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Improvements and limitation of soy protein-based adhesive: A review

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Abstract

Soy protein is known for its eco-friendly, sustainable, and biodegradable qualities that are likely used as raw material in producing bioadhesive. However, soy protein-based adhesive are lacking in terms of adhesive strength and water-resistance compared to commercial formaldehyde-based adhesives such as phenol and urea-formaldehyde resin. Therefore, continuous research has been done to improve adhesive performance. This can be done via physical or modification methods, including the usage of cross-linking agents, structural modification, enzymatic modification, and the addition of additives. This review will cover these modification methods that give significant enhancement to the water-resistance and adhesive strength of soy protein-based adhesives.

KEYWORDS

adhesive performance, adhesive strength, modification, soy protein-based adhesive, water-resistance

1 | INTRODUCTION

Adhesives have been used in many different products such as, shoes, plasters, packaging, self-adhesive notes/envelopes, as well as in wood composites. Formaldehyde-based adhesives such as urea-formaldehyde (UF), melamine-formaldehyde (MF) and phenol-formaldehyde

(PF) have been used as adhesives in the preparation of composite panels for many years since they offer superior strength and good water-resistance to the composite[1]. Today, urea-formaldehyde adhesive is being used in the manufacturing of wood panels and/or particleboards for interior use, while phenol formaldehyde is being used for exterior purposes[2, 3]. However, concerns arise since they

release free formaldehyde into the air during use, and it is hazardous to the environment and human health[4, 5]. Besides, the International Agency for Research on Cancer (IARC) has also reported that formaldehyde is carcinogenic to humans[6]. Moreover, the formaldehyde-based adhesives are from oil resources (petroleum) that are nonrenewable and limited[1, 7]. Due to the growing concern about environmental issues and human health, an adhesive made from natural and renewable resources as well as formaldehyde-free products has become a targeted product for the industry of adhesives[8, 9]. Therefore, many studies have been done to test the compatibility of adhesives from natural resources with wood-based composites.

Agricultural biomass resources such as proteins, polysaccharides, gelatin, lignin, and tannin have been used as raw materials to produce adhesives for coatings, packaging, and furnishings[10]. Conventionally, protein-based adhesives based on resources from animals originally came from the hoof, hide, blood, milk, and fish scales, while soybeans were the leading resource for plant protein[11, 12]. Among other plant-based proteins reported, soybean (soy protein) and wheat (wheat gluten) were the primary protein resources for producing protein-based adhesives[13]. The wood products that were manufactured using protein-based adhesives include interior plywood (soybean adhesives) and glued laminated timber beams (casein adhesives from milk)[14].

Soy protein is one of the environmental-friendly biomass with preferable qualities since it is biodegradable, abundant, annually renewable[15], inexpensive, nontoxic[16] easy to handle material[17] and holds significant potential in the wood industry as a raw material for producing an adhesive[18]. The biocompatibility, biodegradability and strength of soy protein can be improved through chemical or physical modification[19]. Before the 1960s, the plywood industry used soy-based adhesive as a main binder in their manufacturing process before it was replaced with synthetic resins[1]. However, in the 1990s, it was once again back in the research field as a wood adhesive and has been used as a research material until now[20]. However, these adhesives have low water-resistance[13, 21]. Many ways could be used to resolve this problem, including modification by hydrolysis, chemical denaturation, cross-linking, enzyme modification, and so on[20]. Some researchers have combined soy protein with different types of protein, such as casein and blood, or with synthetic polymers to enhance their performance and properties[13, 22]. Based on studies conducted by previous researchers, the effects of various methods of modification on soy protein used on different types of wood products (particleboard, fiberboard and plywood) are addressed in this paper.

2 | SOY PROTEIN

Soy protein is one of the most valuable industrial crops product containing a high level of edible oil (about 20%) and protein (about 40%). Soy protein has been used as an excellent nutritional source in the food industry because it contains significant amounts of essential amino acids [23]. Soy protein has good properties, such as fast growth, biocompatibility, and biodegradability. These properties have attracted research interest in the development of environmentally friendly materials for adhesives [24]. Soy protein can be classified into three commercially available products based on their protein content, which are defatted soy flour (SF), soy protein concentrate (SPC), and soy protein isolate (SPI). The SF contains 40%–60% protein, combined with carbohydrates and fats [25], while the SPC contains 65%–72% protein, 20%–22% carbohydrates and 7.5%–10% fiber and ash [26]. The SPI contains approximately 90% protein [18, 23, 27]. The different types of soy protein content of each product are due to different producing methods. The SF is the least refined soy protein product that is produced by grinding soybean to a particle size of <100 mesh or finer [28]. Whereas, the more refined form of protein is SPC, which was prepared by removing part of carbohydrates (oligosaccharide) dehulled and defatted soybeans [29]. The removal of carbohydrates can be done through three possible methods. Which are by washing with 60%–80% aqueous alcohol, use of an acid at pH 4.5 and use of moist heat [28]. The SPI is the most refined form of soy protein and it can be produced by removing nonprotein components, fat, and carbohydrates from defatted SF. They are produced through several steps (i) the defatted SF is stirred in warm water plus alkali at pH 7–8.5 (ii) through centrifugation, the solution containing the protein and soluble carbohydrates is separated from the insoluble fraction (iii) the pH of the solution is then adjusted to pH 4.2–4.5 (iv) finally, the sugars are washed away and the protein precipitate is obtained [28, 30]. The least expensive of soy protein product is SF, followed by SPC and lastly, SPI [24, 31, 32]. Soy protein has great potential to be applied in many possible ways including as in drug delivery products [33, 34], fiber products [35, 36], biodegradable film [37, 38], foams [39], packaging [40, 41] and adhesives that will be discussed in this paper. Soy-based protein compositions consist of a mixture of four main protein categories. It is known as 2S (conglycinin), 7S (β-conglycinin), 11S (glycinin) and 15S (globulins), and differentiated from each other by their Svedberg sedimentation coefficients [42, 43]. Among the four protein categories stated, 7S and 11S are the major proteins reported, which denote more than 80% of the total protein [44].

Proteins are polymers comprising **20** different types of amino acids, and the structure of the side chain of an

amino acid that is indigenous to a protein will determine whether it is acidic, basic, or natural. Proteins are linear polyamides built-up by amino acids, linked together with polypeptide bonds, and together with DNA, fat, and polysaccharides, form the most fundamental elements in living species [45]. The amount of amino acid residue and its placement along the polypeptide chain become the main factors that will determine the chemical and physical characteristics of soy protein [46]. The polypeptide backbone of the protein determines the molecular structure of soy protein. The polypeptide backbone of protein is made up of different types, numbers, and sequences of amino acids [45]. Proteins have primary, secondary, tertiary, and quaternary structures. Figure 1 shows the complex structure of the protein that will denote the properties of a protein where the primary structure consists of a string of amino acids coupled by peptide bonds and will partially assemble into the secondary structure of α-helices and β-pleated sheets that are stabilized by hydrogen bonds. The tertiary structure is a form of a 3D-structure that occurs when side-chains interact with each other and they are stabilized by a series of hydrophobic amino acid residues and disulfide bonds formed between two cysteine amino acids. Lastly, the quaternary structure will be created when the whole protein molecule engages with other protein molecules to form an entire unit [46–48]. The functional groups in the side-chains of the polypeptide chain are responsible for defining the amino acid whether it is hydrophilic or hydrophobic. It provides feasibilities for interaction with hydroxyl or carboxyl groups in wood, as well as for crosslinking sites [47].

Commonly, protein-based adhesives have low solid content, high viscosity, and due to their low water-resistance, they can usually only fulfill the requirements for indoor applications [47]. Some methods are used to overcome the drawbacks of the soy protein-based adhesive, which are low water-resistance and low adhesive strength. The methods used to modify the soy adhesive, include

cross-linking, chemical denaturation, hydrolysis, enzyme modification, and others [20], as depicted in Table 1. The alteration of the secondary, tertiary, and quaternary structure levels of protein molecules during the modification will allow further interaction between soy protein-based adhesives and the substrate, since it will change the soy protein conformation from a folded structure to a loose and disordered structure [51, 65].

3 | MODIFICATION OF SOY PROTEIN

3.1 | Cross-linking agents

Cross-linking modification is a relatively common method used for the modification of soy-based adhesives nowadays. Typically, cross-linkers are introduced into the formulation in two ways: by directly mixing them with soy adhesive prior to application or by adding them during the soy adhesive preparation[20]. Nevertheless, the handling process of soy adhesive is much easier in the latter way. Choosing a compatible and effective cross-linker is the crucial point in this type of modification method, since it can affect the resultant modified adhesives. Soy proteins contain many reactive groups, namely hydroxyl ($-OH$), thiol ($-SH$), carboxyl ($-COOH$), and amino ($-NH_2$), that allow numerous chemicals to be used for the cross-linking of soy adhesives[20, 66]. The cross-linked structures that help in improving the water-resistance of the adhesive are generated by the reaction of the active function of the cross-linker with the active groups of the protein ($-NH$, $-COOH$, and $-NH_2$)[16].

Soy protein has been combined with polyamide epichlorohydrin (PAE) to enhance the adhesive properties. Li et al.[50] have modified a soy protein-based adhesive with Kymene, an aqueous solution of PAE resin that was
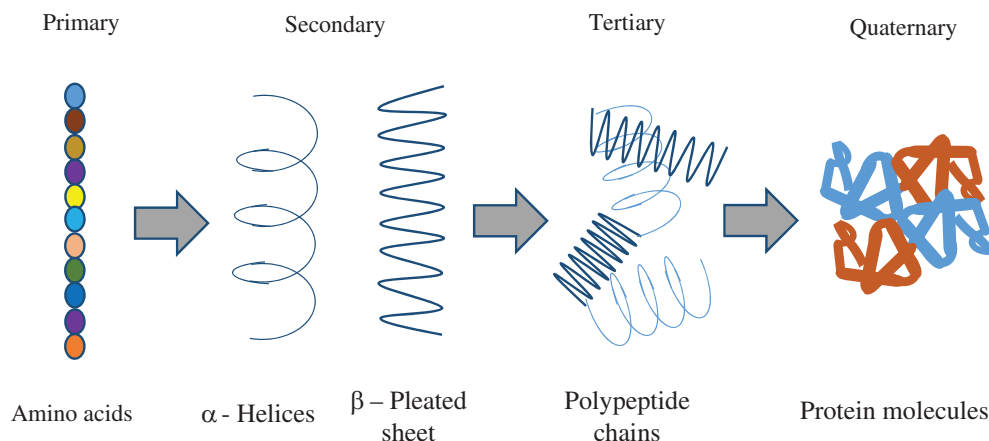

FIGURE 1 Simplify structure of protein molecule

Primary   Secondary   Tertiary   Quaternary

Amino acids   α - Helices   β – Pleated sheet   Polypeptide chains   Protein molecules

TABLE 1 Summary of previous studies on the modification of soy protein

Type of modification	Soy protein type	Substrate	Findings	Reference
Cross-linking agent	Soy protein isolate (SPI)	Cherry wood veneer	• Complex formation of ionic interaction between SPI and polyamide epichlorohydrin (PAE) is formed at room temperature and at a pH of 4–9. • Thermal properties (denaturation temperature, T_d and denaturation enthalpy, ΔH_d) of modified soy protein increased when PAE concentration increased and the highest value recorded was at a 15% PEA concentration (T_d: 82.6°C and ΔH_d: 11.05 J/g). • The maximum adhesive strength was recorded on modified SPI with 5% PAE concentration at pH 5.5.	Zhong et al. [49]
Additives	Soy protein isolate (SPI)	Sugar maple veneer	• The reaction between SPI and Kymene formed a water-insoluble 3D cross-linking network. • The SPI-Kymene adhesive reported the highest shear strength and water resistance compared to SPI, Kymene and phenol-formaldehyde.	Li et al. [50]
Cross-linking agent	Soy meal (SM)	Poplar veneer plywood	• There is no cross-linking reaction detected between polyethylene glycol diacrylate (PEGDA) and SM adhesive, but a cross-linking reaction successfully occurs during the curing process of PEGDA modified SM adhesive. • The water-resistance of plywood bonded with modified SM with 4% PEGDA shows an improvement since the wet shear strength recorded has increased from 0.48 MPa to 0.90 MPa.	Gao et al. [51]
Cross-linking agent	Soybean meal (SM)	Poplar veneer plywood	• The addition of 8% triglycidylamine (TGA) to the SM adhesive improved the water-resistance to 15.1% of the modified SM adhesive and 86.6% in wet shear strength of the plywood. • Addition of 85 acrylic emulsion (AE) into the SM/TGA adhesive successfully enhanced the water resistance from 1.25 MPa to 1.80 MPa and from 0.71 MPa to 1.05 MPa of wet shear strength compared to the TGA/SM adhesive.	Luo et al. [52]

TABLE 1   (Continued)

Type of modification	Soy protein type	Substrate	Findings	Reference
Cross-linking agent	Soy protein isolate (SPI)	Poplar veneer plywood	• The dry/wet shear strength of plywood bonded with SPI/TGA/7% TPU adhesive was increased by 115 and 68% respectively compared to SPI/TGA adhesives. • Further improvement in dry/wet shear strength of plywood was observed when it was bonded with SPI/TGA/TPU/KG-560, which increased by 23%/34% when compared to SPI/TGA/TPU (thermoplastic polyurethane elastomer) adhesives.	Xu et al. [16]
Cross-linking agent	Soy protein isolate (SPI)	Poplar veneer plywood	• Incorporation of 3 wt% hyperbranched aminated soybean soluble polysaccharide (A-SSPS) into SPI/TGA adhesive shows reduction in viscosity, moisture uptake and improvement in residual rate of cured adhesive. • The highest wet shear strength (1.07 MPa) was recorded on plywood bonded with SPI/TGA/A-SSPS-3 while the highest dry shear strength (2.08 MPa) was displayed on plywood bonded with SPI/TGA/A-SSPS-7.	Zhang et al. [53]
Cross-linking agent	Soybean meal (SM)	Polplar veneer plywood	• High-pressure homogenization (HPH) treatment successfully unmasks the active functional group in the protein structure, reduces the particle size and increases the particle size distribution for reaction with cross-linker and bonding enhancement. • The resultant plywood when bonded with SM/HPH-7/TGA adhesive shows improvement in wet shear strength (from 0.33 MPa-1.03 MPa) and dry shear strength (from 0.85 MPa-1.83 MPa) compared to the SM adhesive.	Zhang et al. [54]
Denaturation agent	Soy protein isolate (SPI)	Soft maple wood blocks	• Water-resistance properties of modified soy protein adhesive with alkali (AMSP) and trypsin (TMSP) were improved due to the presence of a higher amount of hydrophobic groups present in the AMSP and TMSP structures. • The highest adhesive strength (743 N) on wood blocks is recorded on TMSP, followed by AMSP (730 N) and unmodified adhesive (340 N).	Hettiarachchy et al. [55]

(Continues)

TABLE 1 (Continued)

Type of modification	Soy protein type	Substrate	Findings	Reference
Denaturation agent	Soy protein isolate (SPI)	Wheat straw particleboard	• Beach straw particleboard bonded with NaOH-modified adhesive shows the ideal mechanical properties compared to other particleboards (different soy protein adhesive and straw surface treatment) tested.	Mo et al. [56]
Denaturation agent	Soy protein isolate (SPI)	Pine, maple, poplar and walnut plywood	• Comparing plywood bonded with urea- modified with alkali-modified, heat–treated protein and unmodified protein adhesive, the former modification show the higher water resistance.	Sun and Bian [57]
Denaturation agent	Soy protein isolate (SPI)	Walnut, cherry and pine plywood	• The shear strength and water resistance of modified soy protein with urea and guanidine hydrochloride (GH) are enhanced compared to unmodified soy protein adhesive. • Among all the concentrates tested, soy protein adhesive modified with 3 M urea, 0.5 M and 1 M GH was reported to give good shear and water-resistance to the composite.	Huang and Sun [58]
Denaturation agent	Soy protein isolate (SPI)	Fiberboard	• The maximum shear strength value reported was 1.93 MPa at 1 M concentration of guanidine hydrochloride (GuHCl) and increasing the concentration will only decrease the value of shear strength. • Press temperature (120°C), press time and assembly time (5 min and 10–15 min) give maximum shear strength to the final composite.	Zhong et al. [59]
Denaturation agent	Soy protein isolate (SPI)	Walnut, cherry and pine plywood	• Soy protein modified with 0.5% and 1% sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) showed improvement in shear strength in all wood samples tested compared to unmodified soy protein.	Huang and Sun [60]
Denaturation agent	Soy protein isolate (SPI)	Fiberboard	• The shear strength of the modified SPI adhesives with sodium dodecyl sulfate (SDS) was reported to have increased when the assembly time, press time and/or press temperature increased.	Zhong et al. [61]
Enzymatic modification	Soy protein isolate (SPI)	Walnut, cherry, soft maple, poplar and yellow pine wood	• Increasing the glue concentration will also increase the adhesive strength of trypsin-modified soy protein (TMSP).	Kalapathy et al. [62]

TABLE 1   (Continued)

Type of modification	Soy protein type	Substrate	Findings	Reference
			• Among the woods tested, the 2 mg/cm² glue concentration of TMSP applied on soft maple and subjected to a cold press gave the highest adhesion strength.	
Enzymatic modification	Soy protein isolate (SPI)	Rubberwood, Bhutan pine, teakwood and plywood	• The extent of hydrolysis determines the hydrophobicity of the modified adhesives, where chrymotypsin-modified SPI shows the maximum value of hydrophobicity, followed by papain modified SPI and trypsin-modified SPI. • The best shear strength on plywood was recorded by the urea-modified SPI.	Kumar et al. [63]
Additives	Defatted soy flour (DSF)	Cherry wood plywood	• An improvement in adhesion strength is recorded from 2.9 MPa in control adhesives to 4.3 MPa upon the addition of 8% sodium montmorillonite clay (Na MMT) to the adhesive.	Qi et al. [64]

used in paper manufacturing as a wet strength additive to improve the properties of a soy-based adhesive and was tested on a wood veneer composite. They discovered that the strength and water resistance of modified soy protein adhesives had been greatly improved. This is because, at elevated temperatures, the active azetidinium group in PAE can react with active hydrogen groups in soy protein structures such as carboxyl, hydroxyl, and amino groups, to increase the water resistance of the final product by creating an insoluble network and forming a crosslink between the resin and the substrate[10, 67, 68]. However, because the soy protein structure naturally has an abundance of amide linkage, the properties of their modified soy protein adhesive are still very low when compared to the phenol formaldehyde resin. On the other hand, Zhong et al.[49] studied the effect of pH and temperature on the performance of PAE/SPI adhesive applied to cherry wood veneer composite. They discovered that the strength and water-resistance ability of PAE/SPI adhesives were affected by pH and complexation interaction (acting as physical interaction) between PAEs. In their case, complex interaction has two main functions: (i) forming an insoluble three-dimension network by promoting crosslinking between PAE and SPI to improve strength and water-resistance, (ii) reducing the penetration of water into the interfacial layer between substrate and adhesive by forming complexation reaction and such crosslinkage during reaction. Nonetheless, the use of these cross-linking agents has raised a number of concerns[10, 66, 69]. It is a fossil-based material, and the vast amount of this cross-linker is used in the formulation (ratio of protein/cross-linker is 1.5:1). Also, the use of PAE added to the brittleness of the adhesive, thus lowering the dry bond strength of the final product.

Polyethylene glycol diacrylate (PEGDA) is a type of polyfunctional methacrylate. It has been added to soymeal protein-based adhesive as a viscosity reducing agent as well as a cross-linking agent[51]. With the addition of PEGDA, the interaction between protein molecules is weakened because PEGDA can form a shield between proteins, reducing the viscosity of the modified adhesive to provide good flowability on the wood surface and easy handling[70]. It was reported that the highest gel content and the lowest value of water absorption could be achieved on soymeal adhesive added with 4% PEGDA because of the high possibility of an increase in the amount of cross-linking density on cured adhesive. Increasing the amount of PEGDA by more than 4%, on the other hand, will result in the opposite trend in the results. It is shown that PEGDA improved the water-resistance of the modified soymeal protein-based adhesive compared to the unmodified soymeal protein-based adhesive. The improvement in water-resistance is due to an increase in solid content and a decrease in viscosity

after the addition of PEGDA that aids in the easy formation of glue attachment between the poplar plywood used. Based on their FTIR and NMR results, there are no new absorption peaks and spectrums detected that can indicate the reaction between PEGDA and soy protein. However, the disappearance of the C=C peak at 1636.6 cm^{-1} and at 125 ppm on FTIR and NMR confirms that the crosslinking reaction of PEGDA occurs during the curing process. As a result, they conclude that the interaction form of cured PEGDA and protein adhesive could be interpenetrating polymer networks. This polymer network might also contribute to an improvement in the water-resistance of adhesives[71, 72].

As reported by Xu et al.[16], the soy protein isolate adhesive (SPIA) itself is brittle, and the brittleness of this adhesive will be increased even after the addition of the cross-linker, resulting in low dry bond strength and impact resistance properties of the bonded panel. This is due to the fact that, during the manufacturing process, there will be unavoidable residual stresses present inside the panel, and they will ratchet up along with the increase/decrease in moisture content within the panel during the application process. The bond force of the cured adhesive can usually balance these residual stresses. Yet, this balance can be easily broken when the residual stress increases (the cured adhesive is brittle). Past studies have indicated that a more compact structure of adhesive can be obtained by increasing the cross-linking agent dosage, but at the same time, this will reduce the bond strength of the resultant panel[51]. Therefore, increasing the toughness of the SPIAs will benefit from balancing the internal forces, thus enhancing the bond strength and water-resistance of the adhesive.

The toughness of soy protein-based adhesive can be improved by incorporating thermoplastic polyurethane elastomer (TPU) and -(2,3-epoxypropoxy) propyltrimethoxysilane (KH-560) into the soy protein isolate (SPI)/ triglycidylamine (TGA) formulation to develop a high-performance SPI-based adhesive[16]. They discovered that when a cross-linker TGA and KH-560 are added into the formulation, the reactive group of TGA and KH-560 will react with the active of -NH$_2$ and.

—OH in soy protein, thus increasing the water-resistance of the resultant adhesive. This can be proven by the FTIR results, where there is a reduction in —COOH spectra and a blue shift of amide I/II detected. The ability of KH-560 to form a joined crosslinking structure by acting as a bridge linked with protein molecules and TPU. This joined crosslinking network gives other advantages to the final product, such as improving the interfacial force between the adhesive and the substrate (polplar veneer plywood), thus improving board performance, thermostability and toughness, as well as being able to create a uniform ductile fracture section of the adhesive.

Luo et al.[52] also used triglycidylamine (TGA) but with the addition of water-based acrylic emulsion (AE) into their soy protein adhesive to focus on improving its toughness and water-resistance and tested it on poplar plywood. The AE is produced through the emulsion polymerization of acrylic/methacrylic acid with vinyl ester monomer[73]. The addition of TGA and AE to SPAs increased the solid content of the cured adhesive and decreased water evaporation, hence improving the water-resistance of the cured adhesive. It was also discovered that the toughness of the resultant adhesive was increased after the addition of TGA and AE. Although the addition of TGA is believed to worsen the current brittleness of SPA, the flexible nature of AE will toughen the resultant adhesive. Increasing the toughness of the adhesive increased the crack propagation energy when the system was loaded and improved the mechanical properties of the plywood[74]. The research successfully proved that the addition of flexible AE not only toughens the SPAs but also enhances the water-resistance and increases the strength of the end product.

A high dosage of cross-linking agent is typically added to the formulation. Zhang et al.[53] discovered that the addition of hyperbranched aminated SSPS soybean soluble polysaccharide (A-SSPS) to the mixture of soy protein isolated and bio-based triglycidylamine (TGA) could reduce the quantity of cross-linking agent added into the formulation without forfeiting the water-resistance properties. The addition of A-SSPS to the system will produce an adhesive with a hyperbranched cross-linked structure with an increase in reactivity. The water-resistance of the corresponding adhesive has improved since the addition of A-SSPS simplified the formation of a highly cross-linked compact three-dimensional network in the adhesive system and as well as reduced the usage of cross-linking agent dosage in the system. Moreover, introducing A-SSPS and TGA to the SPI adhesive can successfully form a compact and homogeneous fracture section, hence significantly improving the toughness and thermal stability of the cured adhesive. Besides, it also helped to reduce the moisture absorption of the adhesive and consequently enhanced the dry/wet bond strength of the final plywood. Nevertheless, the researchers noticed that adding more than 3 wt% A-SSPS would only increase the amount of hydrophilic amino group exposure that leads to an increase in moisture uptake and thus reduced water-resistance.

Recently, Zhang and his team[54] studied the possibility of initially using high-pressure homogenization (HPH) on soy protein adhesives before it was added with TGA and tested on poplar veneer plywood. Similarly, with Luo et al.[52], they also discovered that the reaction

between TGA and soy protein consumed the reactive hydrophilic group on the soy protein adhesive surface and a dense cross-linked network was formed, hence water-resistance was improved. Furthermore, treating soy protein with HPS before adding TGA improves the adhesive properties significantly. This is because HPS can give homogeneous[75] and unmask the active group within protein molecules[76] that can promote effective cross-linking with TGA to increase the adhesive's cross-linking density (improve water-resistance).

3.2 | Structure modification (denaturation agents)

Soy proteins are compact molecules, folded on themselves at numerous locations[77]. Denaturation is referred to all types of modification that lead to changes of the secondary, tertiary, or quaternary structure of the protein molecule without altering the primary amino acid sequences[26–55, 65]. Besides, the acts of protein unfolding through the breaking of hydrogen and sulfate bonds within higher orders of protein structure are also other significant definitions of common denaturation[78]. Denaturation leads to an increase in the accessibility of amino acid side groups which are concealed within the internal structure of proteins to react with other active groups in denaturation agents[79]. Denaturation of protein can be done in many ways, including exposure to heat, acid/alkali, organic solvents, detergents, and urea[55].

Soy protein structure modification refers to the usage of denaturation agents such as alkali, urea, sodium dodecyl sulfate and guanidine hydrochloride. It is to unfold the protein molecules into a loose and disordered structure[51, 53]. The act of unfolding soy protein molecules will expose more of the hydrophobic protein subunit and increase the interaction between the soy protein-based adhesive and the substrate. These interactions, later on, will increase the bonding strength and water-resistance of the end adhesive product.

The FTIR analysis was used to understand the denaturation process of the soy protein. The different secondary structures of soy proteins are reflected in the medium IR range present in amide I ($1720–1600$ cm^{-1}) and amide III ($1400–1200$ cm^{-1}) band patterns[80]. Changes in FTIR spectra indicate that there are changes in the secondary structure of proteins that are caused by modification of soy protein. This can be detected by changes in the absorption peaks on FTIR according to hydrogen bonding, dipole–dipole interaction and peptide backbone geometry[18]. The amide I absorbed in the $1720–1600$ cm^{-1} range is due to C=O stretching and C—N stretching[25], while the amide III is absorbed in the range

of $1400–1200$ cm^{-1} due to N—H bending, C—N stretching with a small contribution from C—O bending and C—C stretching[33].

Soy protein has been modified with urea to enhance the water-resistance of the adhesive and tested on different wood species (pine, poplar, maple, and walnut)[57]. The existence of hydrogen and oxygen atoms in urea enables it to interact actively with the hydroxyl groups of the soy protein molecules. This reaction may lead to an interruption of the hydrogen bonding in the protein chain, and, as a result, the protein complex is unfolded. The authors reported that the viscosity of protein adhesive modified with urea and alkali showed lower viscosity and was thermally stable compared to unmodified soy protein and heat-modified soy protein adhesive. Low viscosity indicates that there are an increasing number of unfolded protein structures on the urea and alkali-modified protein adhesives that provide more considerable contact area for bonding, hence adding to an improvement in gluing strength for both adhesives[11]. Among all the adhesives tested, urea-modified soy protein adhesive showed the most excellent water-resistance, followed by alkali-modified and heat-modified soy protein adhesives, and lastly. Unmodified soy protein adhesive[57].

Guanidine hydrochloride has also been introduced in a soy protein-based adhesive formulation to increase water-resistance and adhesive strength. Huang and Sun[58] prepared a soy protein-based adhesive modified with different concentrations of urea and guanidine hydrochloride tested on different types of plywood; walnut, cherry, and pine. They found that both modified soy protein-based adhesives enhanced water-resistance and increased adhesive strength. Through modification with guanidine hydrochloride, the compact and ordered structure of soy protein is unfolded into a loose and random conformation[59]. The DSC test on protein adhesive modified with urea shows that the peak temperature for conglycinin (7S) and globulin (11S), the main protein subunits, has decreased as well as the total enthalpy. This indicates that urea successfully unfolds protein molecules, hence an increasing degree of denaturation. They discovered that, among all the concentrations, modified adhesives of 3 M urea and 1 M guanidine hydrochloride showed the highest shear strength and water-resistance in all wood specimens compared to unmodified protein adhesive. They believed that the modified adhesive of 3 M urea and 1 M guanidine hydrochloride possibly exhibited a higher content of the secondary structure and more exposed hydrophobic amino acid in which the secondary structure of globular protein contributed to the enhancement of adhesive strength. In contrast, the water-resistance of the final adhesive might be improved by the unveiling of more hydrophobic amino acids.

Adjustment of pH alone or in conjunction with heating is an effective way to modify the properties of soy protein products[43]. Soy protein has also been modified with alkali (sodium hydroxide) and trypsin[55]. When compared to the unmodified soy protein-based adhesives, the modified soy protein-based adhesive is said to have better bond strength and water resistance. However, between the two modifications, alkali and trypsin, the former modified soy protein-based adhesive showed higher adhesive strength and water-resistance compared to the latter. This is explained by the fact that alkali breaks internal hydrogen bonds of protein molecules, and promotes the unfolding of soy protein molecules, which leads to the exposure of more hydrophobic groups for bonding[48, 55]. Mo et al.[56] reported that alkali-modified soy protein gives the best mechanical properties to the particleboard since alkali conditions can hydrolyze soy protein molecules, producing peptide chains that contribute to good bondability.

Zhong et al.[61] used sodium dodecyl sulfate (SDS) to modify soy protein isolate to improve the adhesive properties in fiberboard application. As one protein denaturation agent, SDS and protein molecules were able to bind strongly through hydrophobic interaction between the protein hydrophobic side chains and the hydrophobic moieties of SDS[81].The concentration of SDS, press temperature, press time, and assembly time are important factors to take into consideration in producing of SDS modified soy protein adhesive with good adhesion strength. Increasing SDS concentration up to 3 wt% of SDS will increase the shear strength of the modified adhesive. However, a very high concentration is not ideal since it can elevate the viscosity of the solution, due to swelling and unfolding, which later on will contribute to poor adhesion. A press temperature above the denaturation temperature for 11S (90°C) and 7S (75°C) components is the ideal press temperature for fiberboard manufacturing in this case. At temperatures above the denaturation temperature, protein molecules are unfolded into a loose and disordered structure. Furthermore, it increased the possibility of a chemical reaction between the protein molecules and the substrate at the interface, thereby increasing adhesion strength and water resistance. A long press time and assembly time can also increase the shear strength of the adhesive. Among all the conditions tested, the fiberboard bonded with SPI modified with a 3 wt% concentration of SDS press at a temperature of 100 °C above for 5 min or more demonstrated an increase in adhesion and shear strength.

There is a possibility of using other types of anion detergent aside from sodium dodecyl sulfate (SDS) as a denaturation agent and achieving an almost similar result as SDS. Huang and Sun[60] studied the effects of two different anion detergents; sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulphate (SDBS) with varying concentrations on the modified soy protein isolate adhesive on plywood. Soy protein isolates modified with both SDS and SDBS at 0.5% and 1% concentration gave good shear strength compared to unmodified soy protein adhesives due to the increase in unfolded protein molecules. This was demonstrated by DSC data, which revealed that increasing the SDS concentration resulted in a decrease in the heat capacity (enthalpy) of modified soy protein, indicating that a greater degree of protein unfolding was occurring as previously observed in a study[61]. Since both SDS and SDBS are anion detergents, they can improve the water-resistance of modified soy protein adhesives by increasing the hydrophobicity of the adhesives through anion binding protein modification. Anion binding can bring out some of the inside hydrophobic side chains of protein molecules, so that these hydrophobic side chains can interact with the hydrophobic moieties of detergent molecules and form micelle like regions and hence increase water-resistance[81].

3.3 | Enzymatic modification

Another modification method that has been used to improve the performance of soy protein-based adhesives is by using enzymes as a modification agent. Proteolytic enzymes are commonly used to modify protein structures. Different types of proteolytic enzymes such as chymotrypsin, trypsin, urease, papain, and pepsin have been used by Kumar et al.[63] to modify their SPI adhesives and their compatibility with different types of wood substrates (rubberwood, Bhutan pine, teakwood, and plywood). Based on the hydrophobicity index data collected, the chymotrypsin modified SPI (CSPI) showed the highest value and the unmodified SPI had the lowest value. They believe that hydrolysis plays an important role in improving the hydrophobicity of modified SPI adhesives, since increasing the extent of hydrolysis will expose some more of hydrophobic groups in native protein structures, thus increasing hydrophobicity. Past research by Kumar and team[82] has discovered that the number of the hydrophobic groups exposed is higher in CSPI compared to papain modified SPI (PSPI) and trypsin modified SPI (TSPI). It has been proven that the extension of enzymatic hydrolysis of CSPI is less for PSPI and TSPI compared to CSPI. However, extensive hydrolysis of CSPI led to a decreasing viscosity; thus, CSPI showed no adhesion at all. Among these, urease modified SPI (USPI) showed improvement in adhesion. The rubberwood substrate was the best adherent, while teakwood was the poorest adherent.

The proteolytic enzyme trypsin has been added to the soy protein-based adhesive to improve the performance of the adhesive as investigated by Kalapathy et al.[62]. The work focused on improving the adhesive properties of the final adhesive tested on different types of wood (walnut, cherry, soft maple, poplar, and yellow pine wood). Upon using an enzyme as the modification agent, the enzyme hydrolysis time is vital to take into consideration since it will affect the viscosity and adhesive strength of the modified adhesive since it will enhance the dispersion and unfolding of protein. The viscosity will oversee the adhesive behavior on the flow property, which will affect the adhesive[83, 84]. As reported by Kalapathy et al.[62], the viscosity of modified adhesives decreased with the hydrolysis time while the adhesive strength increased for the first hour before decreasing with increasing hydrolysis time. They noticed that an hour is an ideal hydrolysis time since it produces adhesives with the highest adhesive strength and low viscosity that offer easy handling, smooth spreading and enough penetration into the substrate. Among all the types of wood tested, soft maple showed the highest strength. Trypsin modified soy protein on soft maple wood at 2 mg/cm^2 that underwent cold pressing gave double adhesive strength compared to the unmodified soy protein adhesive. The trypsin modified soy protein adhesives also displayed an improvement in water-resistance compared to unmodified adhesives. This is because trypsin has the ability to degrade soy protein into smaller molecular size and can expose more hydrophobic groups in protein structures to the surface, hence improving the water-resistance[85].

Although limited studies have been done on the modification of soy protein adhesive with enzymes and their effect on the composite, there have been many studies reported using enzyme modification to improve soy protein in food applications. Kim et al.[86] stated that the usage of the proteolytic enzymes (trypsin, alcalase and α-chymotrypsin) is effective in improving SPI functionality. The emulsifying capacity, solubility, and thermal aggregation of SPIs can be elevated to a specific extension by monitoring the duration of proteolytic treatment, types of proteases used, and functional properties of the final SPIs. They also discovered that between protein 7S sub-units and 11S globulins, 7S sub-units show a more extensive enzymatic breakdown compared to 11S globulins. The conforming 7S sub-units possibly contain more hydrophilic surfaces[87], while the 11S globulins may possess more of a compact structure[88]. In order to achieve the desirable functional properties of soy protein hydrolysates, hydrolysis should be performed in strictly controlled conditions. A limited degree of hydrolysis can improve the solubility, emulsifying and foaming capacities of modified soy protein, while excessive hydrolysis often causes loss of some of these functionalities[43].

3.4 | Additives

A few studies have been carried out to test the compatibility of adding different types of additives into the soy protein-based adhesive to enhance the water-resistance and adhesive strength for wood composite applications.

Nanoscale fillers such as sodium montmorillonite clay (Na MMT) were also added to soy protein adhesive to improve its mechanical properties, as investigated by Qi and the team[64]. Na MMT is a silicate clay with a unique nanoscale layered structure and a high expect ratio polymer[89]. At the end of their study, they discovered that the dry and wet adhesion strength of SP/Na MMT modified adhesives was improved, with the most significant water-resistance reported at 8% Na MMT loading. The intercalation structure between Na MMT and protein is achieved through hydrogen bonding and electrostatic bonding, creating a compact cross-linking protein structure. Those compact structures cause the interfacial layer between wood and adhesives to be impenetrable by water, thus improving the water-resistance of the final product.

4 | CONCLUSIONS

A soy protein-based adhesive that was modified through various modification methods showed an improvement in water-resistance and adhesion properties. Previous studies have shown that the reaction between the active groups in cross-linker and the active groups in protein can form a cross linkage structure that enhances the properties of the final adhesives. Moreover, cross-linking agents were also used to reduce the viscosity and increase the solid content of the modified protein adhesive. On the other hand, denaturation agents are more likely used to unfold the complex protein structure so that the hydrophobic groups in soy protein are exposed, hence improving the properties of modified soy protein adhesives, especially the water-resistance. The hydrolysis time plays an important role in the enzymatic modification of soy-based adhesives since it can influence the amount of hydrophobic groups exposed in the protein structure to enhance the water-resistance properties of the resultant adhesive. Since most of the studies done are focusing mainly on soy protein isolate, further research should be done to explain the performance differences between modified soy proteins isolate, soy protein flour, and soy

protein concentrated, and their effects on different types of composite.

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