such as melanoidin helped the improvement of wet adhesion of protein based adhesive after heat treatment.

3.5 Conclusion

Plywood glued with protein based adhesives, such as unmodified soy flour (SF), demonstrated superior improvement in wet adhesion strength after heat treatment. For example, heat treated SF plywood achieved wet strength of 1.28 MPa at 200 °C for 2 h with acceptable loss in bending and tensile strength, while plywood made from UF adhesive become completely delaminated during heat treatment. The wet adhesion strength of SF improved by heat treatment is about equivalent as the effects made by PAE modification. Protein plays a key role in heat treatment attributing to wet adhesion due to its crosslinking reaction and reduction of hydrophilic functional groups (i.e., hydroxyl and amino). Heat treatment temperature and time are two important variables influencing adhesion strength and plywood mechanical properties and color. In addition, Maillard reaction attributing to covalent bonds and melanoidin formation also improved water resistance of SF adhesives. Other nonfood plant protein based flours should be applicable for heat treated plywood production.



(a) (b)

Figure 3.1 Dry and wet strength of 3-layer plywood made with UF adhesive, treated under different conditions (a). Wet strength of plywood made with SF and PAE/SF adhesives, treated under different conditions (b). UF plywood didn't survive heat treatment. PAE/SF plywood remained strong after heat treatment, while SF plywood gained wet strength.

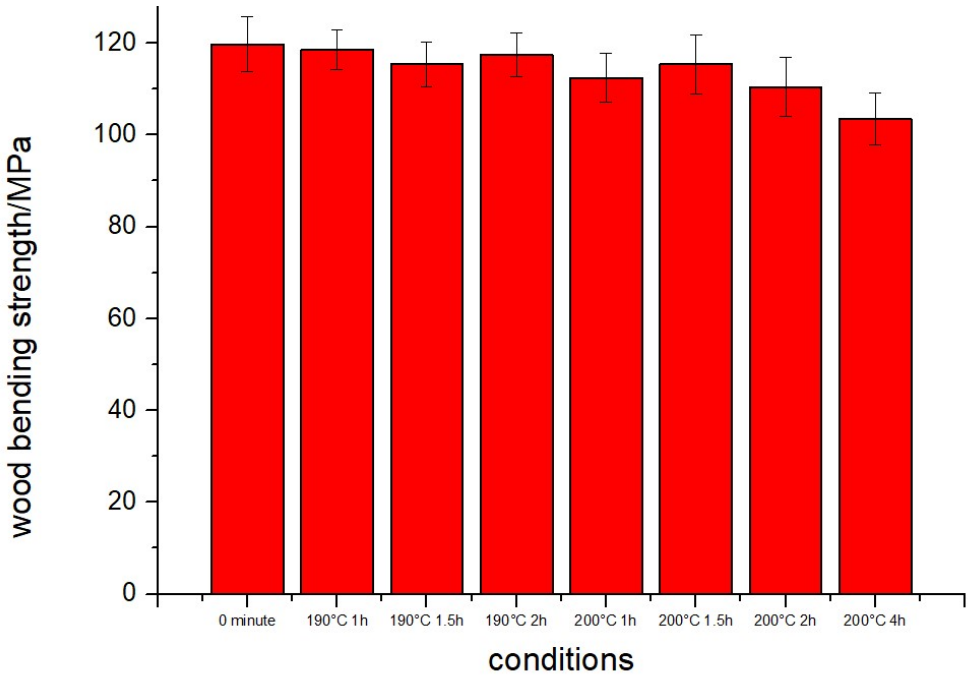


Figure 3.2 Bending strength of raw wood with different heat treatments (stress parallel to grain). Longer treatment time and higher temperature induced weaker bending strength, but the amount of decrease is acceptable.

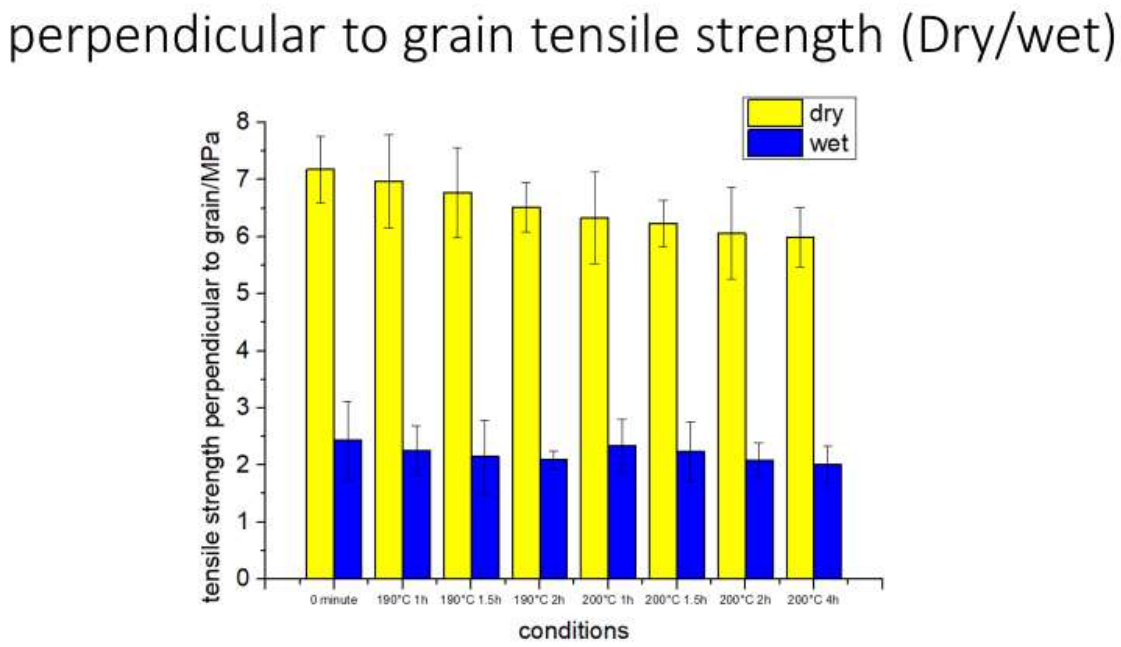


Figure 3.3 Tensile strength of raw pine wood perpendicular to the wood grain. Wood was heat treated with different times and temperatures. Heat treatment reduced tensile strength, but the amount of decrease is acceptable

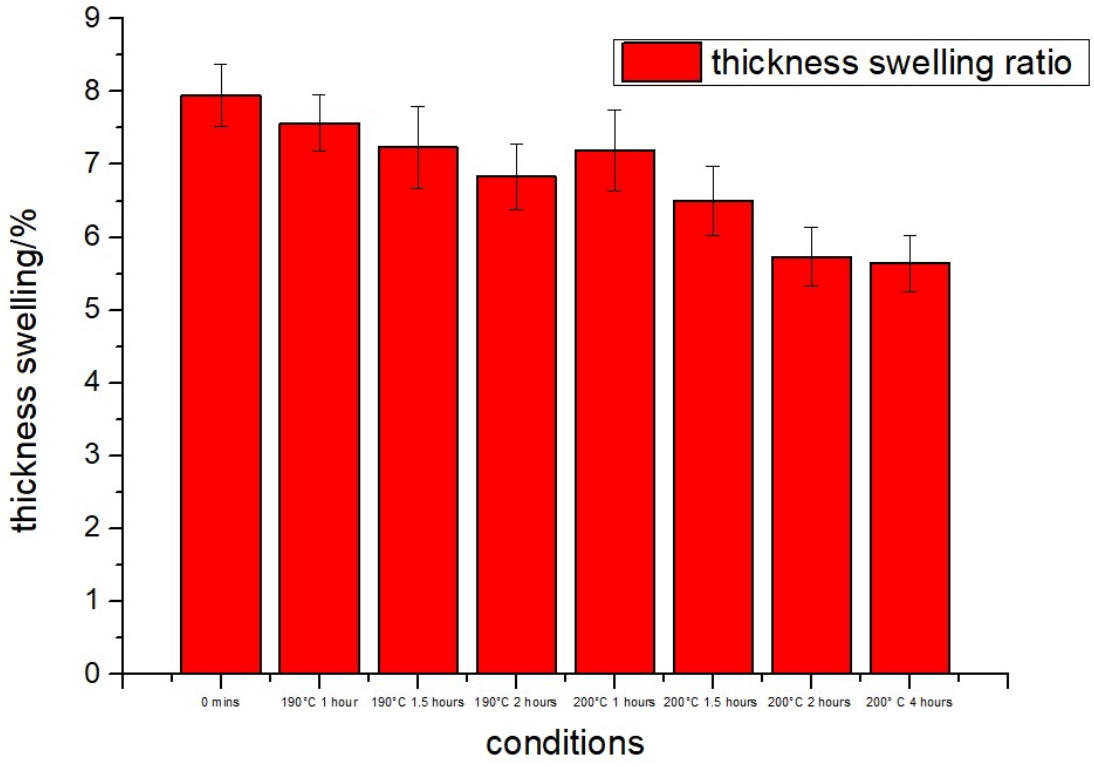


Figure 3.4 Thickness swelling of untreated and treated raw pine wood. Longer treatment time and higher temperature induced lower thickness swelling.

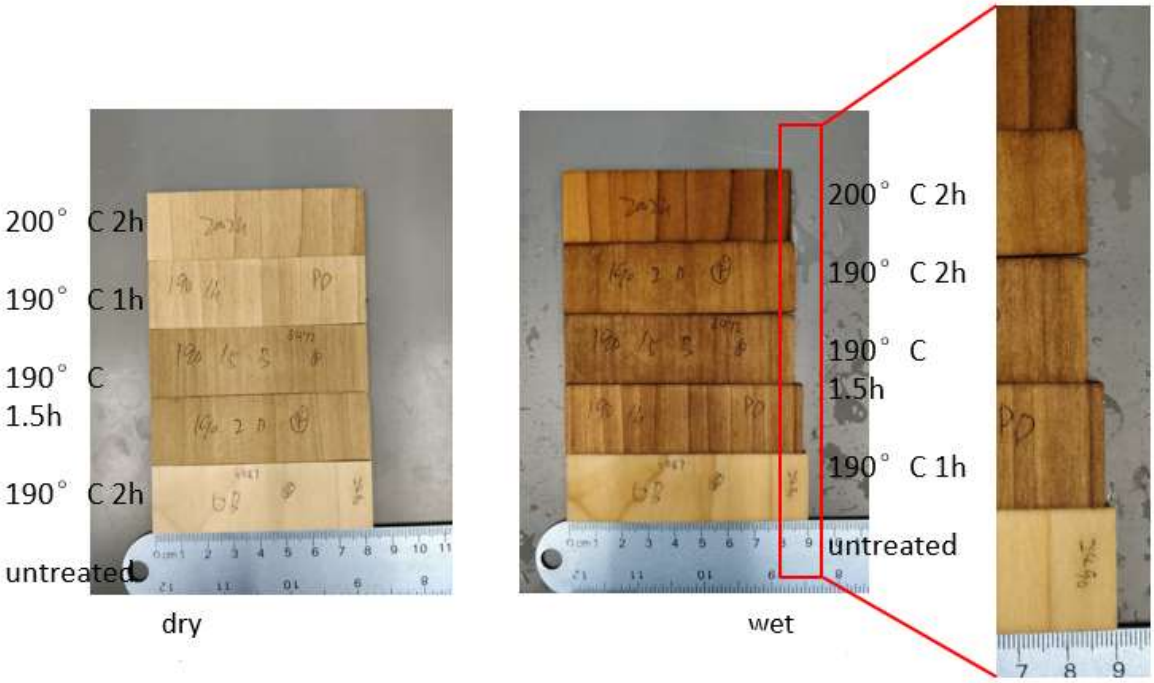


Figure 3.5 Swelling along the direction perpendicular to the wood grain of raw wood samples. Samples were submerged in water for 1 hour.

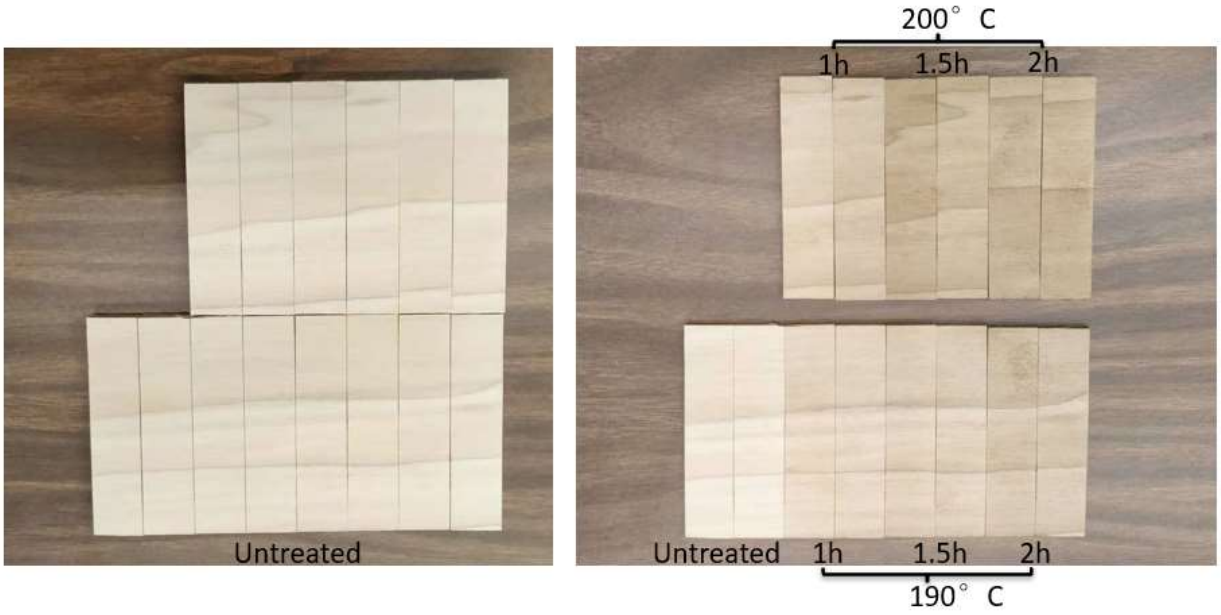


Figure 3.6 Wood color change induced by heat treatment. Longer treatment time and higher temperature induced darker colors.

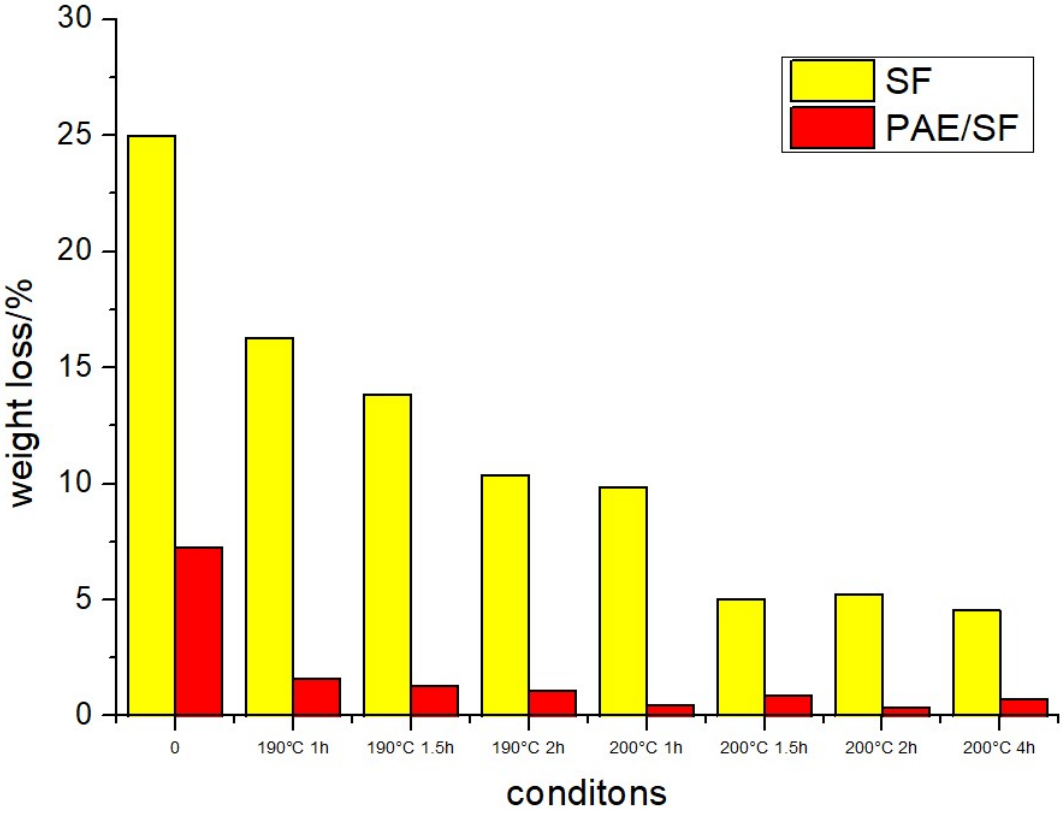


Figure 3.7 Weight loss of SF and PAE/SF film with different treatments after soaking. Longer treatment time and higher temperature made both SF and PAE/SF film more resistant to water soaking.

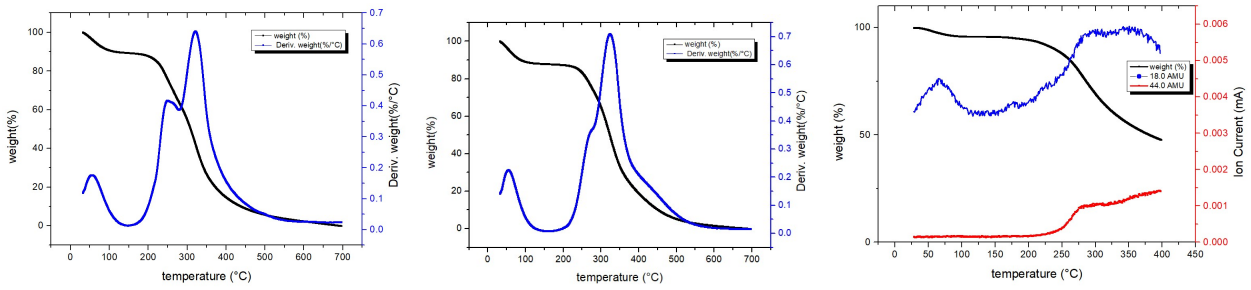


Figure 3.8 Thermogravimetry (TGA) thermal scanning and derivatives of untreated SF (a) and treated (200 °C 2h) SF (b) at 10 ºC/min interval. Thermal scanning and mass spectrum curves (TGA-MS) of evolved gas of soy protein (c).

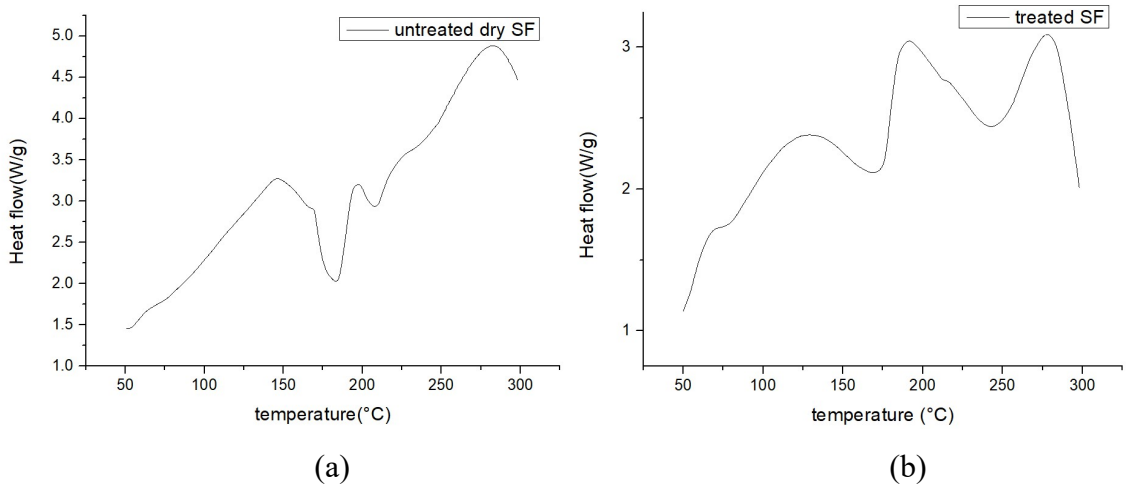
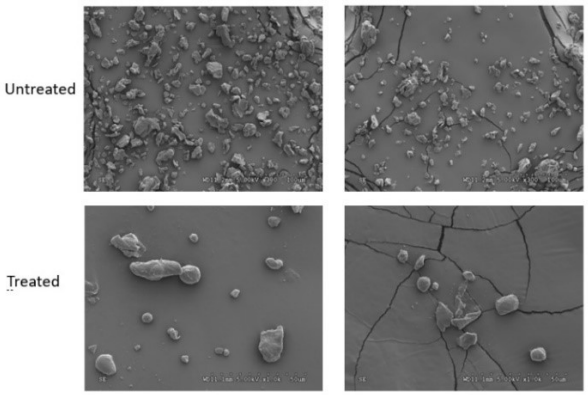
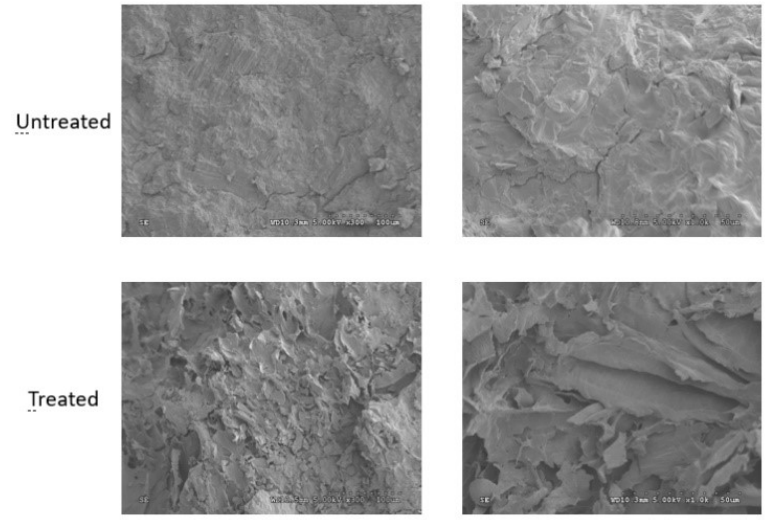


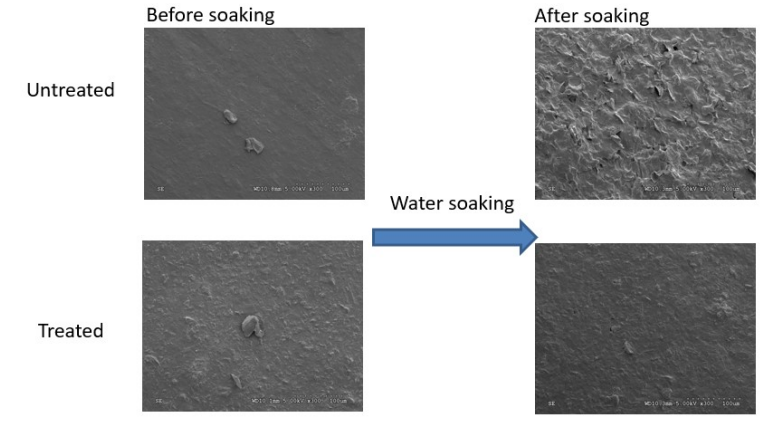
Figure 3.9 DSC thermographs of untreated SF(a) and treated SF(b).



(a)



(b)



(c)

Figure 3.10 SEM images of untreated and heat-treated SF powder (a). Cross-section SEM images of untreated and treated SF film (b). SEM images of SF film surfaces (c). Heat treatment was 200 °C for 2 hours.

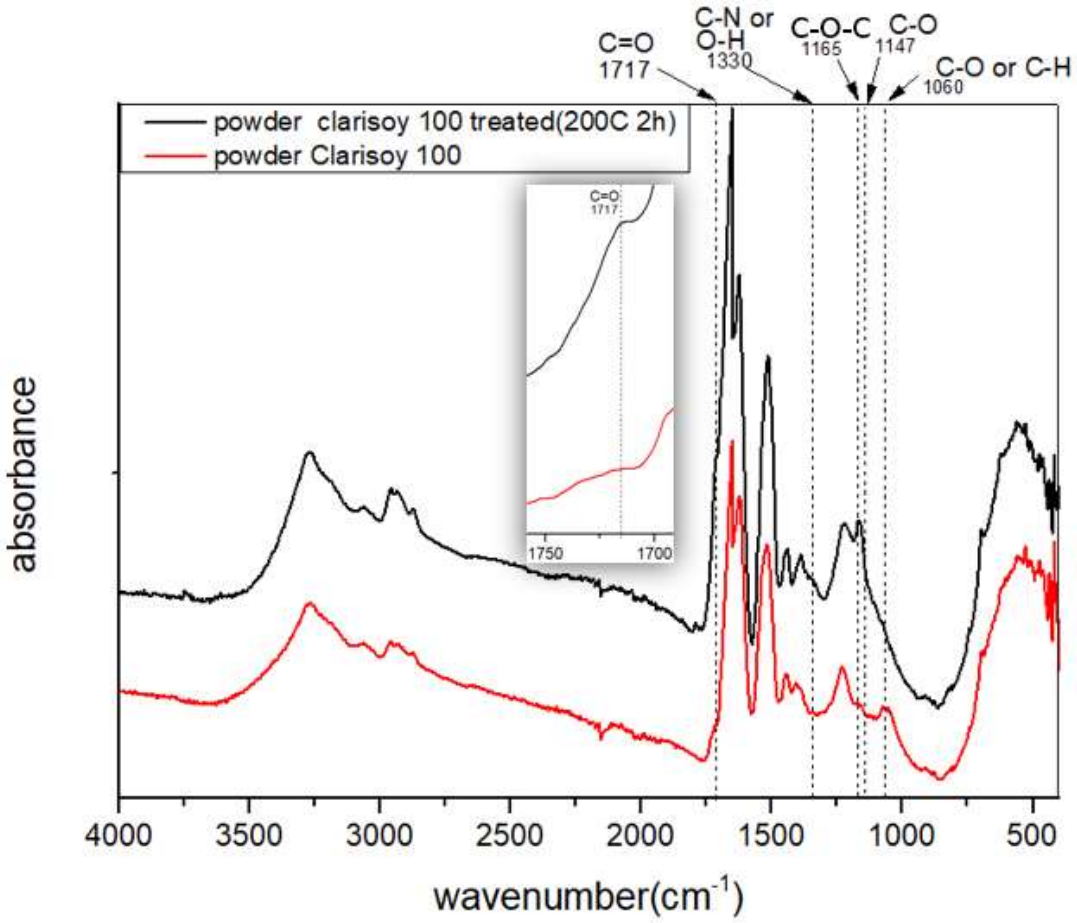


Figure 3.11 FTIR spectrometry of untreated and treated soy protein. Heat treatment was 200 °C for 2 hours.

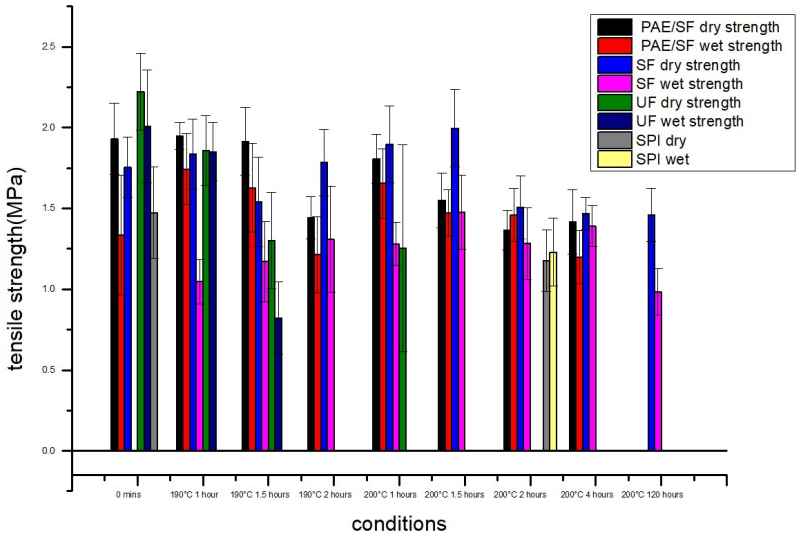


Figure 3.12 Complete adhesion strength data. Dry strength and wet strength of 3-layer plywood made with SPI, SF, PAE/SF, and UF adhesives, treated under different conditions.

Table 3.1 Crosslink densities of SF and PAE/SF films with different treatments, determined by DMA sweep.

Sample	Tg/ °C	E' (Tg+40 °C)/MPa	Crosslink density Ve = E'/3RT (10^3 mol • m^{-3})
SF	182	22.84	1.85
SF 190°C 2h	195	24.9	1.97
SF 200°C 2h	202	26.88	2.09
PAE/SF	156	32.46	2.77
PAE/SF 190°C 2h	163	54.96	4.63
PAE/SF 200°C 2h	184	64.32	5.19

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Chapter 4 – Developing Low Cost Soybean-Based Adhesives for Heat-Treated Plywood with Lignin

4.1 Abstract

Lignin as a low-value byproduct polymer had received attention, and adhesives are one potential application for it. The objective of this research is to develop low cost soy-based adhesives using lignin and optimize the amount of lignin contents to add into the soybean flour (SF) adhesive formula. The pH of the lignin-SF slurry was adjusted to investigate how pH affects adhesion after heat treatment and explore if adjusting the pH allows more lignin content in the adhesive formula. Lignin at 50% content ratio was found to be the maxium that can be added into the formula with a wet strength of 1.31 MPa for treated plywood. Lignin25%-SF75% was found acceptable for practical application with a wet stregnth of 1.43 MPa. The adhesive films were charaterized, and the interactions between soy flour and lignin were studied.

4.2 Introduction

Lignin comes mostly from the cell wall in plants and so is a renewable biomass (Sarkanen and Ludwig, 1971). As a byproduct of the paper pulping and biofuel industry, lignin is considered to have relatively low value. Lignin usually comprises three subunits including H, G and S, all of which posses many phenol groups and hydroxyl groups. Lignin is one of the most abundant aromatic polymers, with functional groups of carbonyl, methoxyl, phenolic hydroxyl, and alcoholic hydroxyl groups. Given these functional groups, many efforts were made to explore the application of lignin, including transforming lignin into adhesives (Ghaffar and Fan, 2014, Pradyawong, Qi, et al., 2019). In most cases, lignin is added as modifiers for protein-based adheisves and the amount added is limited. The phenolic structure of lignin gives it the potential to function similarly as penol-formadehyde (PF) resins. The lignin polymer with aromatic and crosslinked structures has similarity with the phenol formaldehyde network. Synthetic PF resins are made from fossil fuel and have been successfully applied in the wood indursty as a commericial adhesive. Previous work has converted lignin to adheisves to replace phenol-formaldehyde resins (Nada, Abou‐Youssef, et al., 2003). Lower molecular weight fractions of lignin provide better adhesion (Liu, Qiu, et al., 2008). Since heat treatment can degrade lignin and produce smaller molecule contents, this method may increase the adhesion of lignin (Wu, Xi, et al., 2019).

Lignin has a competitive thermal stablity compared with those of other synthetic resins, allowing it to undergo heat treatment without decomposition (Zhang, Resende, et al., 2012). Heat treatment may degrade some parts of lignin into smaller molecule contents, but limited temperature such as 200 °C will not make lignin subunits undergo total pyrolysis (Brebu and Vasile, 2010). When lignin is heat treated with protein or soy flour, heat treatment may also help bond the protein

and lignin content. Phenol formaldehyde acts similarly when added in protein adheisves as a crosslinker.

Heat- treat wood presented many better properties than raw wood, such as durability, mechanical properties and resistance to termites and fungus (Esteves and Pereira, 2009, Homan and Jorissen, 2004). In previous studies, soy flour adhesive was applied to heat heat-treated plywood and exhibited unexpected robust adhesion against moisture. Since the water resistance of the treated plywood is so stronger than the untreated, and additions of small amounts of lignin may help water resistance, in this study, the most content ratio of lignin that can be added was investigated. S so as to mostly decrease the cost of the adhesive for heat treatment application by utilizing lignin content.

The solubility of lignin in water varies depending on pH values. Solubility of lignin is low at a pH of 7 and greatly increases when pH increases. When pH reaches 8, lignin solubility almost doubles (Helander, Theliander, et al., 2013). The pH also influences the diffusion and interaction between lignin and soy flour. Alkali treatment is a common method to improve the digestiblity of lignin in the paper industry (Hartler and Ryrberg, 1985). It also changes the functional groups of lignin and the morphology of soy protein. With sodium hydroxide as a modifier, soy protein based adhesives were found to perform better in the alkaline condition (Sun and Bian, 1999).

In previous studies, soy flour adhesives were used on heat-treated plywood and exhibited robust adhesion against moisture. Since additions of lignin can help improve water resistance, in this study, the content ratio of added lignin was investigated with the aim to decrease the cost of the adhesive for heat treatment applications.

4.3 Material and methods

4.3.1 Materials

Soy flour was provided by Zhengzhou BIO Biological Co. Ltd (Zhengzhou China). Yellow pine wood veneers with dimensions of 300 mm × 300 mm × 1 mm (width × length × thickness) were provided by Veneer One (Oceanside, NY). Kraft Lignin (no. 370959) was purchased from Sigma-Aldrich, Inc. (St. Louis, MO).

4.3.2 Preparation of adhesives

25%LG-75%SF adhesive pH7 (SF): 81g water was uniformly mixed with 37.5g soybean flour and 12.5g lignin, and the slurry was stirred at room temperature for 30 min. The adhesive was used within 1 h.

25%LG-75%SF adhesive pH8 (SF): 81g water was uniformly mixed with 37.5g soybean flour and 12.5g lignin. Sodium hydroxide (30%w) was added to adjust the pH of the slurry to 8, and the slurry was stirred at room temperature for 30 min. The adhesive was used within 1 h.

25%LG-75%SF adhesive pH8-7 (SF): 81g water was uniformly mixed with 37.5g soybean flour and 12.5g lignin. Sodium hydroxide (30%w) was added to adjust the pH of the slurry to 8, and the slurry was stirred at room temperature for 30 min. HCl (30%w) was then used to adjust the pH to 7, and the slurry was stirred for 30 min. The adhesive was used within 1 h.

4.3.3 Preparation of three-layer plywood and adhesive films

Yellow pine wood veneers (300 mm × 300 mm × 1 mm) were preconditioned in a 23 °C, 30% relative humidity (RH) chamber for one week. Three veneers were layered in such a way that the grain line of the middle panel was perpendicular to the grain lines of the top and bottom panels. 20-21g/ft2 (wet basis) adhesives were brushed on the two faces of the middle veneer panel. The assembled wood specimen stood for 15 min before hot press. The hot press conditions were

110 °C for 12 min at 1.03 MPa. The bonded three-layer wood specimens were then conditioned in a chamber at 23 °C and 50% RH for two days. They were then cut into 10 small pieces (82.6 × 25.6 mm) for adhesion tests (ASTMD906-98, 2017).

Adhesive slurries were hot pressed into films at 110 °C for 12 min and cured at 110°C for 30 min. Some of the films were then heat treated at 200 °C for 2h. Both the treated and untreated films were charaterized as detailed below.

4.3.4 Heat treatment

Plywood samples and adhesive films were dried at 105 °C for 5 h to remove moisture. The samples were then placed in an oven set to 200 °C. The oven, connected to a vacuum pump and nitrogen gas source, was vacuumed first and then filled with nitrogen gas. The samples were treated for 2 h. After heat treatment was completed, the samples were cooled in air and then stored in the chamber at 23 °C and 50% RH.

4.3.5 Mechanical strength and water resistance

Five small three-layer wood specimens were soaked in water at 23 °C for 24 h to test wet adhesion strength, and another five specimens were used to test dry adhesion strength. Both wet strength and dry strength were tested with an Instron Tester (Model 4465, Canton, MA) according to ASTM Standard Method D906-98 at a crosshead speed of 1.6 mm/min. Adhesion strength was recorded as stress at the maximum load.

4.3.6 Scanning electron microscopy (SEM)

The surface morphology of the films was observed with SEM (Hitachi S-3500N) at an accelerating voltage of 10 kV. Adhesive slurries were hot pressed into films and dried. Some of the films were heat treated at 200 °C for 2h. Some of the untreated samples were soaked with water

and dried. Prior to SEM, samples were dried and coated with gold/palladium in an argon atmosphere using a Balzers evaporator (model SCD 050, Baltec Lichtenstein, Austria).

4.3.7 Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra were acquired using a PerkinElmer Spectrum 400 FT-IR/FT-NIR Spectrometer (Waltham, MA) over the 4000–400 cm^{-1} region at a resolution of 4 cm^{-1}. Adhesive slurries were hot pressed into films and dried. Some of the films were heat treated at 200 °C for 2h. The treated and untreated films were then characterized by FTIR. Samples were dried at 90 °C for 1 h prior to FTIR.

4.3.8 Thermogravimetric analysis and mass sprectrometry

Thermogravimetric analysis was made via TGA tests (PerkinElmer, Norwalk, CT) in a nitrogen environment, which provided an inert atmosphere during pyrolysis. 5 mg samples were heated from 50 to 400 °C at a heating rate of 10 °C /min. Weight loss and derivative weight loss were detected.

4.3.9 Differential scanning calorimetry (DSC)

The DSC thermal curves were characterized using a differential scanning calorimeter (Q200, TA instrument, Schaumburg, IL). Samples (10 mg) of untreated and treated (200 °C for 2 h) SF were hermetically sealed in aluminum pans. Temperature was held at 20 °C for 1 min and then increased to 250 °C with a heating rate of 10 °C/min.

4.3.10 Water soaking test

Two different adhesives (SF and PAE/SF) were used to make films in pans. Two grams of adhesive slurry was placed in the pan and cured at 110 °C for 30 mins. Curing time was longer than that used in hot press because there was no pressing and the samples were much thicker than

actual adhesive layers between veneers. The samples then went through different heat treatments. After cooling down, the pans were soaked in water for 1 h and dried in oven at 100 °C for 24 h.

Weight loss in water soaking can be calculated as

$$\text{Weight loss}=\frac{W_i-W_f}{W_i-W_g}$$

where W_g is the weight of the pan, W_i is the weight of the pan and cured adhesive film, and W_f is the weight of the pan and adhesive film after soaking and drying.

4.3.11 Viscosity of adhesive slurry

The adhesive slurry was diluted to 30%w, and the apparent viscosity was tested at 25 s^{-1} shear rate for 150s by a Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA). The samples were sheared between parallel 20mm plates with a 500 μm gap. A few drops of silicon oil were used to cover the sample to prevent evaporation during the test. The strain was restricted to 1% to ensure measurements were within the linear viscoelastic region.

4.3.12 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was performed with a DMA machine (Q800 New Castle, DE) using the tension mode at a frequency of 1 Hz and an amplitude of 5μm. The dynamic mechanical properties, moduli, and glass transition of the adhesive films were obtained by heating the films from room temperature to 250 °C at 3°C/min in an atmosphere of nitrogen gas. Measurements were within the linear viscoelastic region of the films.

4.4 Results and discussion

4.4.1 Adhesion strength

As shown in Figure 4.1, the dry strength of untreated 25%LG-75%SF plywood was 1.75 MPa, and the wet strength was 0. After heat treatment at 200 °C for 2 hours, 25%LG-75%SF adhesive had a reduced dry strength of 1.5 MPa and an increased wet strength of 1.48 MPa. These results suggested that heat treatment has a similar effect on LG-SF adhesives as on soy flour adhesives by slightly decreasing dry strength and significantly improving wet adhesion. 25%LG-75%SF-pH8 showed better dry and wet adhesion at pH 8 than at pH 7 regardless of heat treatment. Since alkali influences the morphology of soy flour and adhesion, this improvement may mainly be due to the effect of pH on soy flour. To investigate how much mixing, diffusion and solubility of lignin and soy flour affect the adhesion, lignin and soy flour was firstly mixed at pH of 8 and then the pH was tuned back to 7. The adhesive 25%LG-75%SF-pH87 exhibited better adhesion than pH-7 but weaker than pH-8. Since alkali also influences the morphology of soy flour and adhesion, this improvement by increasing pH may be mainly due to the effect of pH on soy flour. Alkali may help diffusion of lignin to soy flour and increase the chance of interaction. When pH was tuned back to 7, the diffusion effect of lignin may still exist but the alkaline modification effect should disappear. In Under all pH conditions, heat treatment significantly improved wet adhesion.

By increasing lignin content to 50% and 75%, the maximum content of lignin in the formula was investigated. 75%LG-25%SF plywood exhibited weak adhesion under neutral pH and alkaline conditions. Lignin itself has weak cohesion without modification or mixing with other material. The increase of lignin content may decrease the cohesion and induced the weak adhesion. 50%LG-50%SF exhibited acceptable adhesion after heat treatment (Figure 4.1).

4.4.2 Adhesive film soaking test

Weight loss after water soaking is a measure of the water resistance of the cured adhesive. More weight loss after soaking is interpreted as weaker water resistance. Under all pH conditions, heat treatment led to more solid, cured adhesive residue after soaking (Figure 4.2). These results were in accordance with the adhesion strength results, in which heat treatment improved wet adhesion by improving water resistance. Among untreated films, the 25%LG-75%SF-pH8 had the lowest weight loss of 18.3%, possibly due to the hydrophobic functional groups of lignin and better solubility of lignin and alkaline condition unfolding proteins making them more water resistant.

4.4.3 TGA

Lignin powder's derivative thermogravimetry (DTG) curve is shown in Figure 4.3, in which lignin had small peaks under 100 °C showing the moisture in the sample evaporated. Weight loss gradually increased as temperature increased and peaked at 320 °C. Though this weight loss started at a relatively low temperature around 120 °C, the total weight loss at 200 °C was less than 10% of the original weight, which means most lignin remained solid and was not pyrolyzed. This result supports using lignin as an adhesive additive for heat treatment. Heat-treated lignin powder's derivative thermogravimetry (DTG) was also shown in Figure 4.3. The moisture peak disappeared in the treated sample, and the weight loss peak started at 200 °C, which was also the treatment temperature. This means the pyrolysis reaction in lignin was almost finished under 200 °C during the treatment.

4.4.4 DSC

DSC was used to characterize the thermal transitions of LG-SF adhesives. Dry adhesives were scanned using DSC at temperatures ranging from room temperature to 250 °C. The thermographs are shown in Figure 4.4.

The DSC graph of kraft lignin had a crystallization peak at 95° C, which disappeared in treated lignin. Heat treatment may melt and degrade lignin to different and broader molecular weight distributions, making the crystallization temperature in treated sample appear as a band and making it difficult to localize individual molecular weight content. The new peak at 190° C may indicate a new molecule crystallization temperature. In the LG-SF sample, glass transition happened at 50° C, which is almost the same as that of treated samples. The pH conditions seem to have no effect on glass transition and crystallization.

4.4.5 SEM

SEM imaging were used to observe the morphology of untreated and treated lignin powder (200 °C 2h) as shown in Figure 4.5. Untreated lignin powder exhibited a rough and porous surface (Figure 4.5(a)), while treated lignin powder had a more globular shape and smooth surface (Figure 4.5(a)), indicating that heat treatment changed the surface morphology of lignin powder. Recrystallization of lignin would happen in the heat process and hence may induce these changes in surface morphology.

The untreated adhesive films of 25%LG-75%SF had a smooth surface and a less porous and intact structure. After water soaking, more pores appeared and the surface turned rough and scratched. The treated 25%LG-75%SF film remained relatively smooth even after water soaking (Figure 4.5(b)), though some areas appear more damaged. These results indicate that water soaking

can dissolve and damage even the treated adhesive films, but heat treatment significantly improved water resistance.

4.4.6 FTIR

LG-SF powder with different pH values was pressed and dried into films and scanned by FTIR to investigate the chemical changes caused by heat treatment and alkali (Figure 4.6). For untreated 25%LG-75%SF, the typical peaks of soy flour appeared at 3000–3500 cm^{-1} (O–H stretching and N–H bending), 2925 cm^{-1} (C–H stretching), and 1640 cm^{-1} (secondary amide) (González, Strumia, et al., 2011). The peak at 1060 cm^{-1} could be the stretching vibration of C-N of amino groups or C-O of hydroxyl groups (Roeges and Baas, 1994). After heat treatment, most peaks remained, which indicate that heat treatment didn't decompose or completely change the structure of the protein and lignin and that the adhesive can resist heat treatment. However, in some areas such as 1293 cm^{-1}, the peak was mostly due to the formation of phenylpropene, which is believed to crosslink the lignin and soy protein. At 1592 cm^{-1}, the original peak of 25%LG-75%SF considerably weakened, which may indicate that the phenol structure of lignin subunits was consumed during heat treatment.

4.4.7 Viscosity

Rheology properties are important in industry applications and sometimes could be overlooked in laboratory studies. Flowability is important when an adhesive was extruded and brushed on the wood veneer surface. An adhesive that is too viscous is difficult to be uniformly brushed, while a watery adhesive may diffuse too fast into wood veneers and cannot form cohesion. The viscosities after shear at 1 $rads^{-1}$ after 150 s were recorded and shown in Table 4.1. The 25%LG-7%SF had an acceptable viscosity of 5 Pas, and with higher pH values, the viscosity

increased to 15 Pas. The pH shifting sample had higher viscosity than 25%LG-7%SF at pH 7 but lower viscosity than 25%LG-7%SF at pH 8.

4.4.8 DMA

DMA was conducted on LG-SF films (Table 4.2). The crosslinking density was calculated based on the relative calculation method used by Li et al (Li, Li, et al., 2016):

$$V_e = E'/3RT$$

where R is the gas constant, E' is the taken value in the rubbery state, and T is the corresponding absolute temperature. The glass transition temperature of the LG-SF at the neutral pH was 172 ºC; it improved to 188 ºC after heat treatment. The degree of crosslinking changed from 1.65 to 1.93 (Bengoechea, Arrachid, et al., 2007), which indicates that more crosslinked amorphous structures were induced by heat treatment. An alkaline condition with a pH at 8 had the same results. The glass transition temperature improved from 176 ºC to 195 ºC, and the crosslinking degree changed from 1.71 to 1.99 after heat treatment. Among both untreated and treated samples, there was more crosslinking at a pH of 8 than at the neutral pH, indicating that more functional groups of lignin and lignin's better solubility under an alkaline condition may lead to more crosslinked structures in protein and lignin.

4.4.9 Discussions

Based on the results above, we proposed the following mechanism for the LG-SF adhesive. Before the hot press, the hydrophobic structure of lignin units and lignin's low solubility at a low pH help decrease the viscosity of the adhesive, making the slurry easy to flow and apply on the wood surface. At higher pH values, lignin's solubility rapidly increases, and it interacts with protein molecules. Meanwhile, protein molecules expand, unfolding the protein. All of these factors can increase the viscosity of the adhesive.

The hot press provides the adhesion and dry strength of the adhesive, but without heat treatment, the protein is not water resistant, and the crosslinking of lignin and protein is limited. After heat treatment, according to the study in chapter 3, the protein itself forms crosslinks, and hydrophobicity is induced to protein side chains. The high temperature in heat treatment transfers some phenol groups in lignin so that lignin reacts with protein and forms crosslinks via the phenylpropane structure. The crosslinking structure and hydrophobic lignin molecules then link to unfolded protein, improving the water resistance of the adhesive.

4.5 Conclusion

The formation of phenylpropene crosslinking lignin and protein helps improve the strength and wet resistance of the adhesives. An alkaline condition could help improve adhesion, though the effect is not signicant compared with the improvement from heat treatment. The high viscosity induced by alkali is challenging during manufacturing. Adding 25% lignin content into soy flour adhesives was found to be practical. It achieved a wet stregnth of 1.43 MPa after heat treatment, without much deterioation in other properties such as flowablility. The interactions between lignin and protein and between lignin and lignin deserve further research.

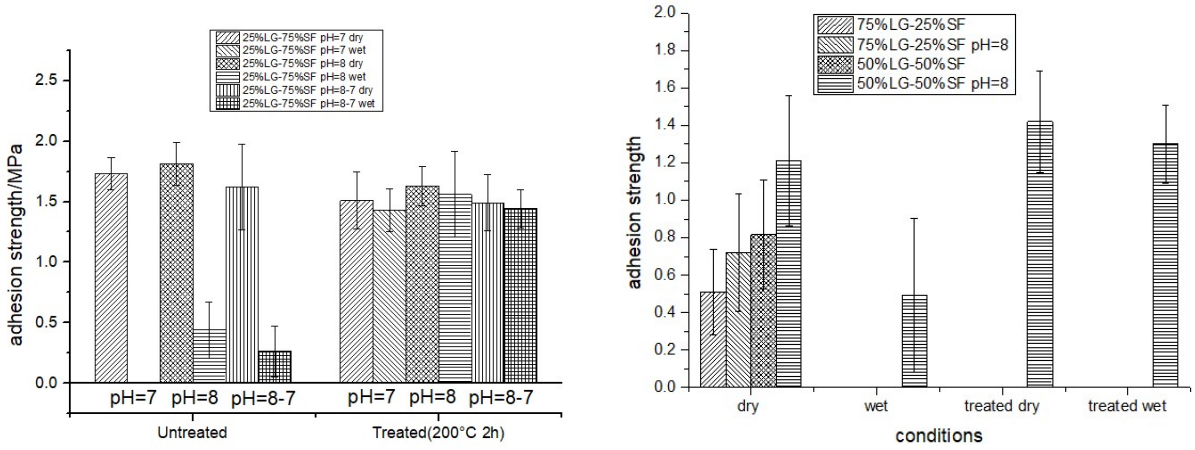


Figure 4.1 Dry and wet strength of untreated and treated 3-layer plywood using LG-SF adhesives. (a) 25%LG-75%SF at different pH (b) 75%LG-25%SF and 50%LG-50%SF at pH-7 and pH-8

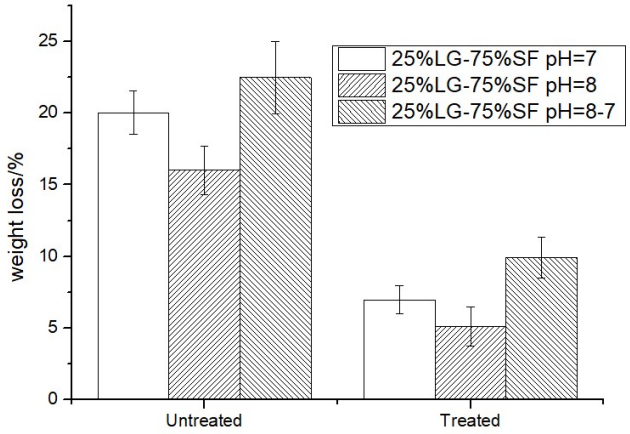


Figure 4.2 Weight loss of adhesive films after soaking

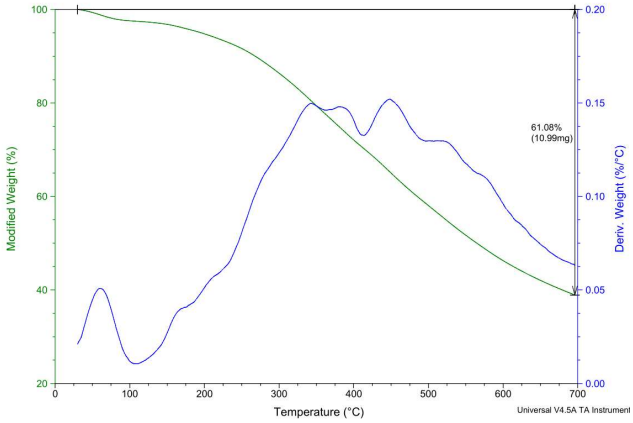
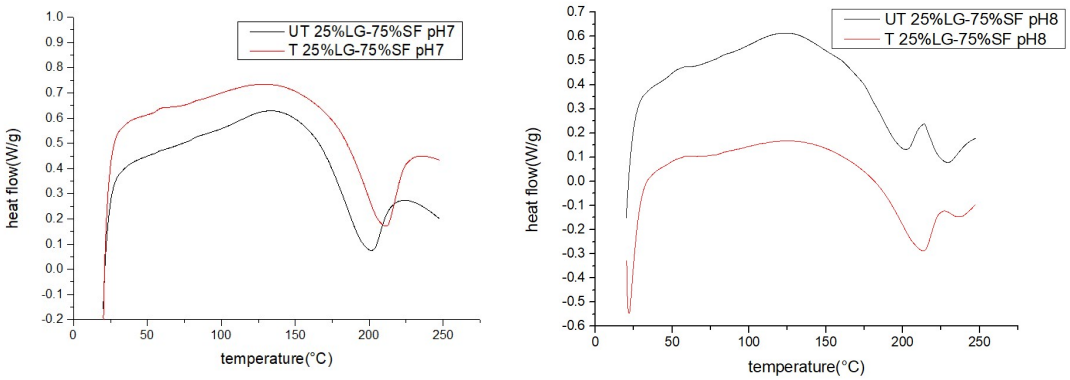
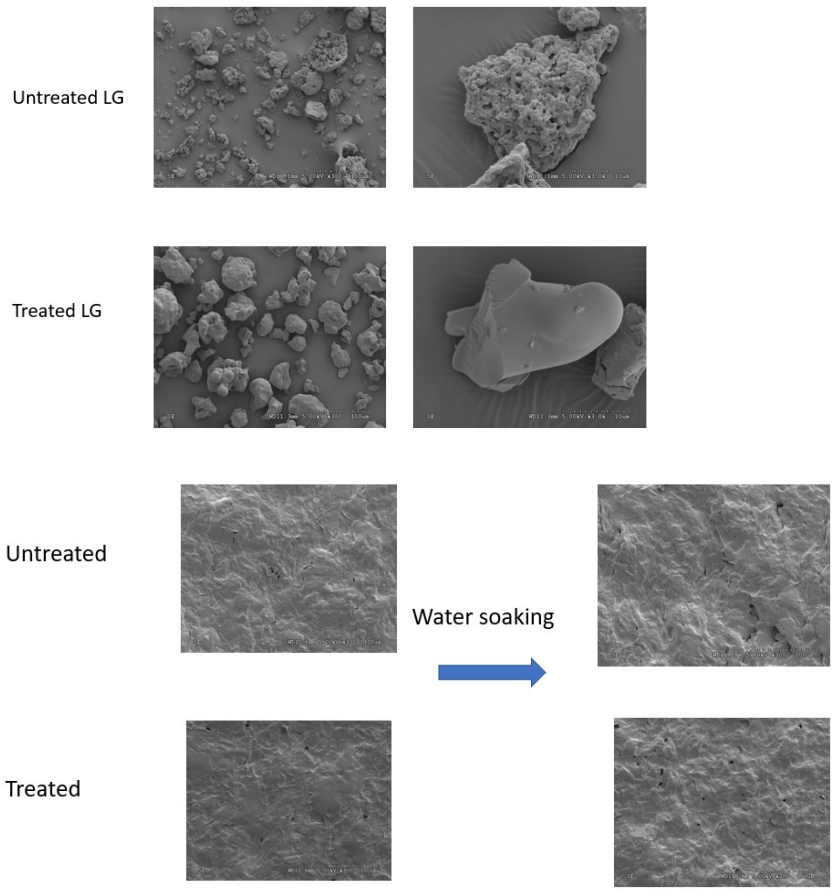


Figure 4.3 TGA graph of lignin powders



(a) (b)

Figure 4.4 Thermal graphs of DSC of LG25%-SF75%pH7 (a) and LG25%-SF75%ph8 (b)



(a) (b)

Figure 4.5 SEM images of lignin powders (a) and adhesive films of LG25%-SF75%pH7(b)

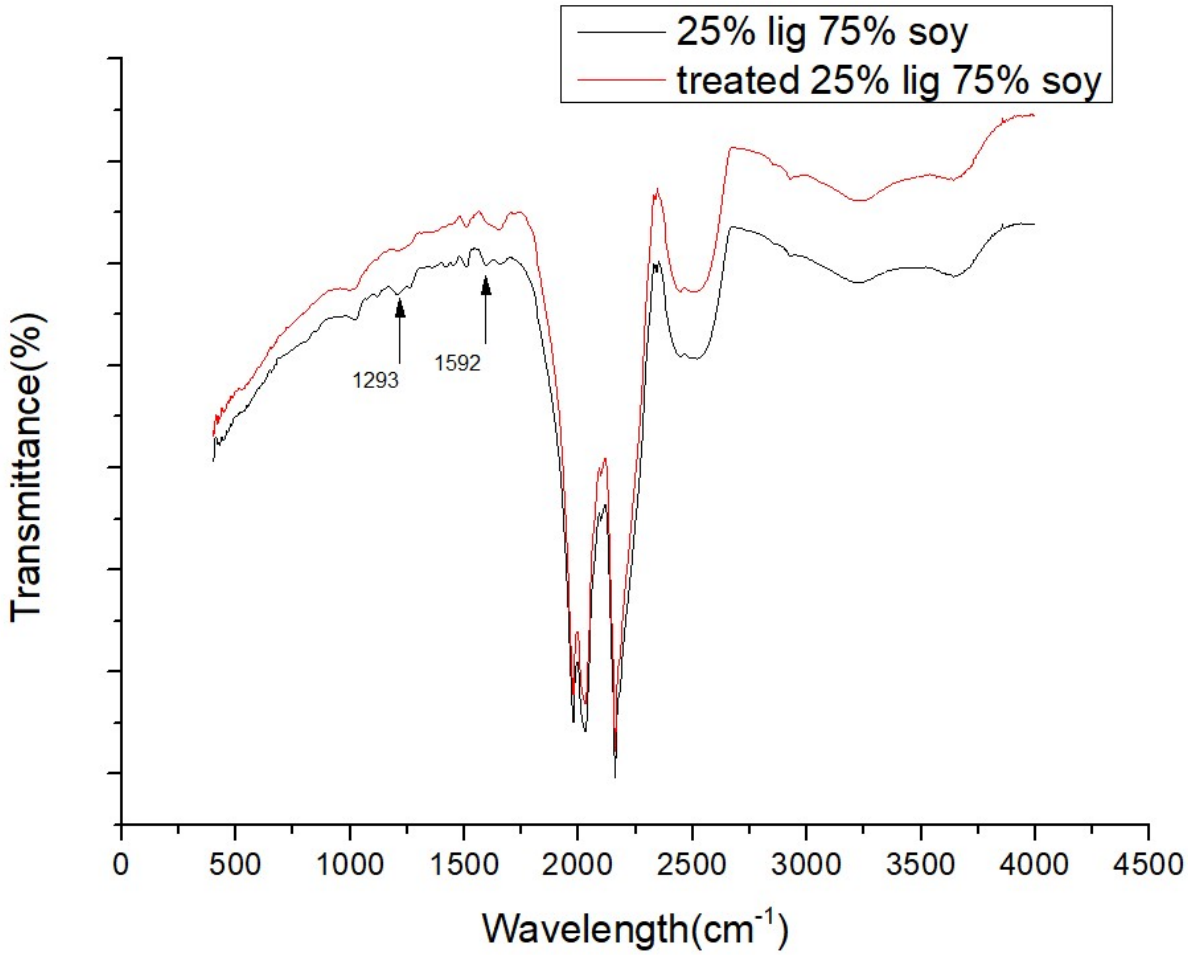


Figure 4.6 FTIR spectrometry of untreated and treated adhesive films of LG25%-SF75%pH7

Table 4.1 Viscosities of SF and SF/LG at different content and pH

	Viscosity at solid content of 30% (CP)
SF	14.25 CP
lignin (untreated)	0.63 CP
25% lignin, 75% SF	5.97 CP
25% 2h (treated) lignin, 75% SF	5.58 CP
75% lignin, 25% soy	1.00 CP
50% lignin, 50% soy	3.23 CP
pH=8, 75% lignin, 25% soy	5.67 CP
pH=8, 50% lignin, 50% soy	15.57 (shear thinning from 35)

Table 4.2 Glass transition temperatures and crosslinking densities of SF and SF/LG films determined by DMA sweep

Sample	Tg/ °C	Crosslinking density Ve = G'/3RT (10^3 mol·m^{-3})
25% lignin and 75% SF	172	1.65
treated 25% lignin and 75% SF	188	1.93
25% lignin and 75% SF, pH=8	176	1.71
treated 25% lignin and 75% SF, pH=8	195	1.99

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Chapter 5 - Enhanced Wet Strength with Heat Treatment: An Investigation Using Glucose as a Model System

5.1 Abstract

The Maillard reaction plays an important role in increasing the water resistance of heat-treated soybean adhesives by forming crosslinking structures. The heat treatment temperature range overlaps with that of the Maillard reaction. The objective of this chapter is to investigate the underlying mechanism of soy flour based adhesives under heat treatment conditions. The main principle of the Mallard reaction is derived from the reactions between proteins and sugars. The limited free soluble sugars from soy flour would react with soy proteins promoting the Mallard reaction. Glucose is the most abundant and common monosaccharide and reducing sugar. Therefore, it was used as an ingredient in soy flour formulation for a model system to study the Mallard reaction. Plywood was prepared following methods similar to those described in Chapter 3 with a typical heat treatment at 200 °C for 2 h. The heat-treated plywood prepared using the soy flour and glucose (SFG) adhesive exhibited better water resistance (1.51MPa), while the untreated plywood had no water resistance. The adhesive films were characterized, and the mechanism of how glucose enhanced the Maillard reaction was proposed. In the proposed mechanism, hydrophilic functional group loss, protein denaturation, and crosslinking after denaturation induced by the heat treatment improved the wet adhesion of soy flour based adhesive.

5.2 Introduction

Soybean protein based adhesive studies have received much attention in the last two decades. Different modification methods have been proposed to enhance soybean-based adhesives. For example, crosslinking soybean proteins and forming a stable hydrophobic network can obtain robust water resistance (Wang, Mo, et al., 2007, Zeng, Xu, et al., 2021). Proteins function fundamentally in soybean flour adhesives, owing to the abundant functional groups that proteins possess. In addition, the Maillard reaction is a common non-enzymic reaction occurring between amino acids and reducing sugars. Roman et al. used ascorbic acids as a reducing sugar to transform protein into soy protein isolate adhesives with improved dry strength (Román and Wilker, 2018).

Carbohydrates and vegetable proteins are abundant renewable resources and have high reactivity. Ancient glues used mainly consisted of biomass materials such as protein and starch, and other carbohydrates (Frihart, 2005). Glucose is the most abundant monosaccharide, with an annual worldwide production of 20 million tons in 2011 (Elvers, 1991). It is one of the most economical sources of reducing sugar that can potentially be applied to soybean adhesives. In previous studies, glucose and sucrose were added in soybean adhesives to enhance water resistance, indicating that amide linkages and ester bonds formed crosslinks (Chen, Lin, et al., 2013). Those studies indicated the possibility of using glucose to modify soybean adhesive. However, the hot press temperature of commercial wood adhesives is usually around 110 °C and lower than the temperature range of the Maillard reaction, because higher temperatures will shrink the wood in thickness causing reduced production. Because of this limitation in temperature, the efficiency of the Maillard reaction is not optimized.

Heat treatment of wood is widely applied and has received commercial success, especially in Europe (Yan-jun, Yi-xing, et al., 2002). The temperature of heat treatment often ranges from

160°C to 250 °C, depending on factors such as end product requirements and wood species. This temperature overlaps with that of the Maillard reaction. Therefore, this research proposes adding glucose to soybean adhesives to enhance the Maillard reaction in heat-treated plywood. In this study, the objective is to investigate the underlying mechanism of soy flour based adhesives under heat treatment conditions. We used soybean-glucose adhesives as a model system to observe the Maillard reaction and test improvements in water resistance. Plywood was prepared and treated under typical heat treatment conditions. The soybean-glucose adhesive was analyzed using the differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and thermogravimetric analysis-mass spectrometry (TGA-MS).

5.3 Material and methods

5.3.1 Materials

Analycial grade glucose was purchased from Sigma Aldrich. Soy flour was provided by Zhengzhou BIO Biological Co. Ltd (Zhengzhou China). Yellow pine wood veneers with dimensions of 300 mm × 300 mm × 1 mm (width × length × thickness) were provided by Veneer One (Oceanside, NY).

5.3.2 Preparation of adhesives

Soy flour adhesive (SF): 81g water was uniformly mixed with 50g soybean flour, and the slurry was stirred at room temperature for 30 min. The adhesive was used within 1 h.
Soy flour and glucose adhesive (SFG): 81g water was uniformly mixed with 47.5g soybean flour and 2.5 glucose. The slurry was stirred for 30 min. The adhesive was used within 1 h.

5.3.3 Preparation of three-layer plywood and adhesive films

Yellow pine wood veneers (300 mm × 300 mm × 1 mm) were preconditioned in a 23 °C, 30% RH chamber for one week. Three veneers were layered in such a way that the grain line of the middle panel was perpendicular to the grain lines of the top and bottom panels. 20-21g/ft2 (wet basis) adhesives were brushed on the two faces of the middle veneer panel. The assembled wood specimen stood for 15 min before hot press. The hot press conditions were 110 °C for12 min at 1.03 MPa. The bonded three-layer wood specimens were conditioned in a chamber at 23 °C and 50% RH for two days. They were then cut into 10 small pieces (82.6 × 25.6 mm) for adhesion tests (ASTMD906-98, 2017).

Adhesive slurries were hot pressed into films at 110 °C for 12 min and cured at 110°C for 30 min. Some of the films were then heat treated at 200 °C for 2h. Both the treated and untreated films were charaterized as detailed below.

5.3.4 Heat treatment

Plywood samples and adhesive films were dried at 105 °C for 5 h to remove moisture. The samples were then placed in an oven set to 200 °C. The oven, connected to a vacuum pump and nitrogen gas source, was vacuumed first and then filled with nitrogen gas. The samples were treated for 2 h. After heat treatment was completed, the samples were cooled in air and then stored in the chamber at 23 °C and 50% RH.

5.3.5 Mechanical strength and water resistance of plywood

Five small three-layer wood specimens were soaked in water at 23 °C for 24 h to test wet adhesion strength, and another five specimens were used to test dry adhesion strength. Both wet strength and dry strength were tested with an Instron Tester (Model 4465, Canton, MA) according

to ASTM Standard Method D906-98 at a crosshead speed of 1.6 mm/min. Adhesion strength was recorded as stress at the maximum load.

5.3.6 Scanning electron microscopy (SEM)

Adhesive slurries were hot pressed into films and dried. Some of the films were heat treated at 200 °C for 2h. Some of the untreated samples were soaked with water. The surface morphology of the films was observed with SEM (Hitachi S-3500N) at an accelerating voltage of 10 kV. Prior to SEM, samples were dried and coated with gold/palladium in an argon atmosphere using a Balzers evaporator (model SCD 050, Baltec Lichtenstein, Austria).

5.3.7 Fourier-transform infrared spectroscopy (FTIR)

Adhesive slurries were hot pressed into films and dried. Some of the films were heat treated at 200 °C for 2h. The treated and untreated films were then characterized by FTIR. Samples were dried at 90 °C for 1 h prior to FTIR. FTIR spectra were acquired using a PerkinElmer Spectrum 400 FT-IR/FT-NIR Spectrometer (Waltham, MA) over the 4000–400 cm−1 region at a resolution of 4 cm^{-1}.

5.3.8 Thermogravimetric analysis – mass spectrometry (TGA-MS)

The thermogravimetric analysis was made via TGA tests (PerkinElmer, Norwalk, CT) in a nitrogen environment, which provided an inert atmosphere during pyrolysis. The 5 mg samples were quickly heated from 50 to 120 °C at a heating rate of 60 °C/min and equilibrated at 120°C for 60 min. The tempearature was then quickly heated from 120 °C to 200 °C at a heating rate of 60°C/min and kept isothermal for 120 min. Weight loss was detected and the evolved gas was analyzed by tandem mass spectrometry (Discovery TGA-MS, TA instrument, Schaumburg, IL).

5.3.9 Differential scanning calorimetry (DSC)

The DSC thermal curves were characterized via a differential scanning calorimeter (Q200, TA instrument, Schaumburg, IL). Samples (10 mg) of untreated and treated (200 °C for 2 h) SF were hermetically sealed in aluminum pans. Temperature was held at 20 °C for 1 min and then increased to 250 °C with a heating rate of 10 °C/min.

5.3.10 Water soaking test

Two different adhesives (SF and SFG) were used to make films in pans. Two grams of adhesive slurries was brushed into the pan and cured at 110 °C for 30 mins. Curing time was longer than that used in hot press because there was no pressing and the samples were much thicker than actual adhesive layers between veneers. The samples then went through heat treatment. After cooling down, the pans were soaked in water for 1 h and dried in oven at 100 °C for 24 h.

Weight loss in water soaking can be calculated as

$$\text{Weight loss}=\frac{W_i-W_f}{W_i-W_g}$$

where W_g is the weight of the pan, W_i is the weight of the pan and cured adhesive film, and W_f is the weight of the pan and adhesive film after soaking and drying.

5.3.11 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was performed with a DMA machine(Q800 New Castle, DE) using the tension mode at a frequency of 1 Hz and an amplitude of 5μm. The dynamic mechanical properties, moduli, and glass transition of the adhesive films were obtained by heating them from room temperature to 250 °C at 3°C/min in the atmosphere of nitrogen gas. The measurements were within the linear viscoelastic region of the films.

5.4 Results and discussion

5.4.1 Adhesion strength

SFG adhesives were used to make three-layer plywood to test how glucose affects plywood performance with heat treatment. As shown in Figure 5.1, the dry and wet strength of untreated 1%SFG plywood were 1.81 MPa and 0.25 MPa, respectively. After heat treatment at 200 °C for 2 h, the dry strength of 1%SFG plywood reduced to 1.61 MPa and the wet strength improved to 1.26 MPa. For 5% SFG plywood , the dry strength was slightly decreased from 1.75 MPa to 1.73 MPa after heat treatment, and the wet strength was improved from 0.41 MPa to 1.5 MPa. The heat treatment had a similar effect on the SFG adhesive, slightly decreasing the dry strength but significantly improving the wet strength. Increasing the ratio of glucose slightly improved the wet strength after heat treatment. Heat treatment had more effect than the ratio of glucose on the improvement of wet adhesion.

5.4.2 Water resistance

The water resistance of adhesives can be quantified by calculating the weight loss of adhesives after water soaking. The weight loss of 1% and 5% SFG samples with and without heat treatment are shown in Figure 5.2. Increasing the content of glucose to 5% didn't reduce the weight loss. It actually increased weight loss from 24.5% to 20.3%. After heat treatment, all samples exhibited strong water resistance against soaking. The weight loss of SF after soaking reduced to 6%, which was significantly lower than that of the untreated SF. With heat treatment and 5% glucose added, the weight loss reduced to 5.9%, which was similar to that of treated SF. These results were consistent with the adhesion strength results, showing that heat treatment seemed to have a major effect on the improvement of water resistance and that the amount of glucose was less influential.

5.4.3 DSC

DSC was used to characterize the thermal transition of SFG adhesives. Dry adhesives were scanned using a differential scanning calorimeter at temperatures ranging from room temperature to 250 °C. The thermographs are shown in Figure 5.3. The decreasing heat flow of the untreated SFG at the range from 160°C to 200°C indicates the occurrence of multiple reactions in this temperature range, including crosslinking, the Maillard reaction, reorganization of S-S bonds, and other structural change reactions. In treated SFG, the decrease was less steep, which indicates that some of the reactions were completed in the earlier heat treatment.

5.4.4 FTIR

SFG powder was pressed and dried into films and scanned by FTIR to investigate the chemical changes by heat treatment. The FTIR spectrum of untreated and treated SFG is shown in Figure 5.4. For untreated SFG, the typical peaks of soy flour appeared at 3000–3500 cm^{-1} (O–H stretching and N–H bending), 2925 cm^{-1} (C–H stretching), and 1640 cm^{-1} (secondary amide) (González, Strumia, et al., 2011). At 1037 cm^{-1}, the peak could represent the stretching vibration of C-N of amino groups (Roeges and Baas, 1994).

For treated SFG at 1014 cm^{-1} and 1159 cm^{-1}, there were absorbances attributed to C-O bond stretching. Hayase et al. indicated that CH_3-COR moiety and C-terminal structures may exist in melanoidins. The C-O and C-C in FTIR may indicate the formation of melanoidins. Melanoidins contain OH, NH, CH_2, CH_3 and amide groups (Kim and Lee, 2009).

5.4.5 SEM

To investigate the surface morphology change of the untreated and treated SF and SFG films, we used SEM imaging to observe the surface of the samples before and after water soaking. The untreated SF and SFG adhesive films had a smooth surface before water soaking as shown in Figure 5.5. After water soaking, the untreated samples showed a rough and damaged surface. The heat-treated samples showed a less damaged surface, and the morphology was more similar to that of unsoaked samples. Heat treatment was effective to improve the water resistance of both the SF and SFG samples. The enhanced water resistance induced by heat treatment made the film surface more integrated and made it harder for water to diffuse and dissolve the films.

5.5.7 TGA-MS

TGA-MS gives information about thermal properties and derivative thermogravimetry. The heating process in TGA-MS tests is set to simulate the heating process of heat treatment, which is to heat and hold at 120°C for 60 min and then increase to 200 °C and hold for 120min. The TGA-MS graph of untread SFG is shown in Figure 5.6. The evolved gas from SFG detected by MS in Figure 5.6(b) and (c) showed the composition of lost protein mass during heat treatment. Evolved water (18 AMU) had one peak. The water is evaporation from pre-existing moisture and water produced by heat treatment. The evolved CO_2 (44 AMU) increased around 60 min, corresponding with the weight loss peak in the TGA graph and indicating the degradation of soy flour. The NH_3 (17AMU), NO (30AMU), and NO2 (46AMU) were detected by mass spectrum. During heat treatment, small amounts of NH_3, NO, and NO_2 would be emitted in the Maillard reaction and thermal degradation of amino acids would occur (Mottram, 1994, Sohn and Ho,

1995). Figure 5.6(c) showed the ion current of the small molecules of NH_3, NO, and NO_2 emitted after 60 min when temperature reached the range of the Maillard reaction.

5.5.8 DMA

DMA tests were conducted on SFG films after hot press or heat treatment. The crosslink density was calculated based on the relative calculation method used by Li et al (Li, Li, et al., 2016):

$$V_e = E'/3RT$$

where R is the gas constant, E' is the taken value of the rubbery elasticity in the rubbery state, and T is the corresponding absolute temperature.

The results are shown in Table 5.1. With heat treatment, SFG films exhibited increased glass transition temperatures from 168 ºC to 196 ºC, which indicates more crosslinked amorphous structures in treated samples. Untreated SFG had a crosslink density of 1.79, and treated SFG had a crosslink density of 2.05, correlating with our understanding that heat treatment improves protein crosslinking in SF. Based on the other data, this improved crosslink density is possibly due to the enhanced Maillard reaction induced by glucose.

5.5.9 Discussion

By using SFG as a model system, we revealed the role of the Maillard reaction in the crosslink of protein adhesives after heat treatment. According to the results obtained from this study, we proposed a possible mechanism for how heat treatment improves water resistance of SF as shown in Figure 5.7. The improvement in water resistance is mainly due to three factors:

hydrophilic functional group loss, protein denaturation, and crosslinking after denaturation. Proteins in SF underwent two major changes upon heat treatment: firstly, hydroxyl groups have dehydration reactions and produce free water, which evaporates; meanwhile, protein becomes denatured, making protein chains more mobile; secondly, functional groups interact with each other, and the Maillard reaction occurs (Román, 2018). As a result, covalent bonds formed and melanoidin was produced among protein-protein, protein-polysaccharide, and polysaccharide-polysaccharide. Heat treatment induces hydroxyl group loss; therefore, treated proteins have a more hydrophobic surface and better water resistance. Compared with the hot press process, heat treatment increases the mobility and denaturation of soy protein chains with its higher temperature. Because natural soy proteins are globular, as mobility and free volume increase, protein chains are more likely to have entanglement, and functional groups are more likely to react. Meanwhile, more physical interactions such as hydrogen bond and hydrophobic interactions may occur to cure the denaturation, inducing new stable structural configurations. Among these factors, crosslinking may be the most important factor for water resistance improvement.

5.5 Conclusion

Glucose was added into the formula of soybean-based adhesives. Plywood was produced using the glucose added adhesive and then heat treated and tested for wet strength and dry strength. Untreated SFG plywood exhibited similar results as plywood made using soy flour adhesives. The heat-treated SFG plywood exhibited water resistance of 1.51MPa. The mechanism of water resistance improvement was proposed as hydrophilic functional group loss, protein denaturation, and crosslinking after denaturation.

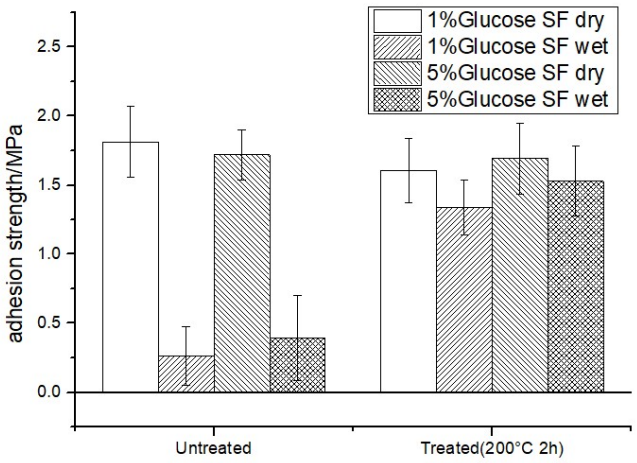


Figure 5.1 Dry and wet strength of untreated and treated 3-layer plywood using SF adhesive and SFG adhesive

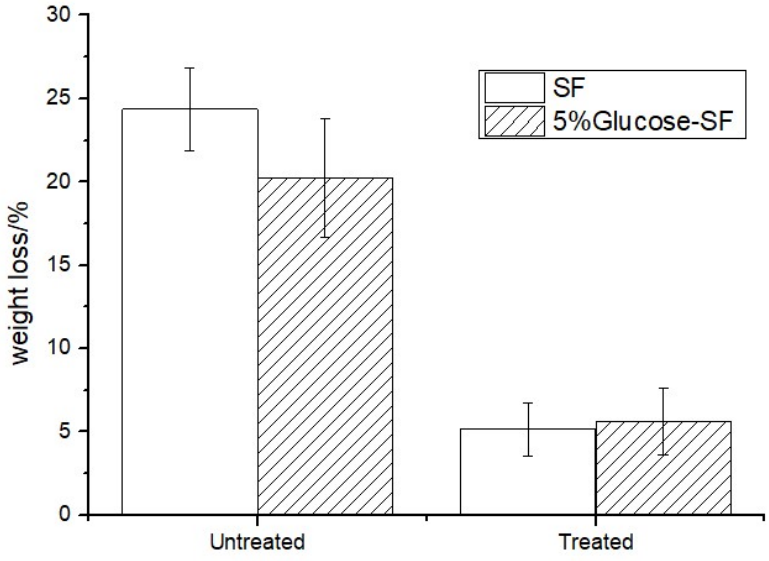


Figure 5.2 Weight loss of untreated and treated SF and SFG films after soaking

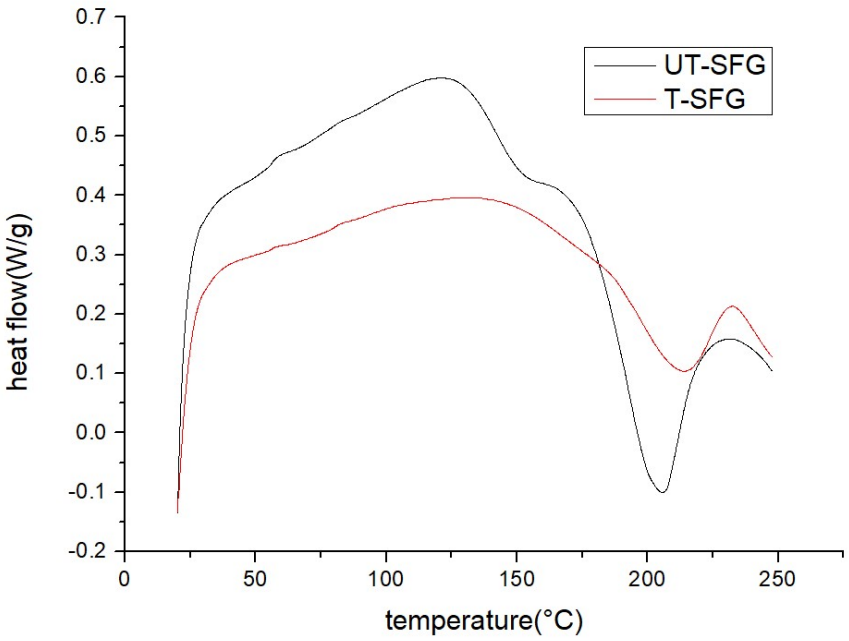


Figure 5.3 DSC thermographs of untreated and treated SFG adhesive

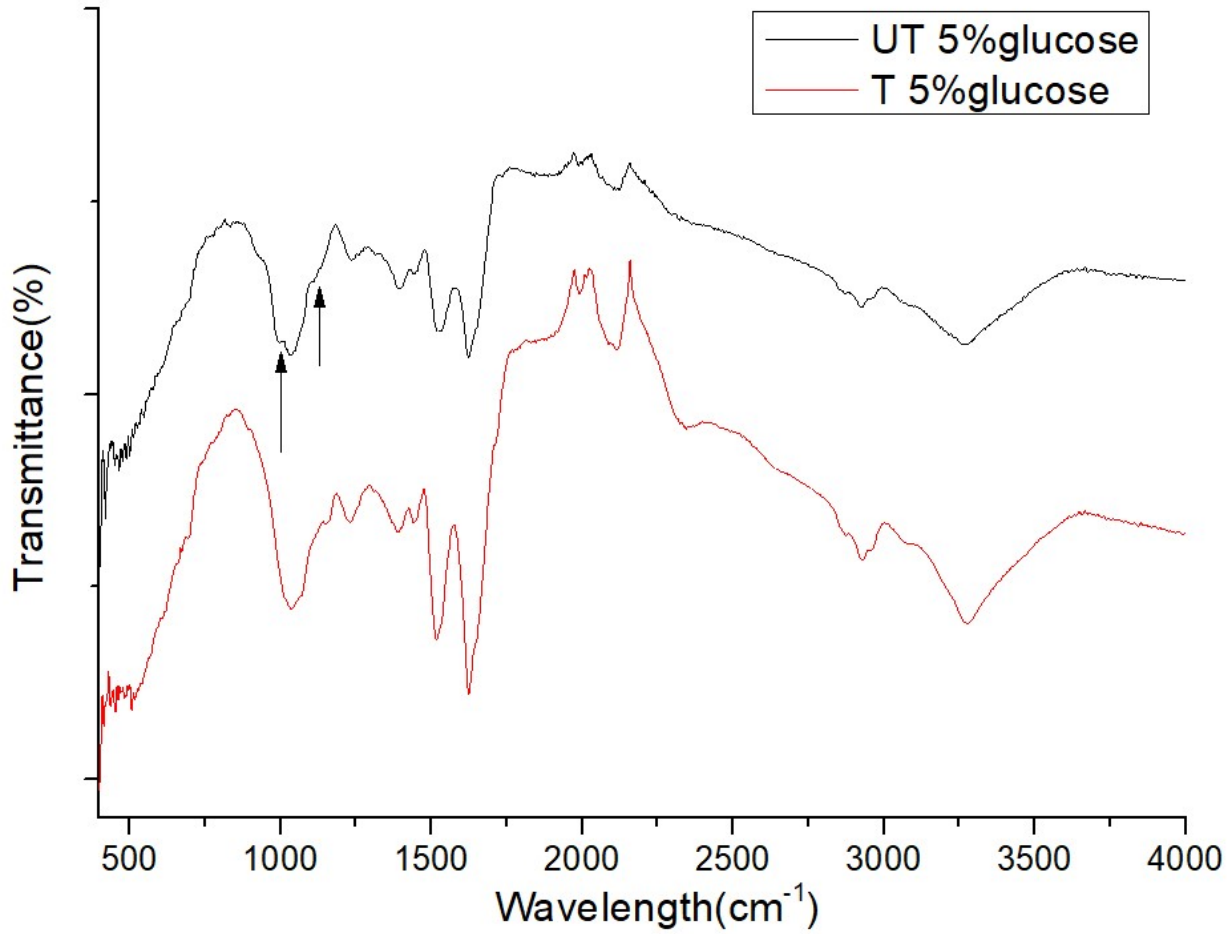


Figure 5.4 FTIR spectrometry of untreated and treated SFG adhesive

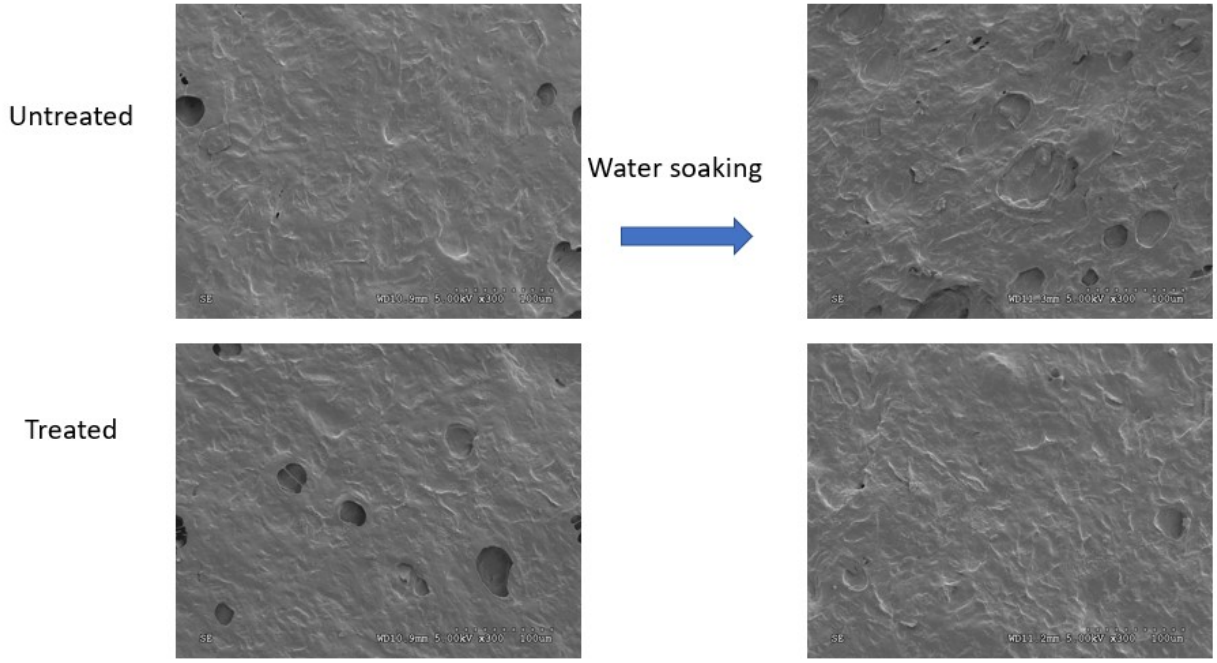
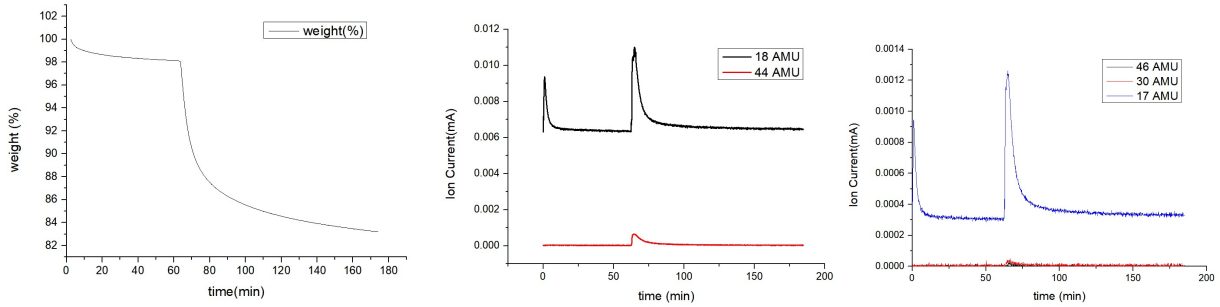


Figure 5.5 SEM images of untreated and treated SFG film before and after water soaking



(a) (b) (c)

Figure 5.6 Thermal graph(a) and evaporated contents of SFG (b)(c) via TGA-MS

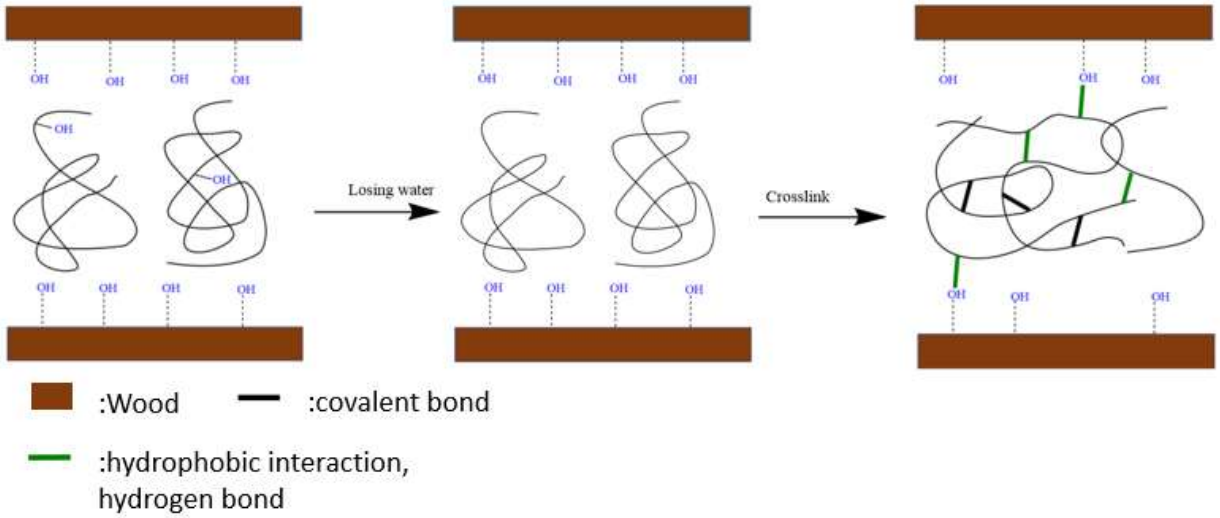


Figure 5.7 Proposed mechanism for protein crosslinking during heat treatment and adhesion with wood surface

Table 5.1 Crosslinking densities of SF and SFG films determined by DMA sweep

Sample	**Tg/ °C**	**Crosslinking density Ve = G'/3RT (10^3 mol·m^{-3})**
5% Glucose and SF	168	1.79
Treated 5% Glucose and SF	196	2.05

5.6 Reference

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Chapter 6 - Conclusion and Future Work

Heat-treated plywood can be successfully prepared using soy flour adhesives with a relatively low cost and acceptable parameters for industry application. The product combines the advantages of plywood and heat-treated wood. Heat treatment of soy flour adhesives was found to improve the wet strength of the plywood products. The thermal stability and chemical structure change of protein are the fundamental reasons of water resistance improvement in heat-treated soybean adhesives.

Lignin was successfully added into the soy flour adhesive formula to reduce cost. 25% lignin best reduces the cost of the adhesive and produces acceptable products, and 50% is the maximum amount that can be added. At a higher pH, more lignin could be added, but viscosity may limit practical applications. Glucose was added to soy flour based adhesives and used as a model system to reveal how heat treatment improves wet adhesion strength. Crosslinking in the Maillard reaction was studied. Hydrophilic functional group loss, protein denaturation, and crosslinking after denaturation were proposed as the main factors that allow heat treatment to improve the wet adhesion of soybean-based adhesives.

The application of protein-based adhesives to heat-treated wood opens a new door for the industry, allowing engineered wood and heat-treated wood to have new features and to be applied to more situations. Our understanding of high temperature modified protein is still limited. Future studies on the mechanism of physical and chemical changes that happen during heat treatment will help us better understand how water resistance form in heat-treated protein-based adhesives and further improve water resistance to allow additional applications. For example, this study only examined plywood, and other engineered wood such as OSB, MDF and particle boards require

more flowable adhesives. Future studies on modifying protein adhesives and improving rheology performance may allow soybean-based adhesives to be used for other engineered wood preparation and heat treatment.