



AN ABSTRACT OF THE THESIS OF

Jian Huang for the degree of Master of Science in Wood Science presented on  
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Title: Development and Characterization of New Formaldehyde-free Soy  
Flour-based Adhesives for Making Interior Plywood

Abstract approved:

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Formaldehyde-based adhesives such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) adhesives dominate the current wood adhesive market. However, these adhesives are derived from petrochemicals and carcinogenic formaldehyde. In this study, we developed two formaldehyde-free adhesives based on abundant, renewable, and inexpensive soy flour (SF).

The first adhesive was mainly composed of SF, polyethylenimine (PEI), and maleic anhydride (MA). The optimum formulation of this adhesive and the optimum hot-press conditions for making plywood were investigated. A three-cycle soak test and a boiling water test (BWT) were employed to evaluate the strength and water-resistance of plywood bonded with the soy flour-based adhesive.

Results showed that SF, PEI, MA and NaOH were all essential components for the adhesive and the SF/PEI/MA weight ratio of 7/1.0/0.32 resulted in the highest water-resistance. When the hot-press temperature was in the range of 140-170 °C, both the water-resistance and the shear strengths of plywood bonded with the adhesive remained statistically the same, except that the dry shear strength of plywood at 170 °C was statistically lower than that at 160 °C. When the hot-press time ranged from 2 to 6 min at 160 °C, the plywood panels made at the hot-press time of 5 min led to the highest boiling water test/wet (BWT/w) shear strength among all samples, and the plywood panel made at the hot-press time of 5 min had a higher dry shear strength than that at 3 min. Plywood panels bonded with this SF/PEI/MA adhesive exceeded the water-resistance requirements for interior applications.

The second adhesive consisted of SF, trimethylolpropane triglycidyl ether (TMTE) and a catalyst. The following catalysts were investigated: calcium hydroxide, sodium carbonate, triethylamine, tetra-n-octylammonium bromide, phosphoric acid and ammonium sulfate. The effects of these catalysts on the water-resistance of plywood bonded with the SF-TMTE adhesive under different hot-press conditions were investigated. It was found that all catalysts improved the water-resistance of the resulting plywood to some extent. Among all catalysts

investigated, calcium hydroxide and triethylamine were better than other catalysts in terms of improving the water-resistance of the resulting plywood panels. These preliminary results also revealed that increasing hot-press temperature and increasing hot-press time enhanced the water-resistance. The water-resistance of plywood panels bonded with these SF-TMTE adhesives still could not meet water-resistance requirements for interior applications.

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DEVELOPMENT AND CHARACTERIZATION OF NEW  
FORMALDEHYDE-FREE SOY FLOUR-BASED ADHESIVES FOR MAKING  
INTERIOR PLYWOOD

by

Jian Huang

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Jian Huang, Author

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# DEVELOPMENT AND CHARACTERIZATION OF NEW FORMALDEHYDE-FREE SOY FLOUR-BASED ADHESIVES FOR MAKING INTERIOR PLYWOOD

## CHAPTER 1 GENERAL INTRODUCTION

### **1.1 Introduction of wood composites**

Wood composites are made from woody materials in various forms such as veneer and particles, and some non-wood materials such as an adhesive. Compared to solid wood, wood composites can provide better mechanical and chemical properties such as higher shear strength, and improved resistance to fire, weathering and biological degradation. Wood composites can be made with various sizes and shapes that are not easily obtainable from logs. In addition, waste materials from saw mills such as chips, sawdust, and shavings can be fully utilized in the production of wood composites. Wood composites can have more uniform properties at different directions than solid wood.

Wood composites can be classified into two categories: I) traditional wood composites including wood-based panels and engineered lumber, and II) advanced hybrid composites such as wood-plastic composites (WPC) and inorganic-bonded composites. The current wood composites market is mostly occupied by traditional wood composites such as plywood, oriented strandboard (OSB), particleboard and medium density fiberboard (MDF)



### **1.1.1 Plywood**

Plywood is composed of veneers bonded with an adhesive under heat and pressure. Wood grains in adjacent layers are typically perpendicular to each other, which imparts plywood panels relatively uniform properties in all directions. Plywood typically has an odd number of layers. Plywood is widely used for making houses, kitchen cabinets, and furniture.

There are two types of plywood: structural softwood plywood and decorative hardwood plywood. Softwood plywood is mainly used for exterior structural applications, and hardwood plywood is generally employed for interior applications. The consumption of softwood plywood has been decreasing in recent years [1]. However, the demand of hardwood plywood will remain strong for many years to come.

#### ***1.1.1.1 Manufacture of plywood***

The raw materials for plywood are a wood adhesive and veneers. An industrial process of making plywood includes veneer preparation, application of an adhesive onto veneers, assembly of adhesive-coated veneers into panels, cold-press, hot-press, and finishing. Logs are first peeled into wood veneers that are dried to about 3-6% moisture content. A wood adhesive is applied onto veneers by different methods. A roller coater is the most commonly used machine for coating an adhesive onto veneers.

An adhesive can also be sprayed or coated onto veneers using a spraying nozzle or a curtain coater. After the gluing operation, adhesive-coated veneers are stacked together to form a panel that is then cold-pressed under certain pressure for several minutes for consolidating the veneers and increasing the contact between the adhesive and the veneers. The panels are hot-pressed under certain temperature and pressure. After the hot-press operation, some finishing steps such as trimming and sanding will follow.

Hot-press pressure is typically in the range of 75 to 250 psi depending on wood species. With low-density wood such as yellow poplar and spruce, 100-150 psi is appropriate. For medium-density wood like Douglas fir, the pressure is usually between 150 and 200 psi. For high-density wood, 200-250 psi is used. Hot-press temperature is typically in the range of 240-285° F. The hot-press time varies with the thickness of panels and the adhesives used. The hot-press time can range from two minutes to an hour [2].

#### ***1.1.1.2 Adhesives used for making plywood***

A variety of adhesives can be employed for making plywood. Phenol-formaldehyde (PF) resins, urea-formaldehyde (UF) resins and protein-based adhesives are widely used in manufacture of plywood. PF is mainly used for making exteriorly used plywood. UF and protein-based adhesives are mainly used for

making interior plywood. The typical adhesive content in plywood is about 3-5 wt% [3].

### **1.1.2 Oriented strandboard (OSB)**

OSB is a structurally used panel made from adhesives and strands under heat and pressure. Strands at adjacent layers are oriented perpendicularly to each other. OSB can be made from small diameter logs and low quality wood, thus being more efficient in the use of woody materials than plywood. OSB also costs less than plywood, but has comparable strength and stiffness to plywood. Therefore, OSB has rapidly been gaining its market share at the expense of softwood plywood since the mid 1980s although OSB has a shorter history than plywood.

OSB can be used for making I-joints, wall sheathing, sub floors, floor underlayment and many other products.

Different adhesives are typically used for making the face layers and the core layer of OSB. PF resins are typically used for making the face layers, and isocyanates are typically used for making the core. Wax is usually employed in the manufacture of OSB for enhancing the moisture resistance and the dimensional stability of OSB[4].

### **1.1.3 Particleboard**

Particleboard is a panel product manufactured from small wood particles and an

adhesive. The raw materials of particleboard are sawdust, planer shavings, or other relatively homogeneous waste materials from wood industry. Particleboard typically has two face layers made with fine wood furnish and one core layer made with coarse wood furnish. Particleboard is less expensive than solid wood. However, particleboard has a lower dimensional stability in the presence of moisture or water than solid wood. Particleboard is mainly used for making furniture and kitchen cabinets.

UF resins are the most commonly used adhesive for making particleboard. PF, melamine-urea-formaldehyde (MUF) and isocyanates are sometimes used [4].

#### **1.1.4 Medium density fiberboard (MDF)**

Fiberboard is a wood composite panel made with wood fibers, an adhesive and some additives such as wax. Fiberboard is typically classified according to its density: low density fiberboard (LDF), MDF and high density fiberboard (HDF). The densities of these fiberboards are 150-450 kg/m<sup>3</sup> for LDF, 600-800 kg/m<sup>3</sup> for MDF, and 850-1100 kg/m<sup>3</sup> for HDF[4]. MDF has a higher strength, and a higher moisture resistance than particleboard.

MDF is widely used for furniture and flooring. It is also used for making interior door skins, moldings and interior trim components.

MDF is predominately made with UF resins. However, UF-bonded MDF has a

low water-resistance and emits formaldehyde, which has generated a need for replacement of UF resins in making MDF[5].

## **1.2 Introduction of wood adhesives**

Adhesives are an indispensable component in traditional wood composites. They can significantly affect the physical, mechanical and chemical properties of wood composites. Wood adhesives can be roughly classified into two categories: adhesives from natural materials and adhesives from petrochemicals

### **1.2.1 Adhesives from natural materials**

#### ***1.2.1.1 Animal glues***

Animal glues are made from the hide and bones of animals such as cattle, sheep, and fish. They are, in fact, hydrolysis products of collagen, i.e., protein-based adhesives. The protein in the animal glues contains a high amount of an amide group (-CONH-), free amino groups (-NH- , -NH<sub>2</sub>) and a carboxylic acid group (-COOH). These functional groups interact with each other within and between protein chains. In addition, these functional groups also interact with wood[6]. These interactions provide the strength of animal glues and the adhesion. Proteins in different animal glues have different structures and contain different amounts of these functional groups. Therefore, the properties of different animal glues vary significantly.

Animal glues are sold as solid or liquid. The solid animal glues have to be

mixed with water before use. Animal glues were once widely used in furniture. However, they have been replaced by synthetic polyvinyl acetate because of their many undesirable properties such as low moisture resistance, susceptibility to biological degradation, and a relatively high price[7].

#### ***1.2.1.2 Casein-based adhesives***

Casein is a milk protein. Casein protein precipitates when milk is treated with acid. Separation and subsequent drying of the precipitate generate casein[8]. Casein has high amounts of carboxylic acid groups and can readily dissolve in an alkaline medium such as lime solution or sodium hydroxide solution. The carboxylic acid groups in casein can react with divalent or polyvalent metal ions to form crosslinked networks. The treatment of casein with the metal ions improves the water-resistance of the resulting plywood. Formaldehyde and dialdehyde starch were used with casein to further improve the water-resistance[9]. However, the treatment of casein with dialdehyde starch significantly increased the viscosity, which made the application of the modified adhesive onto wood furnish difficult[10]. Another undesirable property of casein-based adhesives is that they stain the wood with rich tannic acid[7].

Casein-based adhesives were mainly used for laminated lumbers and doors for interior uses [11]. The wood composite panels bonded with casein-based adhesives

have moderate dry shear strength, moderate water- and moisture-resistance and cannot be used for exterior applications.

#### ***1.2.1.3 Blood-based adhesives***

Blood can also be used as an adhesive. Blood is a byproduct of slaughterhouse and contains a high amount of protein. Lime and sodium hydroxide are typically used to unfold blood protein for adhesive applications[7]. Formaldehyde and PF resins were used to improve water-resistance, strength and mold resistance of plywood bonded with the blood-based adhesive[6]. Blood-based adhesives had a higher moisture resistance, but a lower strength than the casein-based adhesive.

The blood adhesive was used in combinations of PF resins or soybean protein for plywood manufacture [12, 13]. However, it is no longer used in a commercial scale

#### ***1.2.1.4 Soy-based adhesives***

##### ***1.2.1.4.1 Production and composition of soybean***

Soybeans contain about 20% oil, 34% carbohydrates, 40% protein and 4.9% ash[14]. Soybean oil is mainly composed of saturated and unsaturated triglycerides. Soybean carbohydrates consist of the complex polysaccharides including cellulose, hemicelluloses, and pectin. About 18 amino acids can be found in soy protein. Abundant amino acids in soy protein include acidic amino acids (aspartic acid and glutamic acid), non-polar amino acids (alanine, valine and leucine), basic amino acids

(lysine and arginine) and uncharged polar amino acids (glycine). Aspartic acid and glutamic acid account for almost 30% of all amino acids in soy protein[15].

The solubility of soy protein in water is highly dependent upon the pH. In a neutral or alkaline medium, around 80% of the protein can be dissolved[15]. The solubility decreases dramatically in an isoelectric region. The isoelectric region of soy protein is at pH 4.2-4.6. Soy protein can be separated into several fractions with very different characteristics according to their sedimentation constants[15]. The comparison of the fractions in soy protein is shown in Table 1.1

Table 1.1 The comparison of fractions in soy protein

Fraction	Content (%)	Molecular mass (Da)	Principal component
11S	52	320–360 k	glycinin
7S	35	150–190 k	beta-conglycinin
15S	5	640–720 k	dimer of glycinin
2S	8	8000–20,000	polypeptides

Major commercial soybean products include soybean oil, soy flour, defatted soybean meal, soy protein concentrate (SPC) and soy protein isolate (SPI). Soybeans are typically processed to produce soybean powder through the following steps: cleaning, cracking, dehulling and flaking. Soybean oil is typically removed from the soybean powder through a solvent-extraction process. The commonly used solvent is hexane. Soybean oil can also be removed by squashing soybeans. After the removal of soybean oil, the resulting powder is called defatted soybean meal or



soy flour. The defatted soybean meal can be further processed to produce soy protein concentrate (SPC) and soy protein isolate (SPI) through the partial removal of carbohydrates. The protein content for these two products is about 64% for SPC and 90% for SPI[16]. SPC can be produced through treating defatted soybean meal with three methods: moist heating with water leach, aqueous alcohol washing, and leaching with dilute mineral acid. In these treatments, insoluble SPC is obtained and carbohydrates are removed as the solubles. The following is a typical procedure for production of SPI. Defatted soybean meal is dissolved in warm water at the pH value of 7-8.5, and the insolubles are removed through centrifugation or filtration. The resultant solution is acidified to form precipitate that is further neutralized and dried to generate SPI. The compositions of different soy protein products are shown in Table 1.2 [16].

Table 1.2 The compositions of different soy protein products

g/100g product	Soy flour	Soy protein concentrate (SPC)	Soy protein isolate (SPI)
Protein	48	64	92
Fat	0.3	0.3	0.5
Moisture	10	10	<5
Fibers	3.0	4.5	<1
Ash	7	7	4
Carbohydrate	31-32	14-15	-

#### *1.2.1.4.2 Soybeans as a wood adhesive*

Soybean-based adhesives, commonly called soy-based adhesives were widely used in the production of wood composites from the 1930s to the 1960s[17]. Soy-based adhesives have many advantages such as low cost, easy handling and low press temperature[18]. However, wood composite panels bonded with the soy-based adhesives had relatively low strength and low water-resistance, which caused the adhesives to be replaced by formaldehyde-based adhesives.

There is renewed interest in soy-based adhesives in recent years because soybean is abundant, inexpensive, and readily available. Various chemical or enzymatic modifications of soy protein were investigated for improving the strength and water-resistance of wood composite panels bonded with soy-based adhesives. Soybean protein is a storage protein. Its native form has a very compact structure. Inside the compact protein structure, protein chains are held together by disulfide bonds, hydrogen bonds, electrostatic attraction between oppositely charged groups, and hydrophobic interactions. Several studies suggested that unfolding the soy protein structure significantly improved the strength and the water-resistance of wood composite panels bonded with modified soy protein[19-21]. The mechanisms for this improvement were proposed as follows: when the compact protein structure is unfolded, the protein chains can spread well onto wood surfaces and can easily penetrate wood. All those functional groups such as amino groups, carboxylic acid

groups and hydroxyl groups in the unfolded protein can well interact with wood components, thus forming strong bonding with wood. Alkali, organic solvents, surfactants, urea, guanidine, and protease enzymes were used to unfold/modify soy protein[19, 20, 22]. The modified protein was demonstrated to improve the strength and the water-resistance of resulting wood composite panels when compared with an unmodified soy protein[19, 20, 23]. The following mechanisms were proposed to explain the improved water-resistance: those modifications turned some hydrophobic amino acids inside out. The hydrophobic amino acids slowed down water penetration into the modified soy adhesives, thus enhancing the water-resistance [20, 22, 24, 25]. It was demonstrated that the esterification of carboxylic acid groups in SPI with ethanol using hydrochloric acid as a catalyst significantly increased the hydrophobicity of the modified SPI, thus improving the water-resistance of plywood bonded the esterified SPI[26].

The use of curing agents for crosslinking soy protein is another effective method for improving the strength and water-resistance of the soy-based adhesives. Conventional curing agents for soy protein include sulfur-containing compounds, epoxy compounds, aldehydes [21, 27, 28].

Sulfur-containing compounds include carbon disulfide, ethylene thiocarbonate, thiourea and potassium xanthate, and they are very good crosslinkers for soy

protein[21]. Because of their versatility, sulfur-based curing agents are widely used in many industrial applications such as coatings [29]. However, sulfur linkages are susceptible to biological or other degradations. The proposed reaction between proteins and carbon disulfide is shown in Figure 1.1. The amino groups on the protein react with carbon disulfide to produce sulfurized proteins. Then sulfurized proteins can be oxidized to form disulfide linkages.

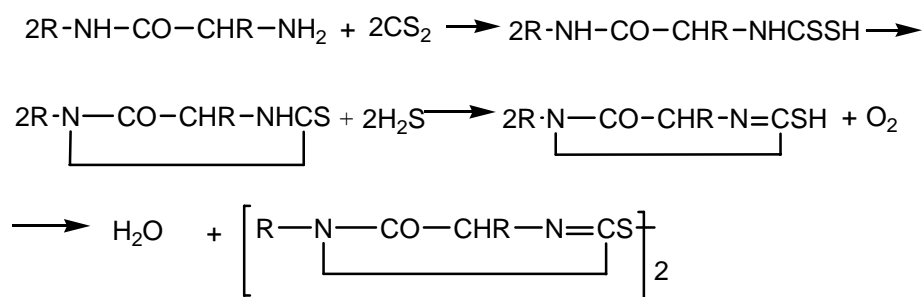


Figure 1.1 The proposed reaction between proteins and carbon disulfide

Epoxies are well known curing agents because the epoxy functional group can react with a wide variety of functional groups. The aliphatic epoxies were extensively investigated as curing agents for soy protein [30, 31]. Lumbuth modified soy protein by grafting aliphatic halohydrin ether to alkaline protein and then de-hydrohalogenating aliphatic halohydrin ether to form the corresponding epoxide in the adhesive system. The modified soy protein resulted in a higher water-resistance than unmodified soy protein [30]. Epoxidized soybean oil and 1, 2, 7,

8-diepoxyoctane (DEO) were investigated as curing agents in the modification of SPI. The modified SPI provided similar adhesive properties to UF resins[31]. Epoxy-modified SPI is expensive although it improved the strength and water-resistance of the resulting plywood panels. The curing mechanism by which epoxy compounds crosslink soy protein relies on the reactions of the epoxy functional group with amino groups, hydroxyl groups and carboxylic acid groups on the soy protein.

Aldehydes are important protein modifiers. They crosslink and denature soy protein, thus resulting in enhanced water-resistance, increased pot life, improved assembly time tolerance, and increased water-holding capacity[21]. Formaldehyde and paraformaldehyde are very active crosslinkers for soy protein, and they can cause pre-mature gelation. Thus they are used in the modification of soy protein with very small quantities such as 0.1-1% based on dry adhesive weight. Linkages from the reactions between formaldehyde and soy protein are reversible under hydrothermal conditions. Therefore, formaldehyde-modified soy protein softens once exposed to tropical temperature and humidity. Other aldehydes such as glutaraldehyde (GA) were also studied for crosslinking proteins[27, 32]. It was proposed that GA mainly reacted with the  $\epsilon$ -amino groups of lysine and N-terminal of polypeptides[27]. GA also reacted with other nucleophilic groups in proteins, such as the mercapto group

(-SH) of cysteine, the amino group on the histidine ring, and the phenolic hydroxyl group of tyrosine[33]. The reactions of these hydrophilic functional groups in proteins with GA enhanced the water-resistance of the GA-modified proteins and the resulting plywood.

It has been demonstrated that modifications of SPI using marine adhesive protein (MAP) as a model were effective ways of improving the adhesive properties of SPI. More specifically, imparting SPI with a 3,4-dihydroxyphenyl group and a mercapto group that are abundant in MAP greatly improved the strength and water-resistance of wood composites bonded with modified SPIs [34, 35]. Wood composites bonded with an adhesive consisting of SPI and a polyamidoamine-epichlorohydrin (PAE) adduct had the shear strength and water-resistance comparable to PF resins [18]. A soy flour-PAE adhesive has been successfully used in a number of plywood plants and a particleboard plant [36]. A novel adhesive system based on SPI, maleic anhydride (MA) and polyethylenimine (PEI) was developed and characterized. This SPI-MA-PEI adhesive was superior to alkali-modified SPI in terms of the enhancing strength and water-resistance of the resulting wood composites [34].

### **1.2.2 Adhesives from petrochemicals**

Synthetic resins are typically derived from petrochemicals. There are two types

of synthetic resins: thermosetting resins and thermoplastic resins. Thermosetting resins become insoluble and infusible materials after being heated at a certain temperature, which is an irreversible process. Thermoplastic resins soften or melt when they are heated, and solidify again when they are cooled. The softening and solidifying are reversible and can be repeated many times [7]. Major thermosetting and thermoplastic wood adhesives are described in detail in the following sections.

### ***1.2.2.1 Thermosetting resins***

The most commonly used commercial thermosetting resins for production of wood composites include phenol-formaldehyde (PF) resins, urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins and phenol-resorcinol-formaldehyde (PRF) resins, and isocyanates[11].

#### ***1.2.2.1.1 phenol-formaldehyde (PF) resins***

PF resins are prepared by addition and condensation reactions of phenol and formaldehyde in the presence of either an acid or base catalyst. The reaction scheme for preparing these two PF resins is shown in Figure 1.2 [6]. Under either an acid catalysis or a base catalysis, the initial reaction is the same, i.e., addition of formaldehyde to phenol to form methylol-substituted phenols. The addition reaction can occur at the *ortho*- and *para*-position of the phenolic hydroxyl group (Figure 1.2). The resulting methylol-substituted phenols react with each other through a

condensation reaction to form linear or branched polymers (Figure 1.2). PF resins prepared with an acid catalyst are called novolacs and those prepared with a base catalyst are called resoles [37]. The reaction parameters for preparing these two PF resins are shown in Table 1.3.

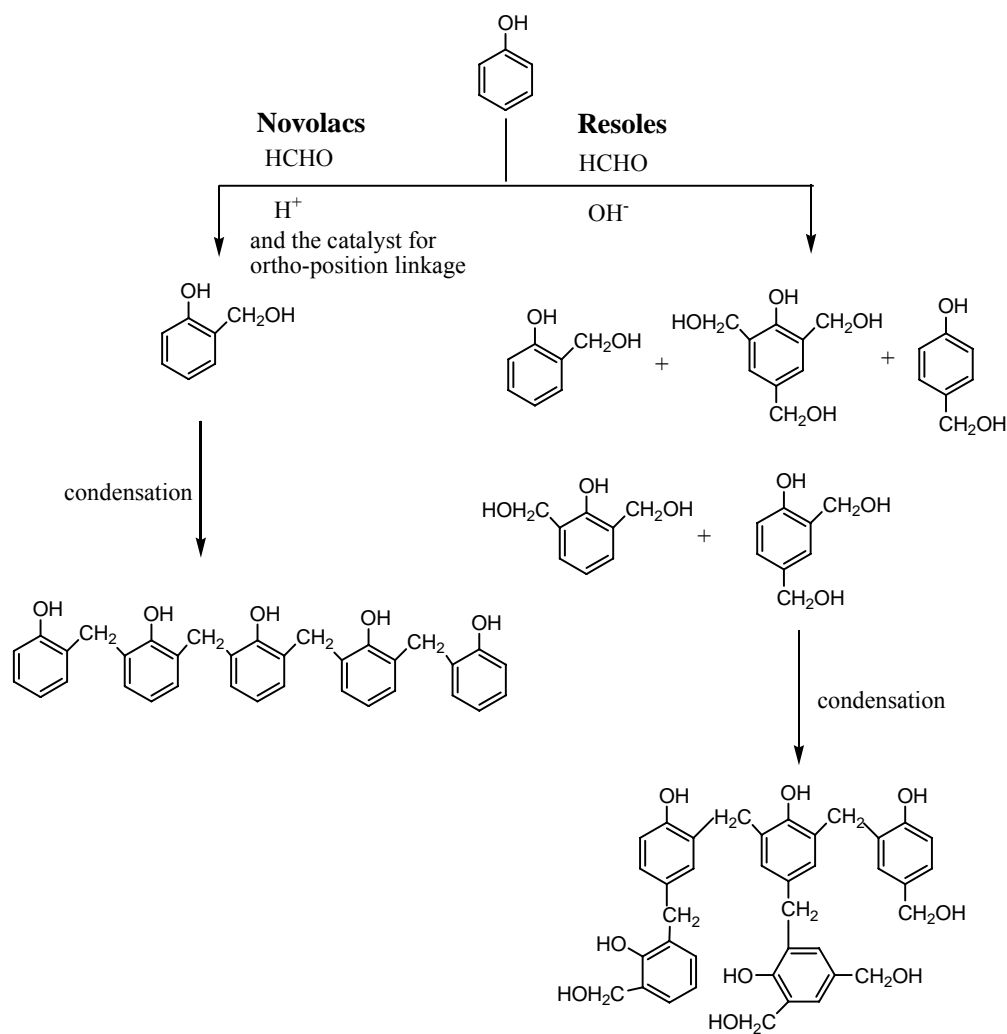


Figure 1.2 The preparations of PF resins by resoles and novolacs

In the preparation of resoles, the molar ratio of formaldehyde to phenol is more



than one. Phenol may be substituted with more than one methylol group. These substituted phenols can further react among themselves to form a mixture of polymers with different sizes and different degrees of branching. Resoles will form highly crosslinked polymer networks when cured at an elevated temperature. In contrast, the formaldehyde/phenol molar ratio is less than one in the initial stage of preparing novolacs. The reason is that the methylol group is not stable under an acidic condition and can quickly react with phenol to form polymers. The low formaldehyde/phenol ratio allows the resulting PF resins to have relatively low molecular weights so that they can flow and penetrate wood. Immediately prior to use for bonding wood, additional amount of formaldehyde has to be added to further react the adhesive, thus forming highly crosslinked polymer networks. With the aid of special catalysts such as divalent metal acetates, phenols can be predominantly linked at *ortho*-positions, thus resulting in novolacs with a linear structure. Because novolacs requires a two step process, almost all commercially used PF resins are now resoles[37].

Table 1.3 Reaction parameters for preparing resoles and novolacs[6]

Name	Type of catalyst	Phenol/formaldehyde molar ratio	Reaction temp. (°F)	Reaction time (hr)	Additional reactants
Resoles	Base	<1:1	175-212	1-3	No
Novolacs	Acid	>1:1	212	3-6	Yes

PF resins are mainly used for production of exteriorly used structural wood composite panels such as plywood and laminated veneer lumber (LVL) because of their good durability and high strength even under harsh weather conditions. PF resins after cured have a dark color, which negatively affects the aesthetics of wood composite products[7, 8]. Therefore, PF resins are normally not used for production of interiorly used wood composite panels.

Lignin, the second most abundant natural polymer, has been extensively investigated for partial replacement of phenol in the preparation of PF resins [38-42]. This replacement is mainly for lowering the cost of PF resins. Studies demonstrated that lignin could potentially replace a wide range (25-100%) of phenol while maintaining the quality of the modified PF resins [41]. However, lignin from different sources or from the same source, but different batches, has highly inconsistent properties and compositions. Lignin also has a much lower reactivity to formaldehyde than phenol. Therefore, only a very limited amount of lignin is currently used for making wood adhesives, despite extensive investigations[43].

#### *1.2.2.1.2 Resorcinol-formaldehyde (RF) resins*

RF resins are derived from resorcinol and formaldehyde and are a special wood adhesive. RF is prepared via the same reaction mechanism as PF resins. Resorcinol is more reactive to formaldehyde than phenol because its two hydroxyl groups at the

*meta*-position to each other greatly activate the aromatic ring. The reactivity of resorcinol to formaldehyde is so high that the polymerization reaction between resorcinol and formaldehyde occurs quickly even at room temperature[44]. Because of the fast polymerization reaction, RF resins are generally prepared in two steps: 1) resorcinol reacts with a part of formaldehyde (the molar ratio of resorcinol to formaldehyde is 1:0.5-0.7) to yield RF pre-polymers, 2) additional formaldehyde called “hardeners” is added to the RF pre-polymers prior to use[37]. The mechanism of addition phase for making RF resins is shown in Figure 1.3.

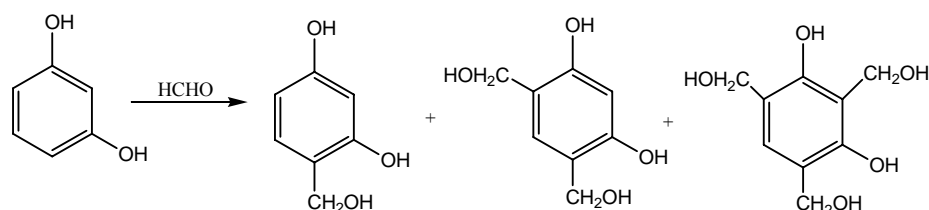


Figure 1.3 The mechanism of addition phase for making RF resins

Because resorcinol can lead to a high degree of crosslinking, RF resins provide a higher strength for wood composites than PF resins. The main drawbacks of RF include a high cost, dark color and a short pot life. Due to the dark color, RF can only be used for making some exteriorly used wood composite panels where the color of the panels is not a concern. Phenol is commonly used to partially replace resorcinol mainly for lowering the overall cost of the adhesive. As a matter of fact,

phenol-resorcinol-formaldehyde (PRF) resins are much more commonly used in the wood composite industry than RF resins. PRF resins are widely used for the production of laminated lumbers and finger-joint applications[45].

#### *1.2.2.1.3 Urea-formaldehyde (UF) resins*

UF resins are derived from urea and formaldehyde in the presence of a catalyst. The reaction scheme of preparing UF resins is shown in Figure 1.4[6]. The reactions between urea and formaldehyde first generate a mixture of mono-, di-, tri- and tetra-methylol ureas that further condense to form crosslinked polymer networks. The molar ratio of formaldehyde to urea is above one, typically around 1.5 to 2. The pH value of the UF resins should be lower than 7 for curing. UF resins can be cured at elevated temperatures (95-130 °C) with ammonium salts of strong acids as catalysts. UF resins can also be cured at room temperature using strong acids as catalysts [8]. But the strong acids such would degrade wood and lower bonding strength[46].

UF resins are colorless and inexpensive, and have a faster curing rate, i.e., a shorter curing time than PF resins. They are widely used for making interior plywood, particleboard and medium density fiberboard. UF resins have a lower water-resistance than PF resins and can easily be hydrolyzed by water to release formaldehyde. Depending on the water-resistance requirements, some melamine may be incorporated into the UF resins to improve their water-resistance[7]. Small

amounts of diisocyanate and polymeric 4,4'-diphenylmethane diisocyanate (pMDI) have been shown to improve the water-resistance of plywood bonded with UF resins as well[47-51].

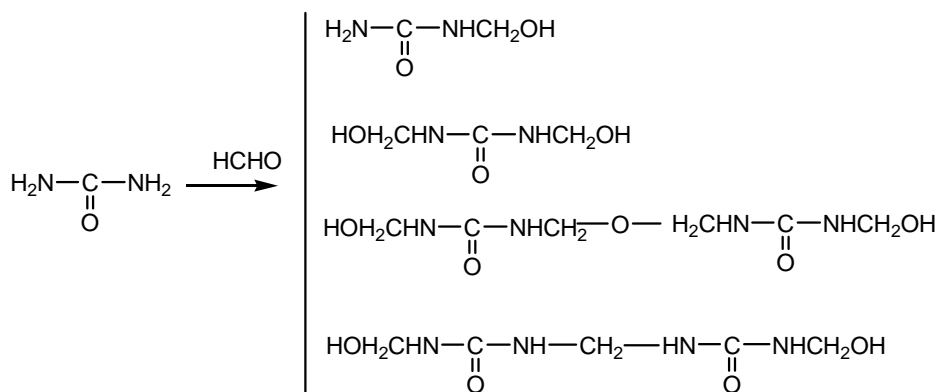


Figure 1.4 The mechanism of preparation of UF resins

#### 1.2.2.1.4 Melamine-formaldehyde (MF) resins

Melamine is derived from urea and is widely used for making MF resins. The reaction scheme for making MF resins is shown in Figure 1.5. Melamine has three amino groups that can react with formaldehyde to form MF resins. The molar ratio of melamine to formaldehyde is about 1:2.5.

MF resins are more resistant against hydrolysis. In other words, wood composite panels bonded with MF resins are much more water-resistant than those bonded with UF resins. MF resins are widely used for making wood composite panels for covered exterior applications. MF resins are also widely used for

saturating paper. MF resins are more brittle than UF resins, thus resulting in brittle joints, blunt tools and hard cleaning of mixing equipment[8, 37]. Because of the high cost of melamine, the annual consumption of MF resins is much less than that of PF and UF resins in the wood adhesive market. The small amount of melamine is often incorporated into UF resins to form melamine-urea-formaldehyde (MUF) resins. MUF resins are more water-resistant than UF resins. MUF resins are used to make wood composite panels for covered exterior applications, such as finger joints, and edge-glued lumber.

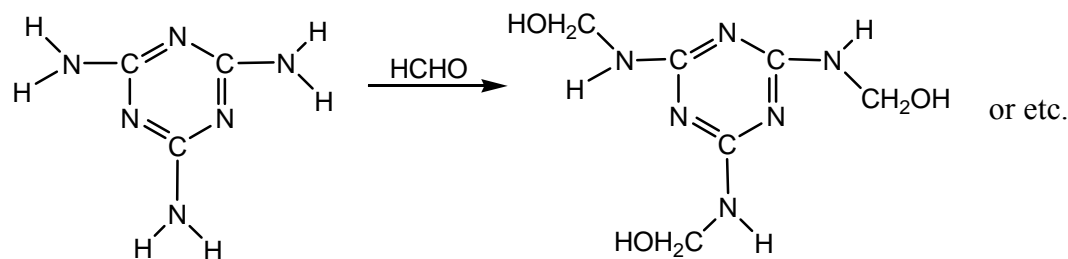


Figure 1.5 The mechanism of addition phase for making MF resins

#### 1.2.2.1.5 Epoxy resins

Epoxy resins are based on compounds containing at least two epoxy functional groups. These compounds polymerize in the presence of a hardener and a catalyst. One of the widely used epoxy resins is bisphenol A diglycidyl ether (BADGE) that is derived from bisphenol A (a condensation product of phenol and acetone) and

epichlorohydrin. A representative structure of BADGE is shown in Figure 1.6. Epoxy resins are widely used in coatings, casting, encapsulation and laminates because they are capable of forming good bonding to many materials. The epoxy functional group can react with a wide variety of functional groups such as hydroxyl groups, amino groups, and carboxylic acid groups. Epoxy resins are thus widely used as crosslinking agents for various substrates in both an organic medium and an aqueous medium. BADGE is rarely used as a crosslinking agent in an aqueous medium because of its poor solubility in water. A number of epoxy resins with high water-solubility, such as trimethylolpropane triglycidyl ether (TMTE), have been used as crosslinking agents in an aqueous medium[52, 53].

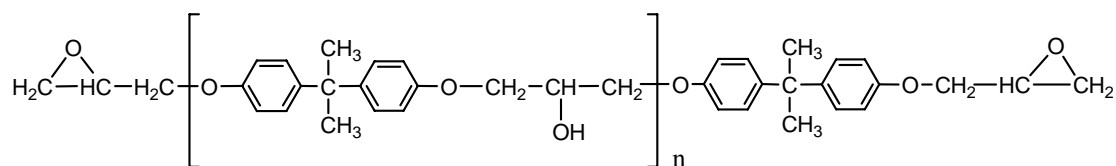


Figure 1.6 The representative structure of bisphenol A diglycidyl ether (BADGE)

Epoxy resins have some outstanding physical properties, such as low cure shrinkage, good wetting ability, excellent chemical and corrosion resistance, superior strength and weather durability[54]. The disadvantages of epoxy resins are inherent brittleness, high cost, high cure requirements for obtaining high strength, and environmental issues related to the emission of volatile organic compounds.

#### 1.2.2.1.5.1 Curing mechanisms for epoxy resins

Curing is referred to a process that transforms an adhesive from a thermoplastic state to a thermosetting state. This process occurs when epoxy resins react with curing agents or themselves to form crosslinked solid materials. The curing is an essential process to impart the adhesive strength and adhesion.

Depending on particular epoxy formulations, curing conditions for epoxy resins vary. The curing can occur at room temperature or elevated temperatures depending on the chemical properties of a curing agent or a catalyst used. Elevated curing temperature is typically needed for many applications.

The ring-opening of an epoxy functional group is the essential reaction in the curing of epoxy resins. The reaction can be carried out under either an acidic or basic conditions. Under a basic condition, a nucleophile opens the epoxy ring via a substitution-nucleophilic-bimolecular-reaction ( $\text{SN}_2$ ) mechanism (Figure 1.7) [55]. Under an acidic condition, the oxygen on an epoxy ring is first protonated, thus weakening the O-C bonds on the ring or breaking the three-membered ring to form a cationic carbon. A nucleophile then breaks the weakened O-C bonds or reacts with the resulting cationic carbon (Figure 1.8) [55]



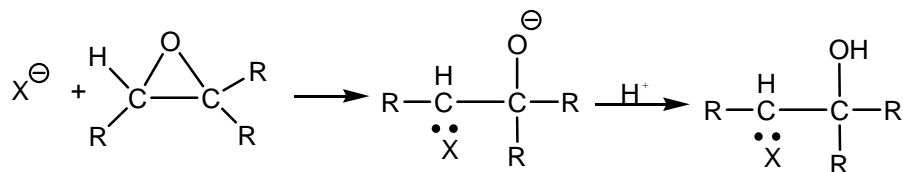


Figure 1.7 The ring-opening mechanism under a basic condition

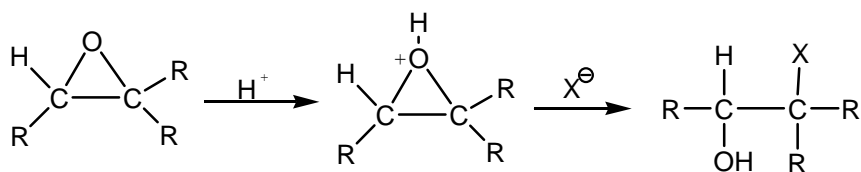


Figure 1.8 The ring-opening mechanism under an acidic condition

There are two main curing reactions for epoxy resins, and both of them increase the molecular weight and crosslinking density of the adhesives. These reactions are polyaddition and homopolymerization.

#### 1.2.2.1.5.1.1 Polyaddition reactions of epoxy resins

A polyaddition reaction refers to a reaction between an epoxy resin and a curing agent containing multiple reactive functional groups. After curing, the curing agent becomes a part of the final adhesive structure. The reactive functional groups in a curing agent must have sufficiently strong nucleophilicity so that they can react with the epoxy functional groups in epoxy resins. A representative polyaddition reaction of an epoxy resin with an effective curing agent is shown in Figure 1.9. In a polyaddition reaction, the reaction rate is significantly affected by the bulkiness of

substituents on the epoxy ring and a curing agent. Small substituents and a small curing agent molecule facilitate the polyaddition reaction and increase the crosslinking density in the final adhesive structure[56].

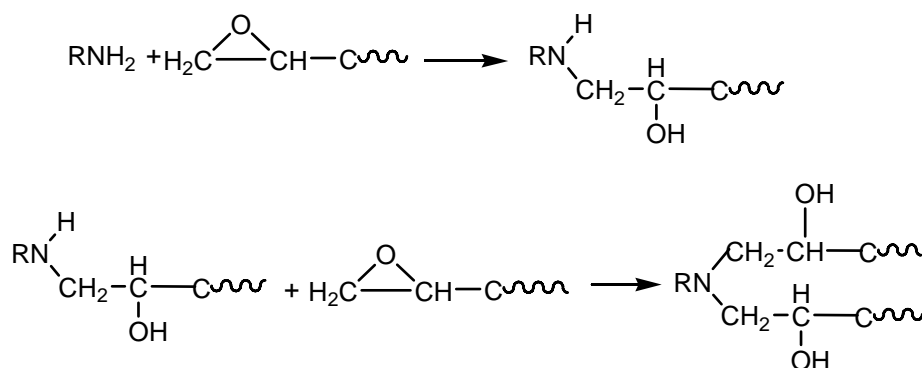


Figure 1.9 A typical mechanism of polyaddition reaction of an epoxy resin with an active hydrogen compound

#### 1.2.2.1.5.1.2 Homopolymerization reactions

An epoxy functional group can polymerize itself in the presence of a catalyst. This process is called homopolymerization. Unlike cured epoxy resins from a polyaddition reaction, the final network structure of the cured epoxy resins from a homopolymerization is solely derived from the epoxy compound. The epoxy compound alone determines the final properties of cured epoxy resins. In addition to a catalyst, an elevated temperature is typically required for carrying out a homopolymerization reaction. A representative mechanism of a homopolymerization reaction of an epoxy resin is shown in Figure 1.10[56].

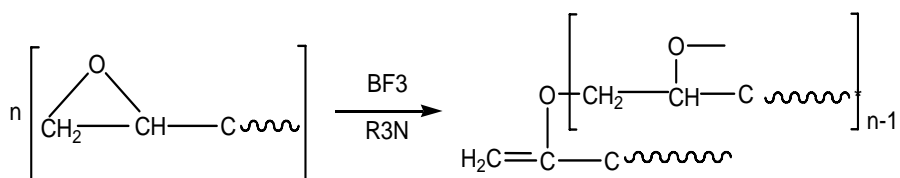


Figure 1.10 The mechanism of a homopolymerization reaction of an epoxy resin

### 1.2.2.1.5.2 Curing agents and catalysts for epoxy resins

#### 1.2.2.1.5.2.1 Curing agents

A wide variety of compounds can be used as curing agents for epoxy resins. Commonly used curing agents include amines, carboxylic acids, carboxylic acid anhydrides, polysulfides and thiols. These curing agents usually react with the epoxy functional group directly. The choice of curing agents is dependent upon end-uses and manufacturing processes. The performance of cured epoxy resins is highly dependent on the types of chemical bonds and the degree of crosslinking from the polyaddition reaction. Amines and carboxylic acid anhydrides are two most commonly used curing agents for epoxy resins.

##### 1.2.2.1.5.2.1.1 Amine curing agents

Amines are the most important curing agents for epoxy resins. Commonly used amine curing agents include aliphatic amines and aromatic amines. Both primary and secondary aliphatic amines can be used as curing agents. Aliphatic amines can

be further classified as acyclic aliphatic amines such as diethylenetriamine (DETA) and cycloaliphatic amines such as isophorone diamine (IPD). Acyclic aliphatic amines can react with epoxy functional groups at a lower temperature than cycloaliphatic amines and aromatic amines. However, at room temperature a long curing time of four to seven days is generally needed for acyclic aliphatic amines[57]. Increase in the curing temperature can significantly shorten the curing time. The effect of curing temperature and curing time on the bond strength of the BADGE epoxy resin with two different acyclic aliphatic amines are shown in Table 1.4[44]. Commonly used cycloaliphatic amine curing agents are diamines such as isophorone diamine (IPD), bis-*p*-aminocyclohexylmethane (PACM) and 1, 2-diaminocyclohexane (DAC). They can be used at both ambient and an elevated temperature. These cycloaliphatic amine curing agents have light color and good chemical resistance. However, they have a low curing rate at low temperature.

Table 1.4 The effect of curing temperature and time on the bond strength (psi) of BADGE epoxy resin cured with two different aliphatic amines

Triethylenetetramine				N, N-diethylaminopropylamine		
Cured at RT		Cured at 95 °C	Cured at 145 °C	Cured at 40 °C	Cured at 95 °C	Cured at 145 °C
3 days	15 days	30 min	30 min	16 h	5 h	30 min
1162	1690	3172	3426	702	3236	4056

Aliphatic amines are corrosive and can cause skin irritation upon prolonged exposure. In addition, unmodified amines can absorb moisture and carbon dioxide

when exposed to ambient environment for a long time, which can cause whitening and thus negatively affect the appearance of cured adhesive in many cases[58]

The most commonly used aromatic amines are *meta*-phenylenediamine (MPDA), methylene dianiline (MDA) and mixtures of the two[56]. Aromatic amines provide cured epoxy resins with superior heat and chemical resistance as well as a long pot life. Generally, elevated temperature is required for aromatic amines to cure epoxy resins when excellent properties are desired. However, aromatic amines can also be cured at ambient temperature in the presence of some special catalysts such as a  $\text{BF}_3$  complex. Aromatic amines have low curing rates. Most of aromatic amine curing agents are in solid forms, which may present a problem in mixing them with an epoxy resin[58]. In addition, some aromatic amine curing agents are human carcinogens.

#### 1.2.1.1.5.2.1.2 Anhydrides

Acid anhydrides are the second most important epoxy curing agents. The most commonly used anhydrides include hexahydrophthalic anhydride (HHPA), phthalic anhydride (PA), nadic methyl anhydride (NMA), and pyromellitic dianhydride (PMDA). The reaction between an anhydride and epoxy resins need the involvement of water, alcohol or an accelerator that may be tertiary amines, metallic salts, and imidazoles etc. The reaction between an acid anhydride and epoxy resins is shown in Figure 1.11. The reaction products are generally complex and both esters and ethers



#### 1.2.2.1.5.2.2 Catalysts

The role of a catalyst in epoxy resins is to facilitate the homopolymerization and polyaddition reactions. The most commonly used catalysts for epoxy resins include metal salts, tertiary amines,  $\text{BF}_3$  complex, imidazoles, and dicyandiamide. They can be roughly classified into two categories: cationic catalysts and anionic catalysts.

##### 1.2.2.1.5.2.2.1 Cationic catalysts

Lewis acids are the most important cationic catalysts for epoxy resins. They typically are inorganic salts of Al (III), B (III), Be (II), Fe (III), Sb (V) and Zn (II) [61]. For example,  $\text{BF}_3$ -Monoethylamine (MEA) is widely used in various commercial applications. This catalyst works well for linear and cycloaliphatic epoxies and glycidyl ethers. The catalytic activity of  $\text{BF}_3$ -MEA is not high until a curing temperature reaches 100-125 °C. Good physical properties of cured epoxy resins with  $\text{BF}_3$ -MEA can only be obtained at a high temperature range of 150-175 °C. The catalytic mechanism of  $\text{BF}_3$ -MEA is shown in Figure 1.12. Quaternary ammoniums conjugated with a weak nucleophilic acid, such as boric acid are well known cationic curing catalysts[32].

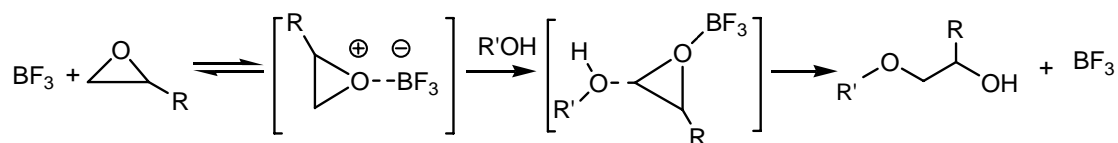


Figure 1.12 A carbonium ion mechanism for  $\text{BF}_3$  and epoxides

#### 1.2.2.1.5.2.2.2 Anionic catalysts

Tertiary amines are widely used as catalysts for epoxy resins. The most commonly used tertiary amines are DMP-10 (tris-(dimethylaminomethyl) phenol) and DMP-30 (*O*-(dimethylaminomethyl) phenol). The tertiary amine-catalyzed epoxy resins can provide excellent adhesion to metal. In addition, tertiary amine catalysts also impart high strength, high toughness and good elongation properties to the cured epoxy resins [56]. Phosphonium salts and water-dispersible polymers containing a tertiary amine functionality were found to be good catalysts for curing of epoxy resins at room temperature[61, 62].

#### 1.2.2.1.5.3 Epoxy resins for bonding wood

Epoxy resins are well known for their high strength and superior durability, but they are seldom used in wood industry because of their high cost and inferior bonding with wood for exterior applications. Wood composite panels bonded with epoxy resins have high strength when they are dry. However, they tend to delaminate once exposed to a water-soaking-and-drying cycle.

Olson and Blmquist invented an epoxy resin, called FPL-16, in the early 1960s.



The plywood panels bonded with FPL-16 endured a 120-hour boil-dry test, although they were still not as durable as those bonded with RF resins. FPL-16A, a modified adhesive from FPL-16, was widely used for making wood aircraft with high dry shear strength and a high wood-failure percentage on various wood species[63]. An epoxy resin was recently synthesized from resorcinol-liquefied wood meal[64]. Epoxy functionality was introduced into the liquefied wood by a glycidyl reaction. This adhesive was superior to BADGE in terms of improving the shear strength and the modulus of elasticity of the resulting plywood panels. But the curing process of this adhesive was too complicated to be practical for wood industry.

Several studies revealed that the mechanical properties and water-resistance of epoxy resin-bonded plywood panels were significantly improved if wood veneers were pre-treated with some chemicals. It was found that pre-treatment of wood with 2% polyethylenimine (PEI) solution prior to bonding with an epoxy resin improved the durability of the epoxy glue lines[65]. It was demonstrated that the pre-treatment of wood with hydroxymethylated resorcinol (HMR) prior to bonding with the BADGE epoxy resin dramatically improved the structural durability of the resulting wood-based panels [66, 67]. This pre-treatment worked well for two softwood (Sitka spruce and Douglas-fir) and one hardwood (yellow-poplar) species, but did not work well for high density Yellow birch [66, 67].

### ***1.2.2.2 Thermoplastic resins***

Polyvinyl acetate (PVA)

PVA, the “white glue”, is typically prepared from an emulsion polymerization of vinyl acetate. The PVA glue is typically sold as an aqueous emulsion. PVA is the most commonly used glue in furniture assembly. Once the PVA glue is applied to wood, it set quickly (typically within 15 min) at ambient temperature and the high strength of adhesive bonds is quickly achieved. The PVA glueline is almost invisible, which is a desirable feature of an adhesive for furniture manufacture. However, The PVA glue has poor gap-filling properties and its water-resistance and heat-resistance are also not good. For improving the water- and heat-resistance, various crosslinkable monomers such as N-(hydroxymethyl)acrylamide have been added in the polymerization of vinyl acetate to modify PVA glues so that the modified PVA glue can form crosslinked polymer networks once cured[68, 69].

## **1.3 Issues associated with formaldehyde-based adhesives**

### **1.3.1 Dependence on non-renewable raw materials**

The raw materials for making UF and PF resins are mostly derived from non-renewable natural gas and petroleum. The finite reserve and expanding consumption of petroleum and natural gas will definitely affect the availability of the raw materials for making these formaldehyde-based adhesives in a long run.

### **1.3.2 Emission of carcinogenic formaldehyde**

Formaldehyde has been re-classified as a human carcinogen by International Agency for Research on Cancer[70]. It is well established that formaldehyde is released in the production and use of wood composites bonded with these formaldehyde-based adhesives, especially UF. The California Air Resources Board (CARB) estimates that as much as 400 tons of formaldehyde is emitted by the products bonded with UF each year in California[71]. The emission of formaldehyde mainly comes from residual free formaldehyde in adhesives and the hydrolytic product of the adhesives. Cured UF resins are susceptible to hydrolysis in the presence of water or moisture to release formaldehyde. Acidic environment and elevated temperatures can speed up the hydrolysis. Cured PF resins are more resistant to hydrolysis than cured UF resins. Thus, residual free formaldehyde is mainly responsible for the formaldehyde emission from PF resins and PF-bonded wood composite panels.

The non-renewable nature of the raw materials for making currently used formaldehyde-based adhesives and the hazardous issues associated with formaldehyde emission have generated a need for the development of a formaldehyde-free wood adhesive from renewable materials.

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CHAPTER 2 A NEW SOY FLOUR-BASED ADHESIVE FOR MAKING  
INTERIOR PLYWOOD

## **2.1 Abstract**

Formaldehyde-based adhesives such as urea-formaldehyde and phenol-formaldehyde resins dominate the current wood adhesive market. However, these adhesives are derived from petrochemicals and carcinogenic formaldehyde. In this study, we developed a formaldehyde-free adhesive from abundant, renewable, and inexpensive soy flour (SF). The main ingredients of this adhesive included SF, polyethylenimine (PEI), and maleic anhydride (MA). The optimum formulation of this adhesive and the optimum hot-press conditions for making plywood were investigated. A three-cycle soak test and a boiling water test (BWT) were employed for evaluating the strength and water-resistance of plywood bonded with this adhesive. Results showed that SF, PEI, MA and sodium hydroxide were all essential components for the adhesive and the SF/PEI/MA weight ratio of 7/1.0/0.32 resulted in the highest water-resistance. When the hot-press temperature was in the range of 140-170 °C, both water-resistances and shear strengths of plywood bonded with the adhesive remained statistically the same, except that the dry shear strength of plywood at 170 °C was statistically lower than that at 160 °C. When the hot-press time ranged from 2 to 6 min, the plywood panels at 5 min had the highest BWT/w shear strength. The plywood panels made at the hot-press time of 5 min had a higher dry shear strength than those made at the hot-press time of 3 min. Plywood

panels bonded with this SF/PEI/MA adhesive exceeded the water-resistance requirements for interior application.

## **2.2 Keywords**

Wood adhesives, soy protein, plywood, water-resistance

## **2.3 Introduction**

In 2001, the worldwide wood adhesive consumption was 13.3 million tonnes and total sale value reached \$6.1 billion. Formaldehyde-based adhesive accounted for 99% of the total volume and 97% of the total sale value, which indicated that formaldehyde-based adhesives played a dominant role in the wood adhesive market[1]. However, formaldehyde-based adhesives are derived from non-renewable petrochemicals and natural gas. In addition, the emission of formaldehyde, especially from the breakdown of UF resins in wood composites, poses a great hazard to human health because formaldehyde is a human carcinogen[2]. Finite oil reserves, the expanding wood adhesive market and hazardous issues associated with formaldehyde-based adhesives generate an urgent need for the development of environmentally friendly alternative wood adhesives from renewable materials.

Soybean, originated from eastern Asia, is one of the most important crops in the United States. Soybean oil and soybean meal are two major products of

soybean. At present, soybean meal is mainly used as food and animal feeds. In the United States, about 98% of soybean meal is consumed by livestock and poultry[3]. Only a small portion of soybean meal is currently used in non-food industrial applications such as surfactants, inks, fuels and lubricants. The worldwide production of soybean has been increasing in recent years. The US farmers produced about 3.19 billion bushels of soybean in 2006[4]. The traditional soybean market as food and animal feeds has been saturated. New non-food industrial applications have to be developed for consuming the oversupplied soybean.

Wood adhesives are potentially a huge market for the oversupplied soybean. As a matter of fact, soy-based adhesive was widely used in the commercial production of plywood in the 1930s-1960s. Soy-based wood adhesives have many advantages such as low cost, easy handling, low pressing temperature[5]. However, they also have many inferior properties such as low strength and water-resistance of the resulting wood composite panels. Because of their inferior properties, they have been virtually replaced by formaldehyde-based adhesives since the 1960s. However, soybean represents an ideal raw material for making wood adhesives because it is abundant, renewable, environmentally friendly, and readily available.

There has been a renewed interest in development of soy-based wood adhesives in recent years. Various new methods have been investigated for improving the

strength and water-resistance of wood composite panels bonded with soy-based adhesives. It was demonstrated that the treatment of soybean protein with alkali and protease enzymes significantly improved the strength and water-resistance of plywood samples bonded with the modified soy proteins [6-8]. The treatments of soy protein with urea, guanidine hydrochloride, and sodium dodecyl sulfate (SDS) were also found to improve the strength and water-resistance of the resulting plywood panels[9-12]. Chemical modifications of soybean protein using mussel adhesive protein as a model have been demonstrated to be effective ways of converting soybean protein to a strong and water-resistant wood adhesive[13, 14]. A polyamidoamine-epichlorohydrin (PAE) resin has been found to be an excellent curing agent for soybean protein[5, 15, 16]. A patented technology based on soybean flour and the PAE resin has been successfully used in the commercial production of plywood and particleboard[17].

A novel adhesive based on soy protein isolate (SPI), MA, and PEI has been developed[18]. However, this adhesive is not practical for commercial application because SPI is too expensive to be used as a raw material for making wood adhesives. In this study, we investigated if SF, the most abundant and the most inexpensive form of soybean meal, can be used to replace SPI for bonding wood.

## **2.4 Materials and experimental methods**

### **2.4.1 Materials**

SF (7% moisture content) was provided by Cargill Incorporated (Minneapolis, MN); A 50 wt% aqueous PEI solution ( $M_w=750,000$ ) and MA were purchased from Sigma-Aldrich (Milwaukee, WI). Yellow-poplar veneer was a gift from Columbia Forest Products (Portland, OR).

### **2.4.2 Preparation of soy flour (SF)-polyethyleneimine (PEI)-maleic anhydride (MA) adhesives**

The following is a representative procedure for the preparation of SF-PEI-MA adhesives. A 50% PEI solution (228 g wet PEI, 114 g dry PEI), de-ionized water (1517 mL) and MA (36.5 g), and 1 N NaOH (285 mL) were sequentially added to a KitchenAid mixer and mixed for 5 min at room temperature. SF (859 g, wet weight) was added and further mixed for 10 min. The total solids content of the resulting adhesive was 36%.

### **2.4.3 Preparation of three-ply plywood samples**

The adhesive was applied to two sides of a yellow-poplar veneer (2 ft × 2 ft; moisture content, 12%) by a roller coater. The spread rate of the adhesive was 8 mg/cm<sup>2</sup> on a dry weight basis. The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. The stacked veneers were put on a table for 5 min, cold-pressed at 100



psi for 5min, put on a table again for 5 min and hot-pressed at 150 psi with predetermined time and temperature. After hot-press, the panel was stored at ambient environment for at least 24 h before it was evaluated for its shear strength and water-resistance.

#### **2.4.4 Determination of the water-resistance and the shear strength of plywood panels**

##### ***2.4.4.1 Three-cycle soak test***

The water-resistance of plywood panels was determined with a three-cycle soak test in accord with the American National Standard for Hardwood and Decorative Plywood; Hardwood Plywood & Veneer Association; 2004 (ANSI/HPVA HP-1). ANSI/HPVA HP-1 is the commonly accepted standard for evaluating the water-resistance of interior plywood. The following is a detailed testing procedure defined by the standard. Twenty plywood specimens (2 in × 5 in) cut from each plywood panel were soaked in water at  $24 \pm 3$  °C for 4 h, and then dried at 49 °C-52 °C for 19 h. All specimens were inspected to see whether they were delaminated. This soaking/drying cycle was repeated until three cycles were completed. According to the standard, a plywood panel meets water-resistance requirement for interior applications if 95% of the specimens, i.e., 19 out of the 20 specimens do not delaminate after the 1<sup>st</sup> soaking/drying cycle and 85% of specimens, i.e., 17 out of 20 specimens do not delaminate after the 3<sup>rd</sup> soaking/drying cycle. The ANSI/HPVA

HP-1 specifically provides the following definition of delamination: any continuous opening between two layers has to be longer than two inches and deeper than 0.25 inch and wider than 0.003 inch.

#### ***2.4.4.2 Boiling water test***

In accordance with US Voluntary Product Standard PS 1-95 for Construction and Industrial Plywood (published by the U.S. Department of Commerce through APA-The Engineered Wood Composites, Tacoma, WA), the following boiling water test (BWT) can be used to evaluate whether plywood panels can meet one of the water-resistance requirements for exterior applications. At least nine specimens (3.25 in × 1 in) were boiled in water for 4 h, dried at  $63 \pm 3$  °C for 20 h, boiled again for 4 h, cooled down with tap water and then evaluated for shear strength while the specimens were still wet. The shear strength determined by this way was called BWT/w. The shear strength was measured with an Instron testing machine. The crosshead speed was 1mm/min.

#### ***2.4.4.3 Statistical analysis of strength data***

Strength data were analyzed with a two-sample t-test using S-PLUS® statistical software (Edition version 7.0, Insightful Corp. Seattle, WA). All comparisons were based on a 95% confidence level.

## 2.5 Results

### **2.5.1 Effect of the adhesive components on the water-resistance of plywood bonded with the adhesives**

Table 2.1 Effect of the adhesive components on the water-resistance of plywood bonded with the adhesive (SF/PEI/MA weight ratio, 7/1/0.4; hot- press conditions: 150 psi, 160 °C and 5 min; Y represents that the component was present in the adhesive and N represents that the component was not present in the adhesive. The sign “-” means that no test was taken. Each row in the table represents one independently made panel).

Components				The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test
SF	PEI	MA	NaOH	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
Y	N	Y	N	20/20	-	F
				20/20	-	F
				20/20	-	F
				20/20	-	F
				20/20	-	F
Y	Y	N	N	6/20	-	F
				0/20	0/20	P
				0/20	1/20	P
				7/20	-	F
				0/20	0/20	P
Y	Y	Y	N	0/20	1/20	P
				0/20	1/20	P
				0/20	1/20	P
				0/20	0/20	P
				0/20	4/20	F
Y	Y	Y	Y	0/20	0/20	P
				0/20	0/20	P
				0/20	1/20	P
				0/20	0/20	P
				0/20	0/20	P

All specimens from all five panels delaminated after the 1<sup>st</sup> cycle soak test in the absence of PEI and NaOH, i.e., when the adhesive only consisted of SF and MA, (Table 2.1). Three panels passed the three-cycle soak test and two panels failed when MA and NaOH were absent, i.e., when the adhesive only consisted of SF and PEI. The SF-PEI adhesive was better than the SF-MA adhesive. However, this SF-PEI adhesive generated inconsistent results. Four panels passed the three-cycle soak test and only one panel failed when NaOH was absent, i.e., when the adhesive consisted of SF, MA and PEI. This SF-MA-PEI adhesive appeared to be slightly better than the SF-PEI adhesive. When SF, PEI, MA and sodium hydroxide were all present, all panels passed the three-cycle soak test and almost no specimens delaminated.

### 2.5.2 Effect of SF/PEI weight ratio on the water-resistance of plywood bonded with the adhesives

Table 2.2 Effect of SF/PEI weight ratio on the water-resistance of plywood bonded with the adhesives (PEI/MA weight ratio, 1/0.4; 1N NaOH solution, 285 mL, hot-press conditions: 150 psi, 160 °C and 5 min. The sign “-” means that no test was taken. Each row in the table represents one independently made panel).

Weight ratio (SF/PEI)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test
	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
5/1	2/20	3/20	F
	0/20	0/20	P
	1/20	1/20	P
	0/20	0/20	P
	0/20	0/20	P
7/1	0/20	0/20	P
	0/20	0/20	P
	0/20	1/20	P
	0/20	0/20	P
	0/20	0/20	P
9/1	0/20	0/20	P
	2/20	5/20	F
	0/20	0/20	P
	0/20	5/20	F
	6/20	-	F
11/1	1/20	4/20	F
	0/20	0/20	P
	0/20	0/20	P
	0/20	2/20	P
	3/20	-	F
13/1	2/20	5/20	F
	0/20	5/20	F
	0/20	4/20	F
	4/20	-	F
	0/20	4/20	F

At the 5/1 SF/PEI ratio, four panels passed the three-cycle soak test. However, one panel failed because two of 20 specimens failed after the 1<sup>st</sup> soaking/drying cycle. Strictly speaking, plywood panels bonded with the adhesive at the 5/1 SF/PEI ratio failed to meet the water-resistance requirements for interiorly application. However, only three of 20 specimens failed after the 3<sup>rd</sup> cycle, which implied that this panel passed the 3<sup>rd</sup> test. It is still possible that the adhesive at this SF/PEI ratio can be used for production of interior plywood when a large number of plywood panels are made and evaluated. At the 7/1 SF/PEI weight ratio, all panels passed the three-cycle soak test and all test specimens showed little opening or crack on the gluelines. At the 9/1 SF/PEI weight ratio, two panels passed the three-cycle soak test and three failed. At the 11/1 SF/PEI weight ratio, three panels passed the three-cycle soak test, but two failed. These results indicated that plywood panels had inconsistent water-resistance at the 9/1 and 11/1 SF/PEI weight ratios. All panels failed to pass the three-cycle soak test when the SF/PEI weight ratio was further increased to 13/1 (Table 2.2).

### 2.5.3 Effect of the MA dosage on the water-resistance of plywood bonded with the adhesives

Table 2.3 Effect of the MA dosage on the water-resistance of plywood bonded with the adhesives (SF/PEI weight ratio, 7/1; 1N NaOH solution, 285 mL; hot-press conditions: 150 psi, 160 °C and 5 min, The sign “-” means that no test was taken. Each row in the table represents the three-cycle soak test of one independently made panel).

wt % MA on PEI (Dry basis)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test	The number of specimens delaminated after a BWT/total specimens
	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle		
40	0/20	0/20	P	4/12
	0/20	0/20	P	4/12
32	0/20	1/20	P	0/9
	0/20	0/20	P	0/9
24	0/20	0/20	P	1/9
	0/20	0/20	P	1/9
16	2/20	5/20	F	-
	0/20	0/20	P	8/9
8	8/20	-	F	-
	0/20	0/20	P	3/9

As the 40 wt% MA, both plywood panels passed the three-cycle soak test, but four out of 12 specimens delaminated after a BWT. At the 32 wt% MA, both panels passed the three-cycle soak test and no specimens delaminated after a BWT. At the 24 wt% MA, both panels passed the three-cycle soak test, but one out of nine specimens delaminated after a BWT. At the 16 wt% MA or 8 wt% MA, one panel passed the three-cycle soak test and one failed. However, a high percentage of

specimens delaminated at these two dosages after a BWT. In summary, all plywood panels passed the three-cycle soak test at the 24-40 wt% MA, and all test specimens had little opening or crack on the gluelines, which means that the adhesive at this range of MA usage can be used to make interior plywood. Plywood panels bonded with the adhesive at the 32 wt% MA had the highest water-resistance. Reduction of the MA usage to 16 wt% or 8 wt% significantly decreased the water-resistance of the resulting plywood panels. At the 8-16 wt% MA, the resulting plywood panels could not meet the water-resistance requirement for interior applications.



### 2.5.4 Effect of hot-press temperature on the water-resistance and shear strength of plywood bonded with the adhesives

Table 2.4 Effect of hot-press temperature on the water-resistance of plywood panels (SF/PEI/MA weight ratio, 7/1/0.32; 1N NaOH solution; 285 mL; hot-press conditions: 150 psi, 160 °C and 5 min. The sign “-” means that no test was taken. Each row in the table represents one independently made panel).

Hot-press temperature (°C)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test	The number of specimens delaminated after a BWT/total specimens
	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle		
110	14/20	-	F	-
	12/20	-	F	-
120	19/20	-	F	-
	0/20	0/20	P	-
130	1/20	1/20	P	-
	3/20	-	F	-
140	1/20	3/20	P	0/9
	0/20	0/20	P	0/9
150	0/20	0/20	P	0/9
	0/20	0/20	P	0/9
160	0/20	1/20	P	0/9
	0/20	0/20	P	0/9
170	0/20	1/20	P	0/9
	0/20	0/20	P	0/9

At 110 °C, both panels failed after the 1<sup>st</sup> soaking/drying cycle. At 120 °C and 130 °C, the resulting plywood panels had inconsistent water-resistance: one panel passed the three-cycle soak test and one failed. When the hot-press temperature was at 140-170 °C, all panels passed the three-cycle soak test and no specimens delaminated after a BWT. Therefore, the hot-press temperature has to be higher than

130 °C for the resulting plywood panels to meet the water-resistance requirements for interior applications.

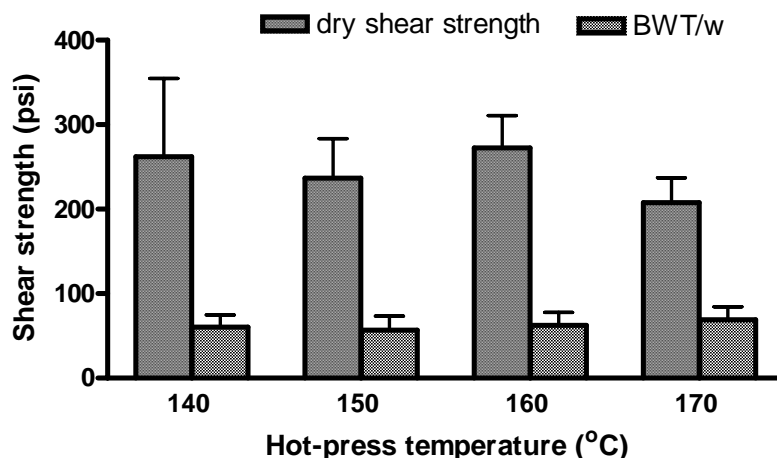


Figure 2.1 Effect of hot-press temperature on dry and BWT/w shear strength of plywood specimens bonded with the adhesives (SF/PEI/MA weight ratio, 7/1/0.32; 1N NaOH solution: 285 mL hot- press conditions: 150 psi, 5min. Data are the means of 18 replicates, and the error bar represents one standard deviation.)

According to the ANSI/HPVA HP-1 standard, there are no shear strength requirements for interior plywood. We measured dry shear strength and BWT/w shear strength to investigate whether a different hot-press temperature in the range of 140-170 °C would make subtle differences on the strength properties of the resulting plywood panels. Results for the shear strengths are shown in the Figure 2.1. When the hot-press temperature was increased from 140 °C to 160 °C, the dry shear strength did not significantly change. When the hot-press temperature was further increased

from 160 °C to 170 °C, the dry shear strength significantly decreased (p-value <0.0005). The BWT/w shear strength did not significantly change when the hot-press temperature was increased from 140 °C to 170 °C.

### 2.5.5 Effect of hot-press time on the water-resistance and shear strength of plywood bonded with the adhesives

Table 2.5 Effect of hot-press time on the water-resistance of the resulting plywood ( SF/PEI/MA weight ratio, 7/1/0.32; 1N NaOH solution, 285 mL; hot-press conditions: 150 psi, 160 °C. The sign “-” means that no test was taken. Each row in the table represents one independently made panel).

Hot-press time (min)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test	The number of specimens delaminated after a BWT/total specimens
	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle		
1	7/20	-	F	-
	3/20	-	F	-
2	0/20	0/20	P	0/9
	0/20	2/20	P	3/9
3	0/20	0/20	P	0/9
	0/20	0/20	P	1/9
4	0/20	0/20	P	0/9
	0/20	0/20	P	0/9
5	0/20	1/20	P	0/9
	0/20	0/20	P	0/9
6	0/20	0/20	P	0/9
	0/20	0/20	P	0/9

At 1 min of hot-press time, both panels failed after the 1st soaking/drying cycle.

At 2 min, both panels passed the three-cycle soak test, but three of nine specimens from one panel delaminated after a BWT. At 3 min, both panels passed the

three-cycle soak test, and only one of nine specimens from one panel delaminated after a BWT. At 4-6 min, not only all panels passed the three-cycle soak test, but also no specimen delaminated after a BWT. Therefore, when the hot-press time was longer than 2 min, the resulting plywood panels met the water-resistance requirements for interior applications. The overall water-resistance increased when the hot-press time increased.

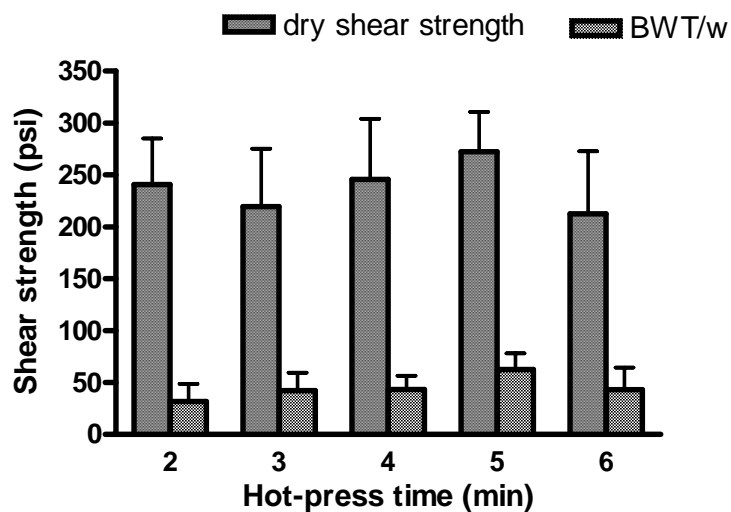


Figure 2.2 Effect of hot-press time on dry and BWT/w shear strength of plywood specimens bonded with the adhesives (SF/PEI/MA weight ratio, 7/1/0.32; 1N NaOH solution, 285 mL; hot-press conditions: 160 °C, 150 psi. Data are the means of at least 15 replicates, and the error bar represents one standard deviation.)

When the hot-press time was in the range of 2 to 6 min, only the dry shear strength of the sample at 5 min was significantly higher than that at 3 min ( $p$ -value = 0.0051) and other comparisons of dry shear strengths did not show significantly

change. The BWT/w shear strength of the sample at 5 min was statistically higher than those at 2 min (p-value<0.0005), 3min (p-value =0.0037), 4 min (p-value=0.0035) and 6 min (p-value=0.01645).

## **2.6 Discussion**

In the previous study on SPI-MA-PEI adhesives, SPI was first modified with MA at 50 °C for 120 min while maintaining a pH value of the reaction mixture at 10, and then mixed with PEI to form the adhesives [18]. We replaced SPI with SF and tried the same preparation procedure described in the literature. We soon found that it was too tedious to make a sufficient quantity of MA-modified SF for making 2'x2' plywood panels because the modification of SPI with MA was carried out in a dilute solution. We then explore different methods of modifying SF with MA. After numerous trials, we found that mixing PEI, MA and NaOH for 5min before adding SF to the mixture was the best procedure for making the adhesive in terms of the simplicity of preparing the adhesive, and the strength and water-resistance of the resulting plywood panels.

The previous publication demonstrated that MA first reacted with amino groups and hydroxyl groups of SPI to form ester-linked maleyl groups and amide-linked maleyl groups on SPI. The reactions between those maleyl groups with amino groups of PEI formed highly crosslinked adhesive networks during the hot-press, thus

curing the adhesives [18]. In this study, the preparation procedure for the SF-MA-PEI adhesives was different from the literature procedure for making SPI-MA-PEI adhesives. The curing mechanisms for the SF-MA-PEI adhesives are expected to be different from those for the SPI-MA-PEI adhesives. We proposed that MA first reacted with PEI to form amide-linked maleyl groups that further reacted with amino groups in SF and PEI during a hot-press of making plywood panels (Figure 2.3). From the proposed reaction mechanisms in Figure 2.3, SF, PEI and MA are all essential components for the final adhesive networks, which is consistent with our results that all these components had to be present for the resulting plywood panels to have superior water-resistance. It is less clear why NaOH also was an essential component. We speculate that NaOH facilitated all those reactions shown in Figure 2.3 and helped unfold soy protein in SF so that amino groups buried inside the compact soy protein structure were made available for the curing reactions.

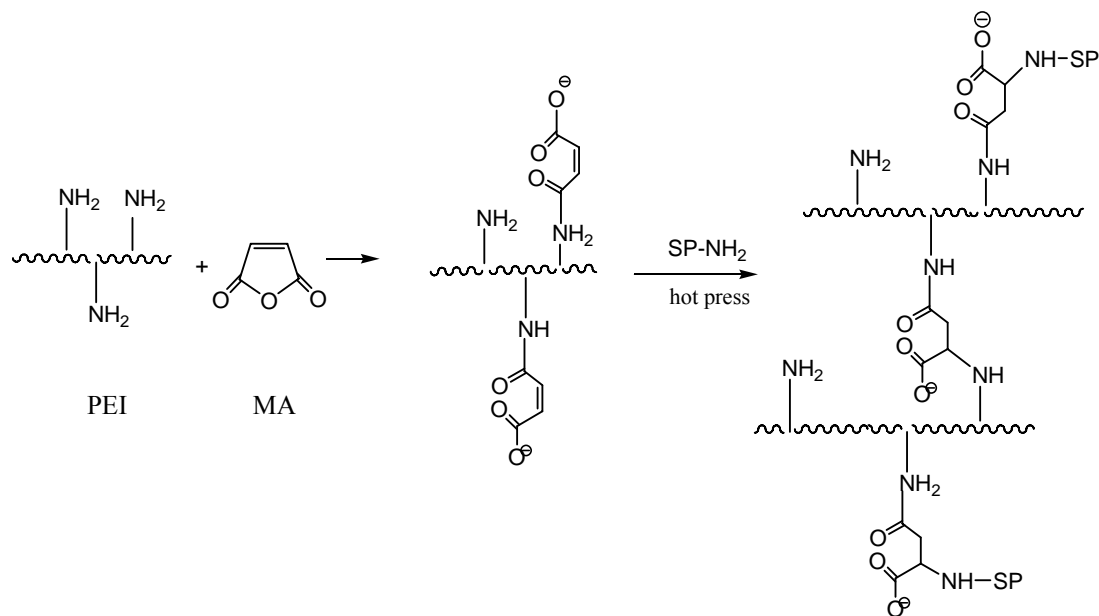


Figure 2.3 Proposed reaction mechanism of SF-MA-PEI

According to the proposed reactions (Figure 2.3), the amount of PEI has to be high enough. Otherwise, the reactive sites for crosslinking may not be sufficient for forming water-resistant adhesive networks. This may explain why the water-resistance of the resulting plywood panels failed to pass the three-cycle soak test when the SF/PEI weight ratio was equal to and higher than 9/1.

MA is susceptible for hydrolysis to form maleic acid and is very water-soluble. A high amount of maleic acid in the final adhesive would definitely reduce the water-resistance of the adhesives. This is why the plywood panels at 40 wt% MA had more specimens delaminated after a BWT than those at 32 wt% MA (Table 2.3). However, the amount of MA has to be sufficiently high. Otherwise, the amount of

amide-linked maleyl groups is not sufficient to form highly crosslinked water-resistant adhesive networks. This explanation is consistent with the results that some plywood panels even could not pass the three-cycle soak test when the amount of MA was equal to and lower than 16 wt%.

The SF-MA-PEI adhesives have to be cured at an elevated temperature for certain time. The optimum hot-press conditions (hot-press time and hot-press temperature) are highly dependent upon the number of plywood layers and the thickness of the plywood panels. For the three-ply panels in this study, it appeared that the adhesives were not fully cured at a hot-press temperature of lower than 130 °C for five min. At 160 °C hot-press temperature, the hot-press time had to be longer than 2 min for the three-ply panels.

## **2.7 Conclusions**

Inexpensive SF was successfully used to replace expensive SPI for making soy-based wood adhesives. SF, PEI, MA and NaOH were all essential components for the adhesives. The SF-MA-PEI adhesives were readily prepared in a large quantity, which was a big improvement over the preparation of the previous studied SPI-MA-PEI adhesives. The water-resistance and shear strength of plywood bonded with the adhesives depended upon the SF/PEI weight ratio, the MA/PEI percentage, and hot-press conditions. The SF/PEI/MA weight ratio of 7/1.0/0.32 resulted in the



highest water-resistance. The water-resistance and shear strength of plywood bonded with the adhesives did not significantly change when the hot-press temperature was at 140-160 °C. Further increasing the hot-press temperature from 160 °C to 170 °C significantly reduced the dry shear strength. At 160 °C, the dry shear strengths of the samples in the range of 2-6 min have no significant difference, except that the dry shear strength of the resulting plywood at 5 min was significantly higher than that at 3 min. The highest BWT/w shear strength was obtained at 5 min with 160 °C. For the three-ply plywood panels, the hot-press time had to be equal to or higher than two min at 160 °C hot-press temperature. Plywood panels bonded with these SF-MA-PEI adhesives could survive a harsh boiling water test without delamination. Plywood panels bonded with the SF-MA-PEI adhesives exceeded the water-resistance requirements for interior plywood.

## **2.8 Acknowledgements**

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CHAPTER 3 PRELIMINARY STUDY OF THE EFFECT OF VARIOUS  
CATALYSTS ON THE SOY FLOUR-(TRIMETHYLOLPROPANE  
TRIGLYCIDYL ETHER) ADHESIVES

### **3.1 Abstract**

In this study, the effects of the following catalysts: calcium hydroxide, sodium carbonate, triethylamine, tetra-n-octylammonium bromide, phosphoric acid and ammonium sulfate on the water-resistance of plywood bonded with a soy flour (SF)-trimethylolpropane triglycidyl ether (TMTE) adhesive under different hot-press conditions were individually investigated. The catalysts improved the water-resistances of bonded plywood panels. Among all catalysts investigated, calcium hydroxide and triethylamine provided the bonded plywood with better water-resistance than other catalysts. Results revealed that the increase in hot-press temperature and hot-press time enhanced the water-resistance of plywood bonded with the adhesives. The plywood panels bonded with these SF-TMTE adhesives could not meet water-resistance requirements for interior applications.

### **3.2 Keywords**

Soy flour, trimethylolpropane triglycidyl ether, water-resistance, plywood, wood adhesive

### **3.3 Introduction**

Wood composites are one of the most important forest products, and widely used in the manufacture of furniture, flooring, kitchen cabinet, houses and bridges. Wood composites typically consist of wood elements, such as veneers, chips, flakes

and fibers, and adhesives. Every year, large quantities of adhesives are consumed for the production of wood composites. In the United States, the consumption of wood adhesives accounted for around 60% of the total adhesive demand in 2004[1]. At present, formaldehyde-based adhesives such as phenol-formaldehyde (PF) resins, urea-formaldehyde (UF) resins are predominantly used in the production of wood composites. However, some serious issues related to the formaldehyde-based adhesives, e.g., petrochemicals as raw materials and the emission of carcinogenic formaldehyde, have generated a need for development of environmentally friendly adhesives from renewable materials.

Soybean is renewable, inexpensive, readily available and abundant. Soy-based adhesives were used in the commercial production of plywood from the 1930s to the 1960s. However, they have been replaced by synthetic resins mainly because of the poor water-resistance of the resulting plywood panels. Soybean represents an ideal raw material for making wood adhesives if the drawbacks of soy-based adhesives can be overcome.

Epoxy resins are widely used in coatings, castings, encapsulation and laminates because of low cure shrinkage, good wetting ability, excellent chemical and corrosion resistance, superior strength and durability[2]. The epoxy functional group can react with a wide variety of functional groups such as hydroxyl groups, amino groups, and

carboxylic acid groups. Epoxy resins are thus widely used as crosslinking agents for various substrates in both an organic medium and aqueous medium. Bisphenol A diglycidyl ether is one of the most commonly used epoxy resins. However, its crosslinking efficacy was not highly probable because it had a poor solubility in water. A number of epoxy resins with a high water-solubility, such as trimethylolpropane triglycidyl ether (TMTE), have been used as crosslinking agents in an aqueous medium[3, 4]. Little has been published about the use of TMTE as a crosslinking agent for soy-based adhesives. Catalysts are typically required when epoxy resins are used as crosslinking agents because the crosslinking reactions proceed very slowly without a catalyst. This paper reveals our preliminary results on the effect of several selected catalysts on the curing of soy flour-TMTE adhesives in making interior plywood.

### **3.4 Materials and experimental methods**

#### **3.4.1 Materials**

SF (7% moisture content) was provided by Cargill Incorporated (Minneapolis, MN). TMTE and calcium hydroxide (95+%) were purchased from Sigma-Aldrich (Milwaukee, WI). Triethylamine and sodium carbonate were purchased from J.T. BAKER chemical Co. (Philipsburg, N.J.). yellow poplar veneers were a gift from Columbia Forest Products (Portland OR). Ammonium sulfate was purchased from

ICN Biomedicals, Inc. (Aurora, OH). tetra-n-octylammonium bromide was purchased from Lancaster Synthesis, Inc. (Pelham, NH). Phosphoric acid was purchased from Fisher Scientific (Fair Lawn, N.J.).

### **3.4.2 Experimental methods**

#### ***3.4.2.1 Preparation of soy flour-(trimethylolpropane triglycidyl ether) adhesives adhesives***

TMTE (114.3 g), triethylamine (8 g, 1% based on dry weight of SF) and water (1641 mL) were mixed in a Kitchen Aid mixer for 5 min at room temperature. Then SF (859 g, wet weight) was added to the mixture and mixed for another 5 min. The total solids content of the resulting adhesive was 36%.

Three types of catalysts were tried for the SF-TMTE adhesive and their dosages were based on dry weight of SF. The following catalysts were individually used to replace triethylamine in the previously described preparation procedure.

Base catalysts: calcium hydroxide, sodium carbonate, and triethylamine

Quaternary ammonium salt: tetra-n-octylammonium bromide

Acidic catalysts: ammonium sulfate, and phosphoric acid

#### ***3.4.2.2 Preparation of three-ply plywood samples***

The adhesive was applied to two sides of a yellow-poplar veneer (2 ft × 2 ft, 12% moisture content) by a roller coater. The spread rate of the adhesive was 8 mg/cm<sup>2</sup> on



a dry weight basis. The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. The stacked veneers were put on a table for 5 min, cold-pressed at 100 psi for 5min, put on a table again for 5 min and hot-pressed at 150 psi with predetermined time and temperature. After hot-press, the panel was stored at ambient environment for at least 24 h before it was evaluated for its water-resistance.

#### ***3.4.2.3 Determination of the water-resistance of plywood panels***

##### Three-cycle soak test

The water-resistance of plywood panels was determined with a three-cycle soak test in accord with the American National Standard for Hardwood and Decorative Plywood; Hardwood Plywood & Veneer Association; 2004 (ANSI/HPVA HP-1). ANSI/HPVA HP-1 is the commonly accepted standard for evaluating the water-resistance of interior plywood. The following is a detailed testing procedure defined by the standard. Twenty plywood specimens (2 in × 5 in) cut from each plywood panel were soaked in water at  $24 \pm 3$  °C for 4 h, and then dried at 49 °C-52 °C for 19 h. All specimens were inspected to see whether they were delaminated. This soaking/drying cycle was repeated until three cycles were completed. According to the standard, a plywood panel meets water-resistance requirement for interior applications if 95% of the specimens, i.e., 19 out of the 20 specimens do not

delaminate after the 1<sup>st</sup> soaking/drying cycle and 85% of specimens, i.e., 17 out of 20 specimens do not delaminate after the 3<sup>rd</sup> soaking/drying cycle. The ANSI/HPVA HP-1 specifically provides the following definition of delamination: any continuous opening between two layers has to be longer than two inches and deeper than 0.25 inch and wider than 0.003 inch.

### **3.5 Results**

#### **3.5.1 Effect of Ca(OH)<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, or triethylamine on the water-resistance of plywood bonded with the adhesives under different hot-press conditions**

Effect of Ca(OH)<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, or triethylamine on the water-resistance of plywood bonded with the adhesives under different hot-press conditions is shown in Table 3.1. All specimens from two plywood panels failed after the 1<sup>st</sup> soaking/drying cycle when the adhesive was only composed of SF or SF and TMTE. It implied that TMTE did not improve the water-resistance. In the presence of Ca(OH)<sub>2</sub>, eight of 20 specimens from one panel and six of 20 specimens from another panel did not pass the 1<sup>st</sup> soaking/drying cycle when the panels were made at 120 °C for 5 min (Table 3.1). This implied that addition of Ca(OH)<sub>2</sub> significantly reduced the number of specimens failed after the 1<sup>st</sup> soaking/drying cycle. With the same SF-TMTE-Ca(OH)<sub>2</sub> adhesive, only one of 20 specimens from one panel delaminated after the 1<sup>st</sup> soaking/drying cycle when the hot-press temperature was further increased from 120 °C to 130 °C. However, this panel did not pass the three-cycle soak test because four

of 20 specimens failed after the 3<sup>rd</sup> soaking/drying cycle. There were still six of 20 specimens from another panel delaminated after the 1<sup>st</sup> soaking/drying cycle (table 3.1). There were insufficient data to convincingly demonstrate that increasing the hot-press temperature from 120 °C to 130 °C significantly improved the water-resistance of the resulting panels. When compared with the SF-TMTE adhesive alone, the addition of Na<sub>2</sub>CO<sub>3</sub> to the SF-TMTE adhesive slightly reduced the number of specimens failed after the 1<sup>st</sup> soaking/drying cycle. Na<sub>2</sub>CO<sub>3</sub> was less effective in improving the water-resistance of the resulting plywood panels than Ca(OH)<sub>2</sub>.

When triethylamine was added to the SF-TMTE adhesive, 15 of 20 specimens from a panel made at 120 °C for 5 min delaminated after 1<sup>st</sup> soaking/drying cycle, which was only slightly better than the water-resistance of plywood panels bonded with the SF-TMTE (Table 3.1). Under hot-press conditions of 140 °C and 2 min, 15 of 20 specimens from one panel and 12 of 20 specimens from another panel delaminated after the 1<sup>st</sup> soaking/drying cycle, which was no better than those under hot-press conditions of 120 °C and 5 min (Table 3.1). Increasing the hot-press time from 2 min to 3 min significantly reduced the number of delaminated specimens after the 1<sup>st</sup> soaking/drying cycle. Under the hot-press conditions of 140 °C and 5 min, one panel passed the three-cycle soak test. However, another panel had seven of 20 panels delaminated after the 1<sup>st</sup> soaking/drying cycle.

Table 3.1 Effect of  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ , or triethylamine on the water-resistance of plywood bonded with the adhesives under different hot-press conditions (SF/TMTE weight ratio, 7/1; hot-press pressure, 150 psi;  $\text{Ca}(\text{OH})_2$ , 16 g ;  $\text{Na}_2\text{CO}_3$ , 16 g, triethylamine, 8 g. The sign “-” means that no test was taken. Each row in the table represents one independently made panel)

Components	Hot-press temperature (°C)	Hot-press time (min)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test
			1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
SF	120	5	20/20	-	F
			20/20	-	F
SF+TMTE	120	5	20/20	-	F
			20/20	-	F
SF+TMTE+ $\text{Ca}(\text{OH})_2$	120	5	8/20	-	F
			6/20	-	F
	130	5	1/20	4/20	F
			6/20	-	F
SF+TMTE+ $\text{Na}_2\text{CO}_3$	130	5	15/20	-	F
			12/20	-	F
SF+TMTE+ triethylamine	120	5	15/20	-	F
	140	2	15/20	-	F
			12/20	-	F
	3	5	5/20	-	F
			2/20	4/20	F
	5	5	0/20	0/20	P
7/20			-	F	

### 3.5.2 Effect of tetra-n-octylammonium bromide on the water-resistance of plywood bonded with the adhesives under different hot-press conditions

In the presence of tetra-n-octylammonium bromide, the number of specimens delaminated after the 1<sup>st</sup> soaking/drying cycle decreased from 16 to 11 when the

hot-press time was increased from 3 min to 5 min. The number of specimens remained at 11 when the hot-press time was increased from 5 min to 7 min. Further increasing the hot-press time from 7 min to 9 min significantly reduced the number of the delaminated specimens from 11 to 4 (Table 3.2).

Table 3.2 Effect of tetra-n-octylammonium bromide on the water-resistance of plywood bonded with the adhesives under different hot-press conditions (SF/TMTE weight ratio, 7/1; hot-press pressure, 150 psi; tetra-n-octylammonium bromide, 4 g. The sign “-” means that no test was taken. Each row in the table represents one independently made panel)

Components	Hot-press temperature (°C)	Hot-Press time (min)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test
			1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
SF+TMTE+ tetra-n-octylammonium bromide	140	3	16/20	-	F
		5	11/20	-	F
		7	11/20	-	F
		9	4/20	-	F

### 3.5.3 Effect of H<sub>3</sub>PO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> on the water-resistance of plywood bonded with the adhesives

In the presence of H<sub>3</sub>PO<sub>4</sub>, at 3 min hot-press time, 11 of 20 specimens from one panel and 8 of 20 from another panel delaminated after the 1<sup>st</sup> soaking/drying cycle (Table 3.3). With the same SF-TMTE-H<sub>3</sub>PO<sub>4</sub> adhesive, increasing the hot-press time

from three min to five min significantly reduced the number of delaminated specimens after the 1<sup>st</sup> soaking/drying cycle. Further increasing the hot-press time from five min to nine min did not substantially reduce the number of delaminated specimens although one panel made at nine min did pass the three-cycle soak test (Table 3.3).  $(\text{NH}_4)_2\text{SO}_4$  was much less effective than  $\text{H}_3\text{PO}_4$  in terms of reducing the number of delaminated specimens under the same hot-press conditions (Table 3.3).

Table 3.3 Effect of  $\text{H}_3\text{PO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  on the water-resistance of plywood bonded with the adhesives (SF/TMTE weight ratio, 7/1; hot-press pressure, 150 psi;  $\text{H}_3\text{PO}_4$ , 0.5 g (+85%);  $(\text{NH}_4)_2\text{SO}_4$ , 8 g. The sign “-” means that no test was taken. Each row in the table represents one independently made panel.)

Components	Hot-press temperature (°C)	Hot-press time (min)	The number of specimens failed in the three-cycle soak test/total specimens		Pass (P) or fail (F) of the three-cycle soak test
			1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
SF+TMTE+ $\text{H}_3\text{PO}_4$	140	3	11/20	-	F
			8/20	-	F
		5	2/20	4/20	F
			2/20	9/20	F
		7	4/20	-	F
			3/20	6/20	F
		9	1/20	5/20	F
			1/20	1/20	P
SF+TMTE+ $(\text{NH}_4)_2\text{SO}_4$	140	3	20/20	-	F
		5	16/20	-	F
		7	14/20	-	F
		9	5/20	-	F

### **3.6 Discussion**

Epoxy resins are generally too expensive to be directly used as wood adhesives. However, it is a viable solution to use a small amount of epoxy resins as crosslinking agents for inexpensive raw materials such as soy flour. It typically takes hours to fully cure epoxy resins. Such a long curing time is unacceptable in the wood composites industry. In practice, the typical hot-press time for making three-ply plywood is about 2-3 min. A highly effective catalyst that can dramatically shorten the curing time has to be developed before epoxy resins can be used as cross-linking agents for soy flour.

A base is known to be able to catalyze epoxy-based crosslinking reactions through enhancing the nucleophilicity of nucleophiles such as hydroxyl groups and carboxylic acid groups. Triethylamine is an organic base. Results shown in Table 3.1 show that both  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$  and triethylamine were all able to improve the water-resistance of the resulting plywood panels to some extent. In addition to enhancing the nucleophilicity of nucleophiles, a base can disrupt the soy protein structure so that nucleophiles such as amino groups buried inside soy protein can be made available for reactions with TMTE. Ca (II) can chelate with two carboxylic acid groups in soy protein to form extra crosslinkages, which may explain why  $\text{Ca}(\text{OH})_2$  was more effective than  $\text{Na}_2\text{CO}_3$  in terms of reducing the number of delaminated specimens after the 1<sup>st</sup> soaking/drying cycle.

A quaternary amine is able to activate an epoxy functional group for its reaction with a nucleophile. The activation mechanism is still not fully understood [5]. A possible mechanism is that the positive charge of a quaternary amine chelates with the oxygen of an epoxy functional group, thus weakening C-O bonds of the epoxy functional group and facilitating the nucleophilic attack of the nucleophile conjugated with the nitrogen atom in the quaternary amine. Tetra-n-octylammonium bromide may be too bulky for its quaternary amine group to effectively activate the epoxy functional groups of TMTE, which may explain why tetra-n-octylammonium bromide had a very limited effect on improving the water-resistance of the resulting plywood panels. More quaternary amines with small substituents will be evaluated in our future studies.

Acids are well known catalysts for epoxy resins. Acids protonate epoxy functional groups, thus weakening the C-O bonds of epoxy and facilitating the reactions between the epoxy functional groups and nucleophiles. Phosphoric acid significantly improved the water-resistance of the resulting plywood panels, especially those made at a relatively long hot-press time. Ammonium sulfate is a very weak acid, which may explain why it had a limited effect on the improvement of the water-resistance of the resulting plywood panels.



### **3.7 Conclusions**

Almost all catalysts studied improved the water-resistance of resulting plywood to some extent. Calcium hydroxide and triethylamine were better than other catalysts in terms of improving the water-resistance of the resulting plywood panels. Increasing the hot-press temperature and the curing time also tended to improve the water-resistance. None of catalysts studied so far enabled the plywood panels bonded with the SF-TMTE adhesive to meet water-resistance requirements for interior applications. More study is warranted to find a highly effective catalyst for this SF-TMTE adhesive.

### **3.8 Acknowledgements**

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## CHAPTER 4 GENERAL CONCLUSIONS

The adhesive consisting of soy flour (SF), polyethyleneimine (PEI) and maleic anhydride (MA) was developed and evaluated for making interior plywood panels. The SF/PEI weight ratio, the MA dosage and hot-press conditions had significant impacts on the water-resistance and shear strength of resulting plywood panels. Under the optimal conditions determined in the study, plywood panels bonded with the adhesive had superior water-resistance, e.g. all test specimens did not delaminate even after a boiling water test. The water-resistance exceeded the requirements for interior plywood

Various catalysts (calcium hydroxide, sodium carbonate, triethylamine, tetra-n-octylammonium bromide,  $H_3PO_4$  and  $(NH_4)_2SO_4$ ) were investigated to facilitate the curing of SF-TMTE (trimethylolpropane triglycidyl ether) adhesives. All catalysts improved the water-resistance of the resulting plywood to some extent. Calcium hydroxide and triethylamine were superior to other catalysts studied in terms of improving the water-resistance. Increase in hot-press time and hot-press temperature also tended to improve the water-resistance. However, none of catalysts studied enabled the resulting plywood panels to meet water-resistance requirements for interior applications.

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