



## AN ABSTRACT OF THE THESIS OF

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Title: Development and Evaluation of a New Formaldehyde-free Wood Adhesive  
from Renewable Materials for Making Interior Plywood

Abstract approved:

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Synthetic adhesives, such as phenol-formaldehyde (PF) resins and urea-formaldehyde (UF) resins, have dominated the wood adhesive market since they were introduced in the wood products industry. Formaldehyde, as a key component in the manufacturing of PF and UF resins, has been classified as a known human carcinogen by the International Agency for Research on Cancer (IARC). The UF and PF resins are derived from petroleum and natural gas. However, petroleum resources are not infinite and not renewable. In recent years, with concerns over fluctuating prices and future-exhaustion of oil, as well environmental issues of the UF resins, soy-based adhesives have again drawn people's attention as one of the most promising alternatives to petroleum-based adhesives. A soy-based adhesive, consisting of soy flour (SF) and a curing agent (CA) (polyamidoamine-epichlorohydrin (PAE) resin) has been commercialized for production of plywood since 2004. The PAE resin is

derived from petrochemicals and is the most expensive component of the soy-based adhesive. In this study, a new formaldehyde-free adhesive, consisting of soy flour (SF) and a new curing agent (CA), was developed and evaluated for making interior plywood. The CA was developed from the reaction of epichlorohydrin (ECH) and ammonium hydroxide in water. ECH can be derived from renewable glycerol.

The weight ratio of SF/CA was 7/1 with the total solids content of 36 wt% for the resulting adhesive. The reaction time, reaction temperature, and addition order of reactants in the preparation of the CA; the heat-treatment and storage time of the CA; and the NaOH usage in the SF-CA adhesive were investigated in terms of their effects on the water resistance of the resulting plywood panels. All adhesives containing the CAs (prepared by adding ECH and ammonium hydroxide all at once in water at the temperature of 45 °C to 60 °C) enabled all types of plywood panels to meet the water-resistance requirements for interior applications. The heat-treatment of all CAs, except the CA prepared at 50 °C for five-ply aspen panels, had no effects on improving the water resistance. The storage time of both heat-treated and untreated CAs within at least two months had no significant effects on their viscosities, and the water resistance of the resulting plywood panels.

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DEVELOPMENT AND EVALUATION OF  
A NEW FORMALDEHYDE-FREE WOOD ADHESIVE FROM RENEWABLE  
MATERIALS FOR MAKING INTERIOR PLYWOOD

by

Yonghwan Jang

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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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Yonghwan Jang, Author

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# **DEVELOPMENT AND EVALUATION OF A NEW FORMALDEHYDE-FREE WOOD ADHESIVE FROM RENEWABLE MATERIALS FOR MAKING INTERIOR PLYWOOD**

## **CHAPTER 1 GENERAL INTRODUCTION**

### **1.1 Introduction of wood composite products**

With the scarcity of forest resources, especially timber resources, corresponding to increase in world population, forest products industry has placed great emphasis on improved utilization of forest resources and has developed numerous wood composite products. The term “wood composite products,” also called engineered wood products, can be defined as a material that mainly consists of wood elements such as veneers, fibers, flakes or strands, or particles. To form composite materials, these elements are bonded together with various adhesives. There are a variety of forms in wood composite products according to the types of wood elements used: *fiberboard* (made from fibers of wood), *particleboard* (made from particles of wood), *chipboard* (made from flakes, stands, or shavings of wood), and *plywood and laminated veneer lumber* (LVL) (made from veneers of wood) [1].

From economic and environmental points of view, wood composite products have become increasingly important in replacing solid wood for many applications due to a shortage of high quality timber for making lumber. Some of the products are constructed from recycled or recovered wood waste. Also, wood composite products

are completely biodegradable when their service life ends. Besides the environmental benefits, the use of wood composite products instead of solid wood provides many other advantages. Wood composite products can have better durability and quality than solid wood. They can be manufactured with various sizes and can also be easily shaped and molded. Compared to solid wood, the price of wood composite products is typically much lower [2].

A variety of chemicals are used in the manufacturing of wood composite products. The use of adhesives such as urea-formaldehyde (UF), melamine-formaldehyde (MF), phenol-formaldehyde (PF) and isocyanates is essential for bonding wood elements together. Moreover, preservatives are employed to prevent the composite products from biological degradation in such a way that the preservatives are applied separately to the products or mixed with the adhesives. Depending on the intended use of the materials, other chemicals such as waxes and fire retardants are often used [3, 4].

### **1.1.1 Classification of wood composite products**

Wood composite products can be largely classified into two categories. Panel products include plywood, oriented strand board (OSB), particleboard and medium density fiberboard (MDF). Lumber and timber products include laminated veneer lumber (LVL), parallel strand lumber (PSL) and oriented strand lumber (OSL), and glued laminated lumber (glulam).

### **1.1.1.1 Panel products**

#### ***1.1.1.1.1 Plywood***

Plywood is one type of the wood composite products and one of the most commonly used materials in the construction industry as well as the manufacturing of household items today. Plywood is made up of thin layers of wood (veneers) by bonding them together with adhesives in such a way that the grain direction of each veneer is perpendicular to that of the adjacent layers. This arrangement provides several advantages to the resulting plywood panel; it is structurally much stronger in the two directions than plain wood in similar dimensions. Also, it prevents the panel from expanding and shrinking [1].

##### ***1.1.1.1.1.1 History of plywood***

Traces of laminated wood have been found in the tombs of the ancient Egyptians. A thousand years ago, the Chinese shaved wood and glued it together to make furniture. They used veneered surfaces and glued thin sheets of high quality wood over a sheet of lower quality wood in order to obtain special effects such as appearance and structural benefits. A modern form of plywood was invented in the mid-1800s. It was made from decorative hardwood and used primarily for household items such as cabinets, desktops and doors. However, structural plywood made from softwood did not come out on the market until the 20<sup>th</sup> century. The commercial production of plywood was established in 1905 in Portland, Oregon and became a major industry in the US in the early 1900s. In the 1940s and 1950s, softwood



plywood was promoted for residential construction in North America, and the production was at its peak in 1960s. However, with the advent of oriented strand board (OSB) technology, softwood plywood was largely replaced by OSB in housing construction. In 2005, softwood plywood accounts for only one-third in the residential construction market in the U.S [1, 5].

#### *1.1.1.1.2 Types of plywood*

Plywood is classified broadly in two categories: construction (softwood) and decorative (hardwood). Construction plywood is generally made from softwood species such as Douglas fir, spruce, pine or fir. It is typically used for construction and industrial purposes such as wall siding, roof decking, floors, and containers. Since construction plywood is generally required to have strength, stiffness, and construction convenience, thermosetting adhesives including phenol-formaldehyde (PF) and melamine-formaldehyde (MF) are employed for the plywood. Decorative plywood, which typically has hardwood veneer faces, is used for interior applications such as furniture, cabinets, and doors. Its face layers have good-looking hardwood including red oak, birch and maple. Decorative plywood is typically produced with a less expensive urea-formaldehyde (UF) adhesive that has limited water resistance [4].

#### *1.1.1.1.3 Manufacturing process of plywood*

Plywood production can typically be divided into three manufacturing stages: veneer manufacture; drying and up-grading; and panel lay-up, pressing and finishing [1].

The process of rotary veneer cutting is essentially to produce veneers from logs, which are peeled perpendicular to the grain. The thickness of veneers depends on their intended use, ranging from 1.6 to 4.8 mm (1/16 to 3/16 in.) for softwood plywood and much thinner for hardwood and decorative plywood. The continuous sheet of veneer is then moved by a conveyor to be clipped into usable sizes and remove defects. After peeling, veneers are too wet to glue, and they need to be dried to 3-6 % moisture content. Properly dried veneers are then sorted into many different grades according to the size and number of knots and other natural and processing defects [1].

An adhesive is spread on the veneers in the lay-up area by spraying, curtain coating, roller coating, extrusion, or foaming. Once built up, panels are moved by the conveyer to the pressing area. The panels are cold pre-pressed for 3-5 minutes for flattening the veneers and transferring the adhesive from one surface of an adhesive-coated veneer to the adjacent uncoated veneer. Hot-pressing is then applied to the cold-pressed panels and cure the adhesive. Press temperature and press time may vary depending on wood species and resins used; a typical press time is 2 to 7 minutes, and the press temperature generally ranges from 132 to 165 °C (270 to 330 °F) for softwood plywood and from 107 to 135 °C (225 to 275 °F) for hardwood plywood [1].

After pressing, the pressed panels are cooled and then taken to a finishing process, where they are graded and trimmed according to the types of the final product, and finally sanded [6].

#### ***1.1.1.1.2 Oriented strandboard (OSB)***

Together with softwood plywood, oriented strandboard (OSB) is one of the major types of structural wood panels and is mainly used for exterior walls, roof sheathing and floor decking. The manufacturing of OSB starts by processing a log into strands that are typically 100 to 150 mm long in the grain direction, 13 mm wide, and 0.6 to 0.7 thick [4]. The strands are then dried below 10% moisture content and mechanically blended with adhesives such as phenol-formaldehyde or isocyanates, to form a 3- or 5-layered mat. In the same way as veneers of plywood are oriented, the adjacent two layers of the mat are aligned at right angles to each other for maximum strength, stiffness and stability [6].

Unlike the plywood industry, the OSB industry does not depend on large diameter logs since small diameter, irregular softwood, or previously unutilized hardwood is generally used for the manufacturing of OSB. In addition to the flexibility of log choices, the competitive cost of OSB in the structural panel market, as compared with softwood plywood, has caused the rapid increase of its production.

#### ***1.1.1.1.3 Particleboard (PB)***

Particleboard (PB) is a non-structural, engineered, wood panel that is manufactured from wood particles of various sizes. Either green or dry wood residues are used as the raw materials to produce PB; green wood residues contain shavings and sawdust from green lumber, and dry residues contain shavings and sawdust from kiln-dried lumber as well as plywood trim. Wood particles are combined with an

adhesive, and sometimes wax in a blender, and then bonded together under heat and pressure in a hot press. Urea-formaldehyde (UF) is predominantly used as an adhesive since PB is mainly used for non-structural, interior applications [7].

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

In the early production of MDF, the same process for manufacturing PB was used for producing MDF in such a way that fibers were dried and then mixed with an adhesive in a blender. However, the process caused dark resin spots in the resulting panels. Today, MDF is manufactured by a very different process, a so-called blowline blending process, which can reduce the problem (dark resin spots). In the process, fibers are carried from a refiner to a flash tube dryer through the blowline, and an adhesive is added before the dryer in the blowline [8].

The raw materials are broken down into wood fibers using a pressurized disk refiner under certain conditions (typically a pressure of 7 to 8 bars and a temperature of 170°C), and wood fibers are then blended, typically with an aqueous urea-formaldehyde (UF) adhesive. Some wax, less than 2% by weight of oven-dry fibers, is often added to the fibers to increase water resistance. The fibers are formed into a mat, and the mat is pressed at temperatures ranging from 160 to 170 °C [2].

MDF is considered as an excellent alternative for solid wood and is widely used in many interior applications. With the employment of phenol-formaldehyde (PF), or urea-melamine-formaldehyde adhesives, MDF can also be used in exterior applications [2].

### **1.1.1.2 Lumber and timber products**

#### ***1.1.1.2.1 Laminated veneer lumber (LVL)***

Laminated veneer lumber (LVL) is a wood-veneer based composite that is used for either structural or nonstructural applications, but is primarily used as the structural framing for residential and commercial construction. LVL is made by bonding thin sheets of wood veneer together with an adhesive under controlled heat and pressure. While the grain in plywood lies at right angles to each other in alternate plies, the grain of each layer of veneers in LVL runs in the same (long) direction [9]. Thus, the main difference between plywood and LVL takes place in the lay-up stage in their manufacturing processes.

Common species used to produce LVL are Douglas fir, larch, southern yellow pine and poplar, which are the same as those for plywood. Typically, veneer thickness varies from 0.10" (2.5mm) to 3/16" (4.8mm) [10]. Its structural use is for support beams, headers, rafters, and I-beams, and nonstructural LVL is used for furniture, window, door frames, and cabinets.

Like plywood manufactures, LVL panels use a variety of adhesives depending on their primary applications. Generally, phenol formaldehyde (PF) resins are used for exterior applications. LVL production is an energy intensive process that requires extensive wood drying (moisture contents of 6-8%) and high temperature hot-pressing (about 200 °C) [11].

In plywood, the way in which the grains alternatively lie in the length and width directions gives the similar strength and stiffness properties in the two directions. LVL can maximize strength and stiffness in the spanned direction because the grain of all veneers is parallel to the long direction.

#### ***1.1.1.2.2 Parallel strand lumber (PSL) and Oriented strand lumber (OSL)***

Parallel strand lumber (PSL) is constructed from long wood veneer strands in the orientation parallel to the length of the member. The strands are bonded together with an adhesive, typically phenol-resorcinol formaldehyde (PRF), to form a finished structural lumber. The veneer strands are cut to 3 mm in thickness, 20 mm in width, and 100-300 mm in length. This product is used for beam and header applications in construction like LVL, and frequently as load bearing columns [12].

Similar to PSL, oriented strand lumber (OSL) consists of flaked wood strands that have a high length-to-thickness ratio. An isocyanate-based adhesive is generally used for making this product, so is a steam-injection pressing. The steam-injection press results in a short press time, and uniform and increased density of the final product. OSL is commonly used for studs and millwork components [13].

#### ***1.1.1.2.3 Glued-laminated lumber (Glulam)***

Glulam, which is an excellent substitute for lumber, is an engineered stress-rated product fabricated by bonding individual pieces of lumber, with a thickness of 2 inches (50 mm). Larger and longer structural wood members can be obtained, which

are not available from small trees. Adhesives used for glulam are generally resorcinol-formaldehyde (RF) or phenol-resorcinol-formaldehyde (PRF). Glulam can be shaped into a straight beam or a complex, curved member, which allows the final product to be used in a variety of construction applications such as headers, floor girders, arches, domes, and bridges [14].

## **1.2 Introduction of wood adhesives**

An adhesive is defined as a substance that can hold the surface of each side of at least two materials together in a strong and permanent manner [15]. Adhesives virtually surround us, as an essential part of our lives. Wood adhesive is a polymeric substance capable of bonding surfaces of wood together through chemical or physical reaction, or both. Wood adhesives have played a central role in the growth and prosperity of the wood products industry and have been attributed to the efficient use of wood materials especially in the construction and housing industries. The demand for wood adhesives has rapidly increased with the increased prosperity of the wood products industry, and the consumption of wood adhesives around the world reached nearly 13.3 million metric tons in 2001 [16]. Currently, the wood adhesive market has largely been dependent on formaldehyde-based adhesive systems including amino resins, and phenolic resins.

### **1.2.1 Classification of wood adhesives**

A large number of adhesives are now used in the manufacture of wood composite products. Adhesives can be grouped in a variety of ways, including source,

function, chemical composition, physical form, and application. A simple classification of wood adhesives is based on whether an adhesive is manufactured from natural or synthetic materials. Also, synthetic adhesives include thermosetting and thermoplastic adhesives.

#### **1.2.1.1 Natural adhesives**

Natural adhesives are produced from organic materials such as animal, casein, vegetable, and blood. Also, adhesives from lignin, tannin, and carbohydrates have been studied for replacement of synthetic adhesives that are dominantly used in the manufacture of wood composite products. These adhesives are generally used for non-structural applications, due to their poor water resistance and low strength properties. This type of adhesive has a long shelf life, ease for applying, and relatively low price. Most of these adhesives are supplied as aqueous solution or as powder that is mixed with water prior to their application. Cross-linking agents are occasionally added to the adhesives [14].

##### ***1.2.1.1.1 Animal glues***

The term “animal glues” can be normally defined as glues derived from collagen, which is a main constituent of animal skin, bone and sinew. Animal glues are classified into two categories depending on where the collagen is obtained: bone glues from animal bones and hide glues from tannery waste. Animal glues are manufactured by the hydrolytic degradation of water-insoluble collagen and composed of approximately carbon (50.7%), hydrogen (6.5%), oxygen (24.9%), and nitrogen



(17.9%) [17]. These glues are initially provided as liquid, jelly, or solid, and are then reconstituted with water for the application [17].

The uses of animal glues were limited to furniture woodworking. However, in the furniture industry, they have been mostly replaced with synthetic and other strong adhesives from natural sources due to their inadequate attributes: low water resistance, degradation by molds and fungi, inconvenience to use, relatively high manufacturing costs, and temperature-sensitive viscosity [18].

#### ***1.2.1.1.2 Casein-based adhesives***

Most casein, the main protein of milk, used for adhesives is manufactured by acid precipitation of milk, but a very small amount is naturally obtained from milk by rennet. These adhesives are provided as powders and are required to mix with water prior to their use. Casein-based adhesives are normally used at room temperature and cured by loss of water through the void volume of wood (porosity) and by cross-linking.

For several decades, casein has been widely used as a wood adhesive for furniture and plywood. In spite of superior properties of synthetic adhesives, these adhesives are still used as wood adhesives. Casein-based adhesives are generally limited to interior structural uses due to several properties. These adhesives have a poor resistance to water, and the attack of molds and fungi, but these properties can be improved by using additives. However, casein-based adhesives have an excellent gap

filling and high strength in a cured bond line. These adhesives are resistant to heat (up to 70°C), and organic solvents [18].

#### ***1.2.1.1.3 Blood-based adhesives***

Blood-based adhesives are preferably produced from soluble dried blood, a by-product of slaughterhouse operation. These adhesives are sold as light colored powders, and powders must then be mixed with water, hydrated lime or sodium hydroxide for their application. Blood-based adhesives have moderate resistance to water and heat, but are subject to being attacked by microorganisms under wet conditions. Phenol-formaldehyde resin can often be added as an antifungal agent, which also provides additional strength [19].

Blood-based adhesives can be hardened by hot-pressing and by loss of water. In the manufacture of softwood plywood, panels bonded with these adhesives are generally hot-pressed at 70-230°C for 10-30 minutes, with pressures ranging from 0.5 to 0.7 MPa [15].

#### ***1.2.1.1.4 Soy-based adhesives***

##### ***1.2.1.1.4.1 Soybeans as a raw material***

Soybeans as one of the most valuable crops are used for a variety of products, ranging from food for human consumption, and animal feed, to industrial products. Soybeans were originally cultivated in Eastern Asia and later introduced to Korea and Japan. Although soybeans were brought to the United States in the late 1800s or early

1900s, the U.S. has been the largest producer in the world for last decades. In 2005-07, the world production of soybeans was approximately 217 million metric tons per year, and the U.S. solely accounted for 37.0% of the world production [20].

Soybeans consist of approximately 40% protein, 20% lipid, 30% carbohydrates and 4.9% ash, but the chemical composition of soybeans can vary according to conditions under which they grow [21].

In the amino acid composition of soy proteins, acidic amino acids (aspartic and glutamic acids) account for 30% of the total amino acids. The remaining composition includes amides (asparagines and glutamine), non-polar amino acids (alanine, valine and leucine), basic amino acids (lysine and arginine), and uncharged polar amino acid (glycine). Table 1.1 summarizes the amino acid composition of soy proteins [21]. Carbohydrates of soybeans can be largely grouped into two categories: soluble sugars (sucrose, stachyose and raffinose) and insoluble polysaccharides (cellulose, hemicelluloses and pectin). Lipids of soybeans generally contain 96% triglycerides, and 4% non-triglycerides including phospholipids, unsaponifiables, and free fatty acids. Most of non-triglycerides are removed from the crude oil during a refinery process for obtaining refined oil [22].

Table 1.1 Amino compositions of soy proteins

Amino Acid	Composition (g/16 g nitrogen)
Isoleucine	4.54
Leucine	7.78
Lysine	6.38
Methionine	1.26
Cystine	1.33
Phenylalanine	4.94
Tyrosine	3.14
Threonine	3.86
Tryptophan	1.28
Valine	4.80
Arginine	7.23
Histidine	2.53
Alanine	4.26
Aspartic acid	11.70
Glutamic acid	18.70
Glycine	4.18
Proline	5.49
Serine	5.12

Almost 90% of proteins in soybeans are globulins that are present in the form of dehydrated storage proteins. The rest of the proteins include intracellular enzymes, hemagglutinins, protein inhibitors and membrane lipoproteins [21]. The solubility of soy proteins is an important physical property. The major proteins in soybeans, globulins, are insoluble at their isoelectric points (pH 4-5), but can be soluble in an adequate solvent (water or dilute salt solutions) with certain pH values above or below the isoelectric points. The solubility of the proteins is significantly influenced by pH

values of a solvent; a pH of above 6.5 results in the maximum solubility of the proteins, and also the high amount of proteins can be extracted around pH 2 [23].

Soy proteins are composed of separate proteins that have a wide range of molecular sizes. The molecular size of each protein is characterized by the use of ultracentrifuge or by gel filtration. Soy proteins are divided into four major fractions (2, 7, 11, 15S) based on their sedimentation rate [24]. Table 1.2 shows the amounts and components of the fractions in soy proteins [24].

Table 1.2 Major fractions of soy proteins

Fraction	Content (%)	Major Components
2S	8	Trypsin inhibitor, cytochrome
7S	35	Lipoxygenase, amylase, globulins
11S	52	Globulins
15S	5	Polymers

Among various products of soy proteins, major products suitable for producing adhesives are soy flour, soy protein concentration (SPC), and soy protein isolate (SPI) [22]. These products are produced from white or defatted flakes, which are residual products after extracting oil from soybeans. Soy flours are obtained by grinding the flakes to 100 mesh or finer (150, 200 and 325 meshes) and contain a minimum of 50% protein. SPCs and SPIs contain minimum 70% and 90% protein on a dry weight basis,

respectively. Both products are obtained by extracting white flakes or ground flour [25].

#### *1.2.1.1.4.2 Soybeans as a wood adhesive*

Increasing environmental concerns and strict regulations on emissions of toxic chemicals have forced the wood composites industry to develop environmentally friendly alternative adhesives from abundant renewable substances such as soy flour. From 1930s to 1960s, soybeans were widely used as wood adhesives, but the synthetic petroleum-based resins quickly replaced the soy-based adhesives after 1960s [26]. While soy-based adhesives have many advantages such as low cost, easy handling, and low press temperatures, the adhesives have low bonding strength and low water resistance [27]. Therefore, their uses in wood composite products are limited to mainly interior applications. In recent years, soy-based adhesives have again drawn people's attention as one of the most promising alternatives to petroleum-based adhesives with concerns over fluctuating prices and future-exhaustion of oil, as well environmental issues associated with petroleum-based synthetic resins. Several studies on improving bond strength and water resistance of soy-based adhesives have been carried out.

Modifications of soy protein structures can be obtained by physical, chemical, and enzymatic treatments. The main principle of using soy proteins as a component of an adhesive is their dispersion and unfolding in solution [28]. Soy protein modification by selected treatments can improve both properties of soy protein

molecules. As a result, soy-based adhesives containing the modified soy proteins have high bonding strength and water resistance [29, 30].

One of the methods used to alter the protein structures is denaturation and disulfide bond cleavage of soy proteins through exposure to heat, acid/alkali, urea, guanidine hydrochloride (GuHCL), sodium dodecyl sulfate (SDS), and sodium dodecylbenzene sulfonate (SDBS) [29-36]. Hettiarachchy *et al.* [32] reported that soy proteins modified by alkali and trypsin resulted in improved bond strength and water resistance of adhesives compared to unmodified soy proteins. In alkali treatment, dispersion and unfolding of the protein structures are enhanced, which leads to better interaction of soy proteins with woody materials [28, 32]. It was found that urea-modified soy protein adhesives provided increased strength and better water resistance to the resulting adhesive than unmodified soy protein adhesives [29, 33, 34]. The mechanism of urea modification is that hydrogen bonding in the soy proteins is broken down by urea, resulting in unfolding the protein structures [29]. The effect of guanidine hydrochloride (GuHCl)-modified soy protein isolate (SPI) on adhesive properties was studied [30, 35]. The modification of soy proteins with GuHCl improved shear strength and water resistance [30]. It was demonstrated that the shear strength of the modified SPI adhesive had the highest value at 1.0 M GuHCl [35]. Huang and Sun [36] investigated the effects of soy proteins modified by sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) on adhesive properties. This research showed that both SDS and SDBS-modified SPI adhesives had greater shear strength and water resistance than unmodified adhesives, specifically

at 0.5 and 1 % concentrations [35]. All these results were obtained from small pieces of veneer laminates in laboratory and have not been consistently confirmed by a commercial plywood production where big multi-ply plywood panels are produced in several minutes.

The performance of soy-based adhesives can be improved by introducing cross-linking agents that are to form covalent linkages between polar functional groups such as amino groups and carboxylic acid groups of amino acid residues in soy proteins [37, 38]. The cross-linking agents that are widely used for enhancing the adhesive performance contain epoxides, and aldehydes [39, 40]. It was demonstrated that the soy proteins modified with aliphatic epoxides, which were used as cross-linking agents in protein-based adhesives, enhanced adhesive performance [39]. In this adhesive system, an aliphatic halohydrin ether cross-links alkaline proteins by reacting with amino groups [39]. Sun *et al.* [41] employed epoxidized soybean oil (ESO) and 1,2,7,8-diepoxyoctane as cross-linking agents, and reported that the modified soy protein isolate (SPI) adhesives showed improved water resistance. Aldehydes can react with amino groups in soy proteins. Formaldehyde is known as a common and very strong cross-linking agent for soy-based adhesives. Formaldehyde provides improved water resistance and bonding strength [37]. Ghorpade *et al.* [42] presented that formaldehyde as a cross-linking agent in soy proteins increased tensile strength (TS) and decreased water vapor permeability (WVP) of soy protein films. Glutaraldehyde (GA), a popular reagent, is also well known for having a good ability to yield cross-linkages by readily reacting with proteins [43]. It was found that cross-



linking by using GA in soy proteins led to improved water resistance and increased tensile strength (TS) [44, 45].

Mussel proteins, also called marine adhesive proteins (MAPs), mainly consist of 3,4-dihydroxyphenylalanine (DOPA), lysine, glycine, and serine or threonine. MAPs are known as strong and water-resistant adhesives [46]. Liu and Li [46, 47] introduced a main functional group of MAPs onto soy proteins. It was found that the modification of the soy proteins with a DOPA group and free mercapto (-SH) provided increased strength and water resistance to their adhesives for wood [46, 47]. Kymene<sup>®</sup> 557H, a commercial wet strength agent for paper, was used as a curing agent in a new soy-adhesive system. The SPI-Kymene adhesives presented very similar properties to phenol-formaldehyde (PF) resins, which were feasible to be used for exterior purposes [48]. However, the new adhesive system was as yet impractical for mass production because SPI is too expensive as a raw material for wood adhesives. Soy flour is a much less expensive soybean product. Soy flour-Kymene adhesive has been commercialized for production of plywood since 2004 [48]. A soy-based adhesive system consisting of soy protein isolate (SPI), maleic anhydride (MA), and polyethyleneimine (PEI) was demonstrated to have improved adhesive properties [49]. Huang and Li [50] developed a new soy flour-based adhesive for making interior plywood. They employed soy flour (SF) instead of SPI as a component of the adhesive, MA (maleic anhydride) and PEI (polyethyleneimine), because SPI is too expensive to be used for commercial productions. The optimum formulation of the main ingredients was 7/1.0/0.32 for the highest water-resistance, and the hot-press temperature (160 °C)

and time (5 min) showed a higher strength and water resistance than other conditions [50].

Presently, one of the soy-based adhesive systems has been successfully used in the wood composites industry, especially for the manufacturing of interior plywood since 2004 [48]. The soy-based adhesive is a sustainable adhesive because it meets all of the economic, social, and environmental demands. Soy flour is relatively inexpensive, abundant and currently of over-supply. Because of increased environmental concerns over toxic chemicals used in wood composites industry, California Air Resource Board and the US federal government have passed strict regulations of limiting formaldehyde emission from wood-based products. From social and environmental viewpoints, soy-based adhesives are excellent alternatives to petroleum-based adhesives.

#### **1.2.1.2 Synthetic adhesives**

Synthetic adhesives are polymers produced from petrochemicals. Synthetic adhesives have dominated the wood adhesive market since they were introduced in wood products industry, especially plywood industry, in the early 1930s [18]. Unlike most natural adhesives, synthetic adhesives generally have superior adhesive performance. Synthetic adhesive used for wood can be classified into two groups based on their behavior when exposed to heat: thermosetting resin adhesives and thermoplastic resin adhesives.

#### ***1.2.1.2.1 Thermosetting resin adhesives***

Thermosetting resins are the most common types of wood adhesives that are used in the wood products industry. The thermosetting resin adhesives include amino resin, phenolic resin, isocyanate-based, and epoxy resin adhesives.

##### ***1.2.1.2.1.1 Amino resin adhesives***

In 1998, amino resins, such as urea-formaldehyde (UF) resins and melamine-formaldehyde (MF) resins, accounted for approximately 60% of the total consumption of wood adhesives in North America [16].

Amino resins are thermosetting resins, which are produced by copolymerizing formaldehyde with an amino compound. The most important amino compounds are urea and melamine [51].

##### **1.2.1.2.1.1.1 Urea-formaldehyde (UF) adhesives**

Urea is a colorless, odorless solid, which is known as the first organic compound made from inorganic raw materials. Urea is manufactured from carbon dioxide ( $\text{CO}_2$ ) and ammonia ( $\text{NH}_3$ ) under high heat and pressure. Formaldehyde is a highly reactive, colorless, strong smelling gas. The method for producing formaldehyde includes the following process: air and methanol vapors are passed through a catalyst bed such as a heated copper or platinum gaze, and the resulting formaldehyde is dissolved in water [51].

Urea-formaldehyde (UF) resins are the most widely used adhesives in the manufacture of wood composite products, such as interior plywood, particleboard, and fiberboard. As compared to other thermosetting resins such as phenol formaldehyde (PF) and isocyanate, UF resins are relatively less resistant to water and moisture, which leads to the limitation of their exterior applications, and releases formaldehyde from products bonded with this UF resins [52]. However, they are less expensive and lighter in color after curing than PF resins. Also, they can be used under a variety of curing conditions. It is possible to improve boiling water resistance of UF-bonded wood composite panels by adding melamine-formaldehyde and phenol-resorcinol-formaldehyde resins [19].

UF resins are obtained by the condensation of urea and formaldehyde in water, and can form both linear and branched molecular chains, as well as three-dimensional networks [53]. There are two major chemical condensations between urea and formaldehyde: alkaline condensation in the first step and acid condensation in the second step. In the alkaline condensation, formaldehyde is added to urea to form mono-, di-, and trimethylolureas by introducing N-hydroxymethyl groups. The second step is the acid condensation of methylolureas with an active hydrogen atom to produce a molecule of water. In this step, higher molecular weight oligomers and polymers are formed by the formation of methylene bridges between amido nitrogens (Equations 1, 3a, and 3b in Figure 1.1), and the formation of methylene ether linkages (Equation 2 in Figure 1.1) [54].

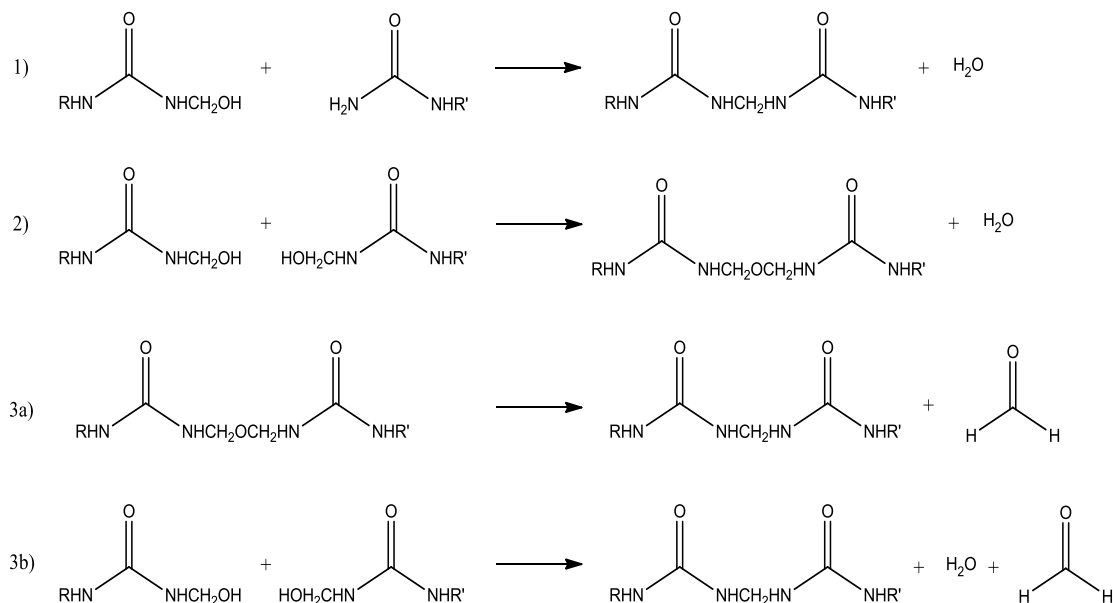


Figure 1.1 Condensation reactions of methylolureas

#### 1.2.1.2.1.1.2 Melamine-formaldehyde (MF) adhesives

Melamine was initially produced from dicyandiamide. However, because of its high production cost, it is presently manufactured from urea by its dehydration [51].

Although melamine-formaldehyde (MF) adhesives have similar properties to urea-formaldehyde (UF) adhesives, there are some superior properties: water and heat resistance, high hardness, and short curing time. Urea dissolves in both cold and hot water, but melamine dissolves in only hot water. MF resins have better resistance to hydrolysis than UF resins. MF is often used with UF resins, thus producing melamine-urea-formaldehyde (MUF) adhesives, for reducing the high cost of MF resins. The addition of UF to MF can improve bonding strength and water resistance, compared to

the use of UF alone. Thus, MF and MUF adhesives can be used for exterior purposes [53].

The other attribute that differentiates MF from UF is that condensation and curing of MF resins are not influenced by pH conditions [53]. MF resins are generally made through the addition and subsequent condensation reactions between melamine and formaldehyde in water. The addition and condensation reactions between melamine and formaldehyde are similar to those between urea and formaldehyde, but the reaction kinetics is very complex because melamine has a higher number of functional group than urea. The synthesis of MF resins involves two different steps. In the first reaction step, methylolmelamines are primarily produced at ambient or higher temperatures. The second step is to form a large number of oligomers and polymers through various condensation reactions among methylolmelamines. In theory, there are two different types of bridge formations between methylolmelamines: methylene bridges at low pH (7-8) and ether bridges above pH 9.0 [53, 55]. A representative chemical structure of MF resins is shown in Figure 1.2 [56].

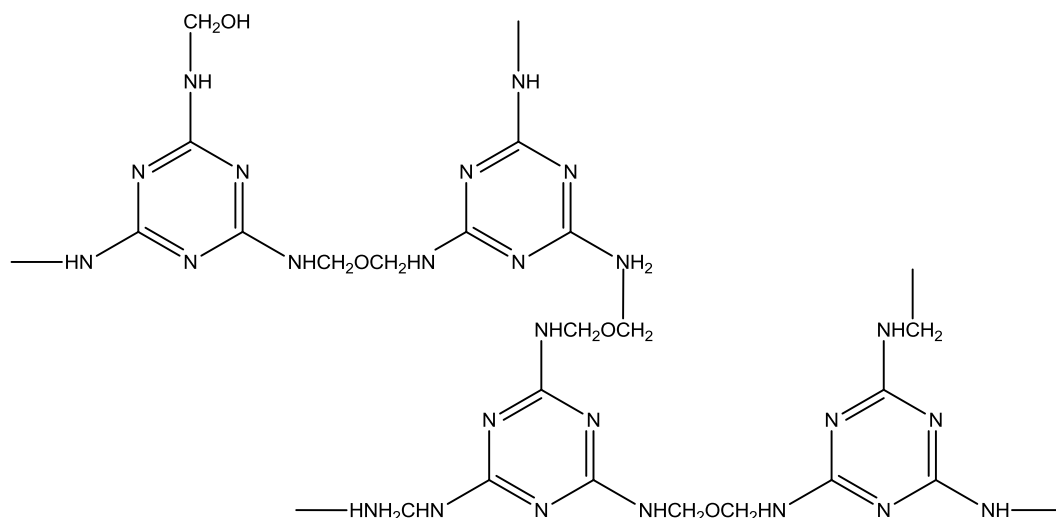


Figure 1.2 Chemical structure of melamine-formaldehyde resin

#### *1.2.1.2.1.2 Phenolic resin adhesives*

Phenolic resins are known as the first true synthetic polymers for commercial purposes. Phenolic resins are made by the condensation of phenol or substituted phenols with formaldehyde. Phenol and resorcinol are two commonly used phenolic compounds for wood adhesives [57].

##### *1.2.1.2.1.2.1 Phenol-formaldehyde (PF) adhesives*

Phenol-formaldehyde (PF) adhesives are relatively inexpensive and primarily used in the manufacturing of exterior plywood and OSB, due to their good resistance to heat, water and biodegradation; good dimensional stability; and high bonding strength [19]. Hydrogen bonding between PF and wood components is believed to play an essential role in the superior strength. Whether covalent bonds between PF and

wood is still not fully understood. The degree of penetration of PF adhesives into wood is also important for the formation of superior bonding [58].

Reactions between phenols and formaldehyde occur at the *ortho*- and *para*-positions of the hydroxyl group in phenols [57].

At the start of the reaction, depending on the pH of a catalyst, phenol reacts with formaldehyde to form a methylol phenol, and then dimethylol phenol. Formaldehyde initially attacks the 2-, 4-, 6-position of the phenol ring. In the second step of the reaction, the methylol groups condense with other available methylol phenol or phenol, resulting in linear and highly branched structures [57].

There are two different resin types based on the use of an acidic or alkaline catalyst: novolak and resol resins.

An acidic catalyst in the reaction of phenol and formaldehyde is used to produce novolak resins. Since there are no reactive methylol groups in the resulting novolak resins, the resins are not able to react further without the addition of more formaldehyde. Thus, formaldehyde is added to completely cure the PF resins [57]. For this reason, novolak resins are commonly referred to as two-stage resins [59]. Resol resins are produced by using an alkaline catalyst, such as sodium hydroxide, and an excess of formaldehyde. In contrast with novolak resins, resol resins have reactive methylol groups. As a result, resol resins are able to be completely polymerized and cured without addition of more formaldehyde during curing; therefore, resol resins are commonly referred as one-stage resins [57, 59].



#### 1.2.1.2.1.2.2 Resorcinol-formaldehyde (RF) adhesives

Resorcinol-formaldehyde (RF) adhesives are more expensive than PF resins. However, unlike PF resins, these adhesives can be cured at room temperature without additional heat input. RF adhesives have excellent properties, such as high bonding strength and high resistance to boiling water, oil, solvents, and mold growth. RF adhesives are generally rated for exterior, structural applications, but often used for interior purposes due to their high reliability [15, 19].

Resorcinol (or resorcin) is derived from phenol, which has an additional hydroxyl group (-OH) on the aromatic ring. The presence of the two hydroxyl groups at the *meta*-position to each other allows resorcinol to react more readily with formaldehyde at the 4- and 6- positions than phenol. A fast cure of RF adhesives at room temperature is attributed to the high reactivity of resorcinol with formaldehyde [60]. The condensation mechanism of RF adhesives is the same as that of PF adhesives. When the molar ratio of resorcinol to formaldehyde is 1:1, the initial condensation reaction causes only the formation of a linear structure, due to the reactivity of the 4- and 6- positions in the phenol ring. The common condensation reaction of resorcinol to formaldehyde is shown in Figure 1.3 [57]. The high reactivity of RF adhesives leads to the absence of methylol groups (-CH<sub>2</sub>OH) and the production of only RF novolaks. The RF polymers are linked by methylene bridges or methylene-ether bridges [57]. Due to its high cost, phenol is often added to RF resins to form phenol-resorcinol-formaldehyde (PRF) [60].

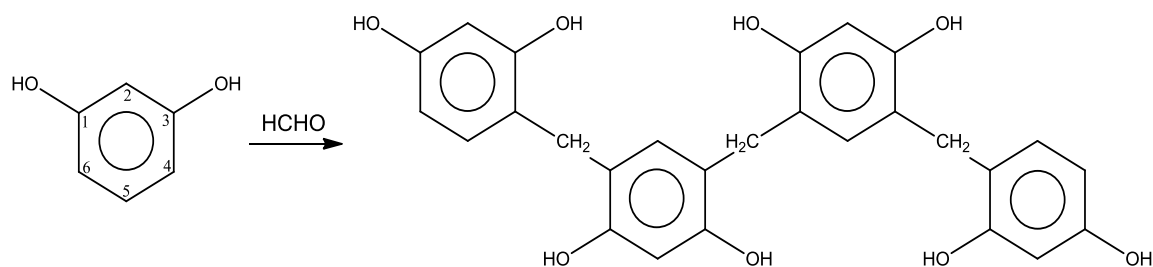


Figure 1.3 Common condensation reaction of resorcinol to formaldehyde

#### 1.2.1.2.1.3 Isocyanate-based Adhesives

The use of isocyanate-based adhesives in the wood composites industry has a relatively short history although diisocyanates have been used for approximately 50 years in the manufacturing of polyurethane resins [61]. 4, 4'-Diphenylmethane diisocyanate (MDI) is predominantly used as an adhesive in the oriented strand board (OSB), medium density fiberboard (MDF), and particleboard (PB) [62]. Advantages of using PMDI (polymeric MDI) as an adhesive for wood composite products are that it has a low vapor pressure, and a low viscosity. Its curing condition is tolerant to fast pressing time and low temperature due to its great reactivity; and it has an excellent resistance to water and a gap-filling property. However, PMDI is more expensive than other thermosetting resins, and there are some concerns about its toxicity. Products bonded with PMDI can adhere to platens of the press; therefore release agents are required in the manufacturing process, leading to an increase in production costs [61].

The reaction mechanism between isocyanates and wood is similar to the polyurethane chemistry. There are two important reactions in bonding wood with

isocyanate: the reactions between isocyanates and hydroxyl groups of wood components, and the reactions between isocyanate and water. These reactions are, as shown in Figure 1.4 [61].

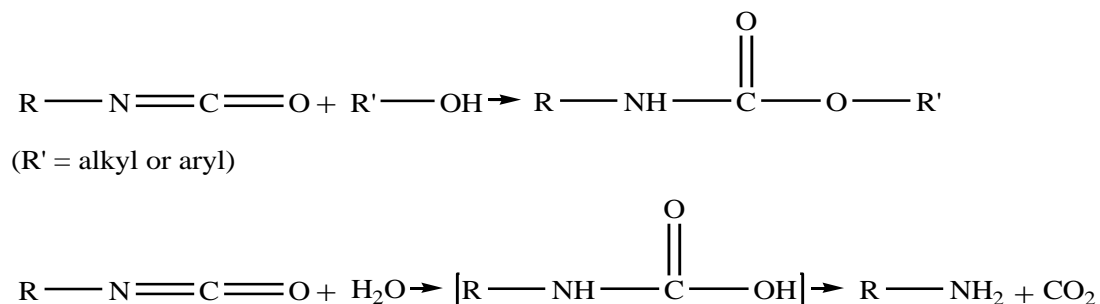


Figure 1.4 Two important reactions in bonding wood with isocyanates

Wood used in the manufacturing of wood composites generally has a moisture content (MC) ranging from 4 to 12%. Also, wood fibers, including cellulose, hemicelluloses, and lignin, contain hydroxyl groups. Therefore, the curing reactions between wood and diisocyanates can be explained through the reaction of water molecules, and hydroxyl groups, with isocyanate groups. The first step is the reaction between water and diisocyanates to form polyamines. Amine groups in polyamines react with isocyanate groups to form polyureas. Polyureas containing terminal isocyanate ( $-\text{N}=\text{C}=\text{O}$ ) groups react with hydroxyl groups of wood fibers to form urethane linkages. The curing reactions of diisocyanates with wood are represented in Figure 1.5 [61].

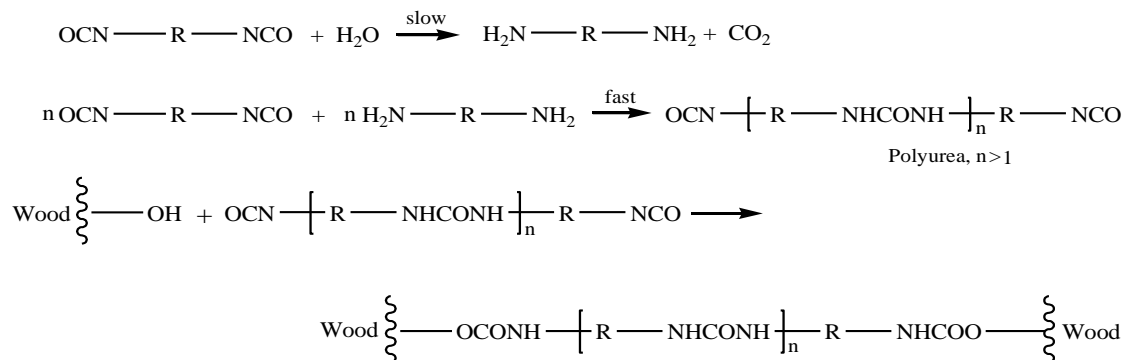


Figure 1.5 Common reaction routes of diisocyanates and wood

The adhesive efficiency of diisocyanates is markedly affected by the degree of polymerization (DP) of diisocyanates. Also, the amount of water in the adhesive system is one of the most important factors for adhesive properties. For example, oversupplied water can lead to insufficient urethane linkages between wood and the adhesive, resulting from a large amount of polyurea that does not have terminal –NCO groups [61].

#### 1.2.1.2.1.4 Epoxy resin adhesives

Commercial application of epoxy resins in bonding structural wood structures started in 1950. Their use has been steadily increased since then even though they have accounted for only a small portion of the total wood adhesive market [63]. Wood based panels bonded with epoxy resins have superior mechanical properties, excellent chemical resistance and durability when compared to those bonded with other conventional thermosetting resins. However, when exposed to the repeated conditions

of soaking in water and drying, products bonded with those adhesives are apt to delaminate [64].

Epoxy resins are synthetic thermosetting resins containing at least two epoxy groups. An epoxy group is a reactive, three-membered ring that consists of an oxygen atom bonded with two different carbon atoms. Epoxy resins have good wetting and adhesion properties with many different types of substrates [19]. Epoxy resins are mainly classified into two categories: glycidyl epoxy and non-glycidyl epoxy resins. The glycidyl epoxy resins include glycidyl-ether, glycidyl-ester and glycidyl amine. The non-glycidyl epoxy resins contain either aliphatic or cycloaliphatic epoxy resins that are generally used in specialty applications [19]. Among various types of epoxy resins, the most commonly used epoxy resin is diglycidyl ether of bisphenol A (DGEBA). DGEBA is produced by the reaction of bisphenol A and epichlorohydrin. The chemical structure of DGEBA is shown in Figure 1.6. The viscosity of DGEBA is dependent on the number of the repeating unit,  $n$  (Figure 1.6). The DGEBA generally exists as viscous liquids when the  $n$  is in the range from 0.1 to 1.0, and as solids when the  $n$  is above 1.0 [63, 65].

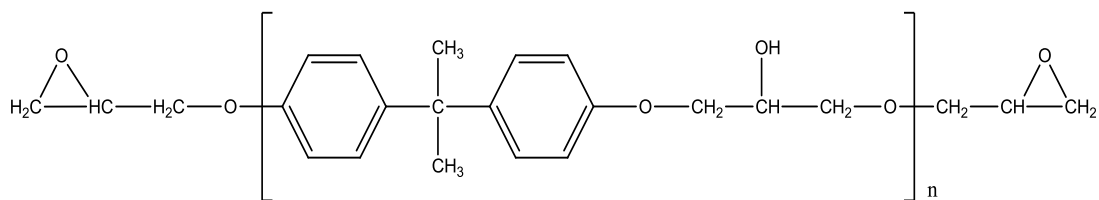


Figure 1.6 Chemical structure of diglycidyl ether of bisphenol A (DGEBA)

Epoxy resins can also be classified as two-part and one-part adhesives. One of the key characteristics of two-part adhesives is their capability to cure at room temperature. Two components of the two-part adhesives are provided separately, and therefore required to be mixed prior to use. The two components are comprised of a base (epoxy resins) and a curing agent that crosslinks with the base for formation of a three-dimensional adhesive network [15]. One-part adhesives do not need to be mixed prior to use. These adhesives, however, require an external energy source such as ultraviolet light and electron beam for facilitating the cross-linking reaction [19].

#### 1.2.1.2.1.4.1 Curing agents for epoxy resins

The use of an effective curing agent in an epoxy resins system is critical since the curing agent significantly affect properties of the resulting (cured) adhesive such as hardness, strength, and durability. Different curing agents may result in different types of chemical structures and the different degree of cross-linking. Epoxy resins can be tailored for different applications through selection of different types of curing agents. There are a wide variety of chemicals that can be used as curing agents for epoxy resins [63]. The characteristics of commonly used curing agents are summarized in Table 1.3 [63].

Table 1.3 Characteristics of curing agents used in epoxy resins

Type	Advantage	Disadvantage
Aliphatic amines	Convenience, room temperature cure, low viscosity, cheap	Sensitive to mix ratios, short pot life, strong irritant, high vapor pressure
Aromatic amines	Good thermal/chemical resistance	Solids at room temperature, slow cure time, requiring elevated temperature for cure
Polyamide	Convenience, room temperature cure, low toxicity	High viscosity, poor thermal resistance, low vapor pressure, expensive
Anhydrides	Long pot life, low viscosity, good thermal/chemical resistance	Slow cure time, requiring elevated temperature for cure, sensitive to mix ratios
Catalytic (e.g., tertiary amines)	Long pot life, high thermal resistance	Poor water resistance, poor physical properties, slow cure time, requiring elevated temperature for cure

The most commonly used curing agents for room temperature curing epoxy resins are aliphatic amines and polyamides. The most commonly used epoxy resins in the epoxy/amine adhesives include diglycidyl ether of bisphenol A (DGEBA), and *N,N,N,N*-tetraglycidyl-4,4'-diamino-diphenylmethane (TGDDM) [66]. An amine is an organic compound containing a nitrogen atom. The reactions of amines with epoxy resins depend upon the number of hydrogen atoms attached to the nitrogen. For example, a primary amine ( $R-NH_2$ ) and a secondary amine ( $R_2-NH$ ) react with two epoxide groups and one epoxide group, respectively. Typically, the reaction of a secondary amine with epoxy resins is slower than that of the primary amine. A tertiary

amine ( $R_3-N$ ) serves as a catalyst, facilitating epoxy reactions, but does not react with an epoxy group for formation of covalent linkages [63, 66]. The mechanism by which epoxy resins react with an amine is described in Figure 1.7. The use of an aliphatic amine in an epoxy resin system results in fast curing of the resins at room temperature. However, the resin system has a short pot life and the resultant adhesive network has poor thermal resistance. The ratio of epoxy/aliphatic amine is critical since adhesive properties are significantly affected by the mix ratio. Diethylenetriamine (DETA) and triethylenetetraamine (TMTE) are the commonly used aliphatic amines [19].

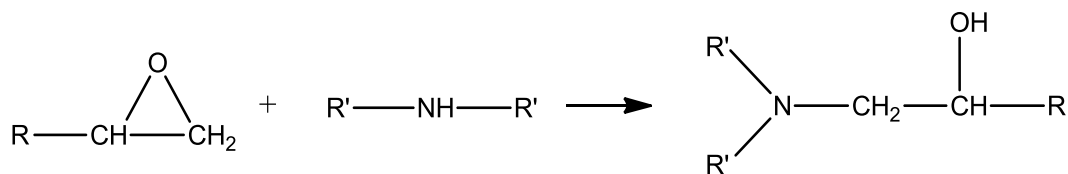


Figure 1.7 Common reaction mechanism of epoxy/amine

The most commonly used polyamides are polymers produced from the condensation of polyamines such as diethylene triamine and unsaturated fatty acids. Polyamides react with epoxide groups through residual amino groups in the polyamides. Unlike aliphatic amines, the mix ratio of epoxy/polyamide is generally less critical due to a wide range of molecular weights of polyamides, which provides flexibility to the resulting adhesives. Epoxy/polyamide adhesives can be cured at room temperature, but may take a long time to cure. The curing time can be significantly shortened through increasing the curing temperature. However,



increasing the curing temperature may reduce the strength of the cured adhesive [19, 63].

The commonly used aromatic amines include *m*-phenylenediamine, diaminodiphenyl methane, and diaminodiphenyl sulfone. In an epoxy/aromatic amine resin system, a catalyst may be used so that the resin can be cured at room temperature [19]. Aromatic amines are relatively expensive, and exist as solids at room temperature, so they have to be melted prior to use [63]. Epoxy/aromatic amine resins generally have poorer adhesive strengths than epoxy/aliphatic amine resins [15]. However, epoxy/aromatic amine resins have a longer pot life, and the cured resins have better chemical and thermal resistance than epoxy/aliphatic amine resins [63].

Epoxy/anhydride resins have several advantages, such as lower viscosity, longer pot life, better chemical resistance (especially to acids), and less exothermal than epoxy/amine resins. The commonly used anhydrides include hexahydrophthalic anhydride (HHPA), phthalic anhydride (PA), nadic methyl anhydride (NMA), and pyromellitic dianhydride (PMDA) [65]. Epoxy/anhydride resin systems require elevated temperatures (up to 200 °C) to cure and long post-cures, resulting in ultimate properties [19, 63]. Since reactions of some anhydrides with epoxy groups are too slow, accelerators such as tertiary amines, metallic salts, and imidazoles may be employed in the resin system. The reaction of anhydrides with epoxy groups is complicated. There are three important reaction mechanisms in the curing of epoxy/anhydride resins: 1) the opening of the anhydride ring by reacting with a

hydroxyl group of an alcohol for formation of the monoester 2) the reaction of an epoxy group with the nascent carboxylic acid group for formation of an ester linkage 3) the reaction of an epoxy group and a hydroxyl group (catalyzed by the acid) for formation of an ether linkage [65]. The common reaction mechanism of epoxy and anhydride is shown in Figure 1.8 [65].

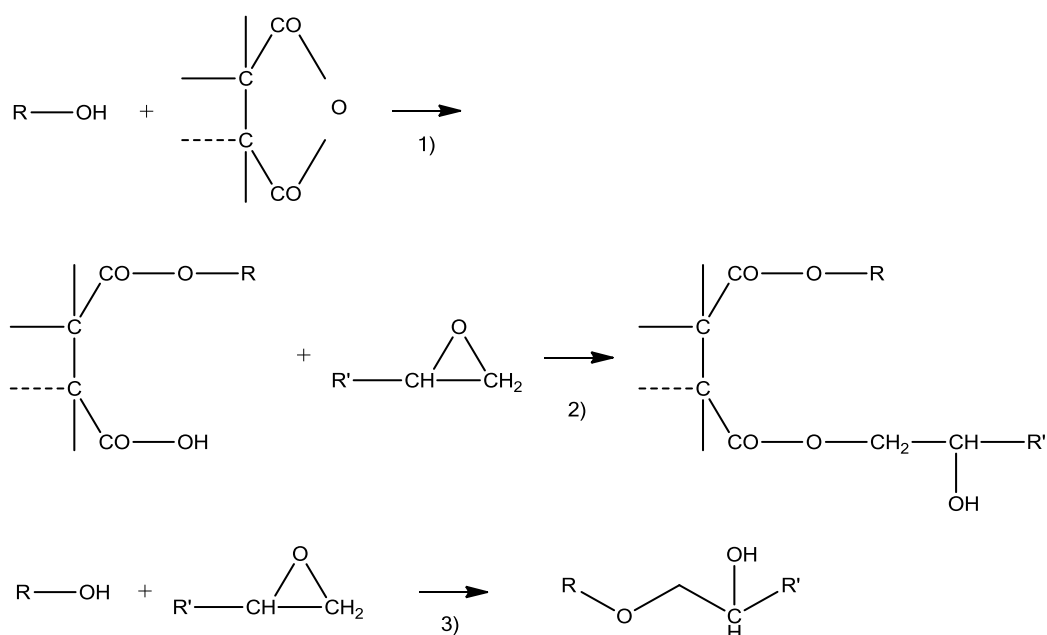


Figure 1.8 Common reaction mechanism in the curing of epoxy/anhydride resins

Epoxy rings can be homopolymerized in the presence of a catalyst such as a strong acid or a strong base. The reaction mechanisms by which epoxy resins polymerize in the presence of an acidic (cationic) or a base (anionic) catalyst are shown in Figure 1.9 [19]. The polymerization is a ring-opening reaction and does not generate any volatile small molecules [67].

Cationic catalysts for polymerizing epoxy resins include Lewis acids (a variety of inorganic salts) such as halides of Al, B, Be, Fe(III), Sb(v), Sn, Ti, Zr and Zn. While epoxy/amine or epoxy/anhydride resin systems generally require a long curing time and high curing temperatures ( $> 130\text{ }^{\circ}\text{C}$ ), curing reactions of epoxy resin systems containing cationic catalysts proceed at a faster rate. Also, initial viscosities of epoxy/cationic catalyst resins are low. Therefore, cationic curing system for epoxy resins can render the curing process simplified, compared to the common curing agents, such as amines and anhydrides [67, 68]. However, the use of cationic catalysts in epoxy resins result in short shelf life and high hygroscopicity while providing fast curing [69]. It has been demonstrated that complexes such as  $\text{BF}_3$ -ether,  $\text{BF}_3$ -amine, or  $\text{SbF}_6$ -epoxide instead of Lewis acids alone can overcome these disadvantages [70]. The cured adhesive with cationic catalysts typically has high thermal and chemical resistance, but has low peel properties and poor impact resistance [19].

Anionic catalysts used in the epoxy resins include Lewis bases. The most commonly used catalysts are tertiary amines such as benzyldimethylamine, pyridine,

triethylamine and 2,4,6-tris(dimethylaminomethyl)phenol. The cured epoxy resins with anionic catalysts have hydrophobic properties against water and high humidity. The mechanical properties, including strength, toughness, and elongation, of the cured epoxy resins are excellent [65]. However, the anionic homopolymerization of epoxy resins has two major drawbacks in the commercial applications of epoxy resins, including slow reaction rate (long curing time) and short primary chains (responsible for relatively low glass transition temperature) [70].

### **1.2.2 Current Issues on conventional adhesives in wood composites industry**

Since conventional wood adhesives (so-called synthetic adhesives) were introduced to the wood composites industry in the 1930s, they have greatly contributed to the prosperity of the whole forest industry, as well as the wood composites industry. The adhesive market had quickly and steadily grown for a considerably long time until recent economic downturn and the rapid increase in oil price in the past decade. The rapid growth of the synthetic resins are mainly due to their superior properties to natural adhesives, ever-increasing demand for wood composite products (corresponding to the increase of world population), and the then relatively stable price of oil. The recent rapid increase in fossil oil price has posed a great concern over whether synthetic resins can support the sustainable growth of the wood composites industry. Emission of toxic chemical such as formaldehyde in the production and use of wood composite panels bonded with synthetic resins, especially urea-formaldehyde resins, has generated great concerns over the negative impacts of

synthetic resins on human health and environment. As a result, the wood composites industry has an urgent need for alternative adhesives that are environmentally friendly and are derived from renewable materials.

Almost all conventional adhesives, such as phenol-formaldehyde resins and urea-formaldehyde resins, are produced from petroleum and natural gas. However, petroleum resources are not infinite and not renewable. Although the exact amount of fossil oil is still unknown, it is predicted that the exhaustion of fossil oil will be in approximately 45 years based on the proven reserves and current world production rates [71]. Also, oil prices have fluctuated over the last few decades, and will probably keep going up in the future. Thus, the development of renewable-material-based alternatives to petroleum-based adhesives is essential for the continued success of the wood composites industry.

Phenol-formaldehyde (PF) resins and urea-formaldehyde (UF) resins are major wood adhesives. In particular, UF resins accounts for over 60% of the wood adhesive market. Formaldehyde is a key component in the manufacturing of PF and UF resins. However, formaldehyde is a hazardous volatile organic compound, and is emitted in the production and use of wood composite panels bonded with UF resins. Formaldehyde has been classified as a known human carcinogen (cancer-causing substance) by the International Agency for Research on Cancer (IARC) [72]. Also, the U.S. Environmental Protection Agency (EPA) has classified formaldehyde as a probable human carcinogen, and the U.S. National Toxicology Program (NTP) has

reported that formaldehyde is reasonably anticipated to be a human carcinogen [73, 74]. It can be an eye, nose, and throat irritant.

Concerns over negative impacts on human health and environment from exposure to formaldehyde have brought about regulations and standards for restricting the amount of formaldehyde that can be emitted from wood-based products. The California Air Resources Board (CARB) passed a regulation on formaldehyde emissions from wood composite products, which is called the “Airborne Toxic Control Measure (ATCM)” in April 2007. Under this regulation, all wood composite products have to meet these strict formaldehyde limits to be sold, distributed, or manufactured in California. Table 1.4 describes the formaldehyde emission standards in two phases [75]. The phase 1 emission standard already went into effect on January 1, 2009. According to the phase 1 emission standard, adhesives are required to have formaldehyde emissions which are equal to or less than 0.08 ppm for hardwood plywood, 0.18 ppm for particleboard (PB), and 0.21 ppm for medium density fiberboard (MDF). Also, the phase 2 standard started on January 1, 2010. By 2012, all the wood composite products should decrease formaldehyde emissions according to the Phase 2 standards (ppm).

Table 1.4 Phase 1 and Phase 2 formaldehyde emission standards for wood composite products\*

Phase	HWPW-VC (ppm)	HWPW-CC (ppm)	PB (ppm)	MDF (ppm)	Effective Date
1	0.08	—	0.18	0.21	Jan 1, 2009
	—	0.08	—	—	Jul 1, 2009
2	0.05	—	—	—	Jan 1, 2010
	—	—	0.09	0.11	Jan 1, 2011
	—	—		0.13	Jan 1, 2012
	—	0.05	—	—	Jul 1, 2012

\*HWPW-VC, hardwood plywood with a veneer core; HWPW-CC, hardwood plywood with a composite core; PB, particleboard; MDF, medium density fiberboard.

More recently, a new federal law for regulating formaldehyde emission, the “Formaldehyde Standards for Composite Wood Products Act (FSA),” was signed into law by President Obama on July 7, 2010. The FSA basically adopts the regulations established by the CARB as federal standards. The FSA revises the Toxic Substances Control Act (TSCA), and EPA requires establishing new regulations for implementation by January 1, 2013.

Reducing or eliminating formaldehyde emissions is one of the major reasons for developing environmentally friendly alternative adhesives from abundant renewable substances. Soy-based adhesives have again drawn attention as one of the most promising alternatives to synthetic petroleum-based adhesives because soybean is abundant, inexpensive, readily available and renewable.

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**CHAPTER 2 A NEW FORMALDEHYDE-FREE WOOD ADHESIVE FROM  
RENEWABLE MATERIALS**

## **2.1 Abstract**

A formaldehyde-free adhesive that consists of soy flour (SF) and a new curing agent (CA) was developed and evaluated for making interior plywood. Three types of plywood panels (seven-ply maple/white fir/pine/white fir/pine/white fir/maple, five-ply yellow poplar, and five-ply aspen) were prepared with the SF-CA adhesives and evaluated for their water resistance. The CA was derived from the reaction of epichlorohydrin (ECH) and ammonium hydroxide in water. Effects of the reaction time, reaction temperature, NaOH usage, heat treatment of CA, addition order of reactants in the preparation of the CA and storage time of the CA on the water resistance of plywood panels bonded with SF-CA adhesives were investigated. The reaction time required for the completion of the reaction significantly decreased as reaction temperatures increased. The addition of NaOH to the SF-CA adhesive improved the water resistance and dry shear strength of the five-ply aspen panels. All plywood panels met the requirements for interior plywood when the CAs were prepared at 45 to 60 °C no matter whether the CA was heat-treated or not. Mixing ECH and ammonium hydroxide all at once resulted in better water resistance of the resulting plywood panels than adding either of ECH or ammonium hydroxide to the other dropwise. The viscosity of heat-treated CA was comparable to that of untreated CA when the CA was prepared at 50 °C. Both heat-treated and untreated CAs could be stored at room temperature for at least two months without compromising the water resistance of the resulting plywood panels.



## **2.2 Keywords**

Adhesives for wood, soy flour, renewable materials, interior plywood, water resistance

## **2.3 Introduction**

In recent years, sustainability has drawn more and more attention due to our heavy dependence on petroleum and natural gas for energy and various products. Development of alternatives for petrochemical-based products from renewable materials will certainly improve the sustainability. At present, petrochemical-based adhesives such as phenol-formaldehyde (PF), urea-formaldehyde (UF) and isocyanates are predominantly used for production of wood composite panels and are not sustainable in a long run. In addition, the emission of carcinogenic formaldehyde in the production and use of wood composite panels bonded with the UF resins has been a big concern in recent years [1]. As a result, the California Air Resources Board (CARB) passed a regulation on limiting formaldehyde emission from wood-based products used and sold in California in April 2007. A national regulation of limiting formaldehyde emission, “formaldehyde standards for composite wood products act,” was signed into law on July 7, 2010. There is an urgent need for development of a formaldehyde-free wood adhesive from renewable materials.

Soybean is abundant, renewable, inexpensive, and readily available. Several soy-based adhesives have been developed in recent years [2-7]. One of the soy-based formaldehyde-free adhesives has been used for production of interior plywood panels

since 2004 [3]. This soy-based adhesive mainly consists of soy flour and a small amount of a curing agent, polyamidoamine-epichlorohydrin (PAE) resin [3]. The PAE resin is derived from petrochemicals and is the most expensive component of the soy-based adhesive. In this study, new curing agents were developed from epichlorohydrin (ECH) and ammonium hydroxide and evaluated as a replacement of PAE. ECH can be derived from renewable glycerol [8-10]. The ECH-NH<sub>3</sub> curing agents can potentially be independent of petrochemicals.

## **2.4 Materials and methods**

### **2.4.1 Materials**

SF (7% moisture content) was provided by Cargill Incorporated (Minneapolis, MN); ECH (99%) and ammonium hydroxide (28%-30% wt% solution of NH<sub>3</sub> in water) were purchased from Acros Organics (Morris Plains, NJ); Sodium hydroxide was purchased from BDH (West Chester, PA); Yellow-poplar, maple, white fir, pine and aspen veneers were provided by Columbia Forest Products (Greensboro, NC).

### **2.4.2 Synthesis of the curing agent (CA) in water**

#### **2.4.2.1 Mixing reactants all at once in water**

Ammonium hydroxide (28-30%, 88 g, 1.5mol) and ECH (99%, 420 g, 4.5mol) were added to the water (150 mL) and stirred at 600 RPM in a 2 L resin kettle equipped with a condenser, a thermometer and an internal cooling coil which was connected with an external cooling circulator. The temperature of the mixture

increased slowly at the beginning and then dramatically went up as time passed. When the temperature reached the predetermined one, the cooling circulator was turned on for maintaining the reaction temperature. The reaction mixture was milky because ECH was not soluble in water. The reaction mixture was stirred for another 30 min after it became clear. The resulting CA was stored at room temperature. The solids content of the CA was about 67%.

#### **2.4.2.2 Adding ECH to a mixture of ammonium hydroxide and water dropwise**

ECH (99%, 420 g, 4.5mol) was dropwise added to a mixture of ammonium hydroxide (28-30%, 88 g, 1.5mol) and water (150 mL) while stirring at 600 RPM in a 2 L resin kettle equipped with a condenser, a thermometer and an internal cooling coil which was connected with an external cooling circulator. The reaction temperature was maintained at 55 °C. The addition time was 1.5 h. The reaction mixture was further stirred at 55 °C for 30 min after it became clear. The resulting CA was stored at room temperature.

#### **2.4.2.3 Adding ammonium hydroxide to a mixture of ECH and water dropwise**

Ammonium hydroxide (28-30%, 88 g, 1.5mol) was dropwise added to a mixture of ECH (99%, 420 g, 4.5mol) and water (150 mL) while stirring at 600 RPM in a 2 L resin kettle equipped with a condenser, a thermometer and an internal cooling coil which was connected with an external cooling circulator. The reaction temperature was maintained at 55 °C. The addition time was 40 min. The reaction

mixture was further stirred at 55 °C for 30 min after it became clear. The resulting CA was stored at room temperature.

#### **2.4.2.4 Heat treatment of the CA**

A portion of the resulting CAs was stirred and heated at 75 °C for one hour before use.

#### **2.4.3 Preparation of SF-CA adhesives**

The following is a representative procedure for the preparation of SF-CA adhesives. A CA (121 g dry weight), water (1533 mL) and a 20% NaOH solution (145 g) were sequentially added to a KitchenAid mixer and mixed for 1 min at room temperature. SF (847 g dry weight) was added and further mixed for 5 min. The total solids content of the resulting adhesive was 36%.

#### **2.4.4 Preparation of plywood panels**

An SF-CA adhesive was applied to two sides of a veneer (60.9 cm × 60.9 cm; moisture content, 12%) by an adhesive roller-coater. The usage 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. When five-ply or seven-ply plywood was made, another adhesive-coated veneer was put on the stacked panel and covered with an uncoated veneer. Previous steps were repeated till a plywood panel with expected plies was made. The structure of five-ply panel was uncoated/coated/uncoated/coated/uncoated. The structure of

seven-ply panel was uncoated maple/coated white fir/uncoated pine/coated white fir/uncoated pine/coated white fir/uncoated maple. The stacked veneers were put on a table at ambient environment for 5 min, cold-pressed at 0.69 MPa and room temperature for 5 min, put on a table at ambient environment again for 5 min and hot-pressed at 1.03 MPa with 120 °C for 6 min. After hot-press, the panel was stored at ambient environment for at least 24 h before being evaluated for its water-resistance.

#### **2.4.5 Water resistance of plywood panels**

##### **2.4.5.1 Three-cycle soak test**

The water-resistance of interior plywood panels was determined with a three-cycle soak test in accordance with the American National Standard for Hardwood and Decorative Plywood-2000 (ANSI/HPVA HP-1-2000). Twenty plywood specimens (5.08 cm × 12.7 cm) 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 after the 1<sup>st</sup> cycle and the 3<sup>rd</sup> cycle if applicable. This soaking/drying cycle was repeated until three cycles were completed. According to the standard, a plywood panel meets water-resistance requirements 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-1-2000 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.

#### **2.4.5.2 Two-cycle boil test**

The two-cycle boil test was also performed in accordance with the ANSI/HPVA HP-1-2000. Four or nine specimens (7.62 cm × 7.62 cm) cut from each plywood panel were submerged in boiling water for 4 h and then dried at 63±3 °C for 20 h. The samples were boiled in water again for 4 h, dried for 3 h at 63±3 °C. The ANSI/HPVA HP-1-2000 has the following definition: any observed delamination greater than 25.4 mm in continuous length constitutes failure of the specimen. Within any given lot of test samples, 90% of the individual specimens must pass.

#### **2.4.6 Statistical analysis of strength data**

Strength data were analyzed with a two-sample t-test using S-PLUS® statistical software (Edition version 8.0, Insightful Corp. Seattle, WA). All comparisons were based on a 95% confidence interval.

#### **2.4.7 Determination of viscosity**

Viscosities of CAs were determined by a Brookfield DV-II+ programmable viscometer with LV spindles at room temperature.

## **2.5 Results and discussion**

### **2.5.1 Preparation of a CA and proposed curing reactions between a CA and SF**

Preparation of a CA and proposed curing reactions are shown in Figure 2.1. The CA (**2**) was prepared with 3/1 molar ratio of ECH to  $\text{NH}_3$  in water (Figure 2.1). The reaction of ECH and ammonium hydroxide in water was highly exo-thermal. Sufficient cooling was required for maintaining the reaction at a predetermined temperature. NMR analysis indicated that all CAs contained abundant chlorohydrins ( $\text{CHOHCH}_2\text{Cl}$ ) and some CAs also contained four-member-ringed azetidinium (**2** in Figure 2.1). It was found that the CAs had very complex structures. The structure of **2** in Figure 2.1 is only used for illustration of functional groups existing in the CA. It has been proposed that the azetidinium group played an essential role in the formation of cross-linkages between PAE resin and soy protein in the curing of soy-PAE adhesive [3]. It has been demonstrated that the azetidinium group is formed from chlorohydrins at 60-100 °C [11, 12]. For increasing the amount of the azetidinium group, some CAs were heated at 75 °C for one hour. It has been demonstrated that chlorohydrins and azetidinium groups could effectively react with amino groups, carboxylic acid group, and other nucleophilic groups in soy protein, thus effectively crosslinking soy protein [3, 13]. The structure of **3** in Figure 2.1 illustrated possible reaction products between a chlorohydrin/azetidinium with an amino group in soy flour.

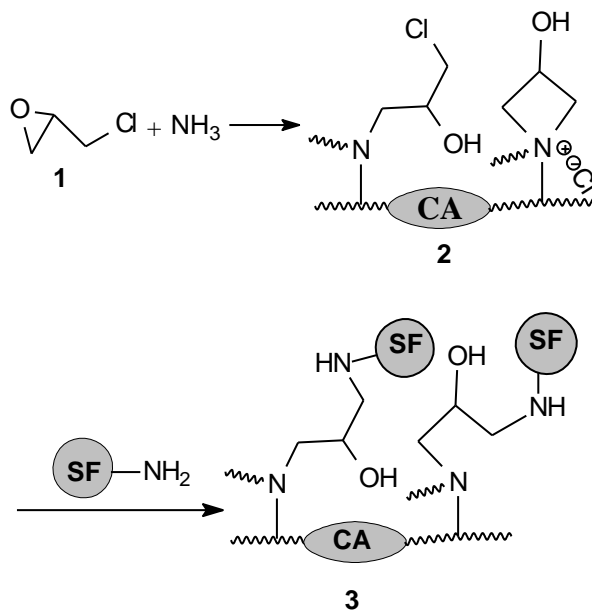


Figure 2.1 Preparation of a curing agent and proposed curing reactions with soy flour

### 2.5.2 The reaction time required for the preparation of a CA at different reaction temperatures

Table 2.1 The reaction times at different reaction temperatures

Temp. (°C )	Reaction time <sup>a</sup> (h)
60	1.5
30	1.8
50	2.8
45	4
40	7.5
35	12
30	24

<sup>a</sup> ECH and ammonium hydroxide were added to water all at once at the beginning of the reaction



The reaction time required for the preparation of a CA at different reaction temperatures are shown in Table 2.1. The reaction time was defined as the time required for the milky reaction mixture to become clear plus 30 min of additional mixing time. The reaction time decreased from 24 h to 7.5 h when the reaction temperature was raised from 30 °C to 40 °C. The reaction time was further reduced from 4 h to 1.5 h when the reaction temperature was raised from 45 °C to 60 °C. We felt that 7.5 h reaction time was too long to be desirable for commercial production of a CA. Therefore, only CAs prepared at 45 °C to 60 °C were thoroughly investigated in this study. A short reaction time implied a high productivity for the production of a CA. In this sense, the higher the reaction temperature, the higher the production efficiency. However, this reaction was highly exothermic. Increase in the reaction temperature accelerated the reaction and generate more heat, which in turn further accelerated the reaction. It was found that the reaction temperature became very difficult to control even at a small laboratory scale when it was set above 60 °C. Therefore, in the production of a large quantity of a CA, the reaction temperature has to be carefully selected so that the productivity can be optimized while the reaction temperature can be controlled.

### 2.5.3 The effect of NaOH usage on the water resistance and dry shear strength of plywood panels bonded with SF-CA adhesives

Table 2.2 Effect of NaOH usage on the water resistance of five-ply aspen plywood bonded with SF-CA adhesives

NaOH % based on dry soy flour and CA <sup>a</sup>	Panel#	Specimens failed in three-cycle soak test		Specimens failed in two-cycle boil test
		1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
3	1	0/20	0/20	3/9
	2	0/20	0/20	2/9
0	1	0/20	0/20	4/9
	2	0/20	3/20	7/9

<sup>a</sup> CAs were prepared at 50 °C by adding ECH and ammonium hydroxide to water all at once at the beginning of the reaction

The CA prepared at 50 °C without further heat treatment was used for this investigation. Based on our previous experience, five-ply aspen panels had smaller variations in shear strength than five-ply yellow poplar panels and the seven-ply panels. The five-ply aspen plywood panels were used in this investigation. The plywood panels bonded with the SF-CA adhesive containing 3% NaOH had much higher shear strength than those containing no NaOH (Figure 2.2). With 3% NaOH, both plywood panels passed the three-cycle soak test without single specimen delaminated (Table 2.2). Without NaOH, both plywood panels also passed the three-cycle soak test, but one of the panels had three specimens failed after the third cycle soak test (Table 2.2). In the two-cycle boil test, the plywood panels bonded with the

SF-CA adhesive containing 3% NaOH had less specimens failed than those without NaOH (Table 2.2). The addition of NaOH appeared to improve both water resistance and dry shear strengths of the plywood panels. An alkaline condition facilitated the generation of azetidinium groups and increased the reactivity of chlorohydrins, thus improving the crosslinking between CA and SF.

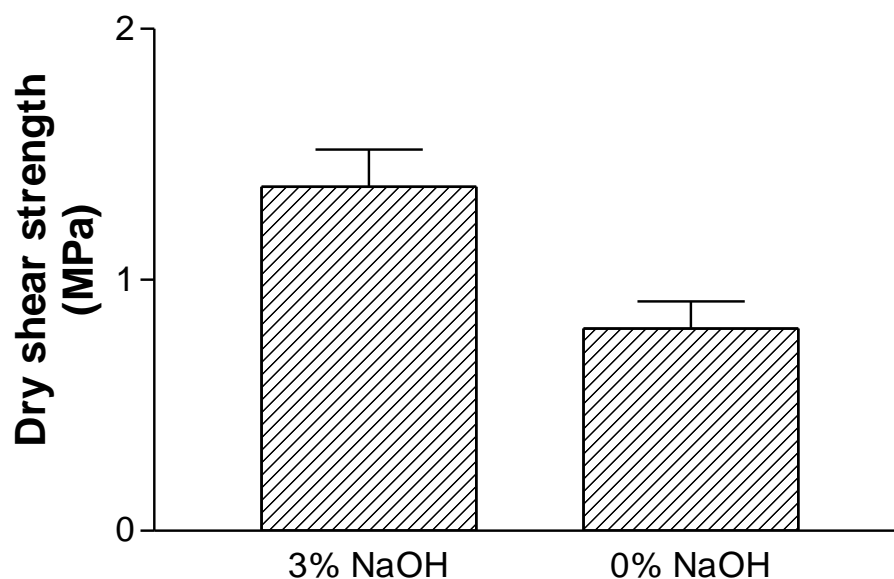


Figure 2.2 The effect of NaOH on the dry shear strengths of five-ply aspen plywood (CAs were prepared at 50 °C by adding ECH and ammonium hydroxide to water all at once at the beginning of the reaction. Data are the mean of at least twelve replicates and the error bars represent one standard error of the mean).

### 2.5.4 Effects of reaction temperature and the heat-treatment of CAs on the water resistance of plywood bonded with SF-CA adhesives

Table 2.3 Effects of reaction temperature on the water resistance of plywood panels bonded with SF-CA adhesives

Reaction temperature <sup>a</sup> (°C)	Structure of plywood	Specimens failed in three-cycle soak test				Specimens failed in two- cycle boil test		
		untreated		Heat-treated		untreated	Heat-treated	
		1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle			
45	7-p <sup>b</sup>	1	0/20	0/20	0/20	1/20	0/4	4/4
		2	0/20	0/20	0/20	0/20	1/4	2/4
	5-pa <sup>c</sup>	1	0/20	0/20	0/20	1/20	0/4	0/4
		2	0/20	0/20	0/20	0/20	0/4	0/4
	5-py <sup>d</sup>	1	0/20	0/20	0/20	0/20	4/4	4/4
		2	0/20	0/20	0/20	0/20	3/4	1/4
50	7-p <sup>b</sup>	1	0/20	0/20	1/20	2/20	0/4	1/4
		2	0/20	0/20	0/20	0/20	0/4	0/4
	5-pa <sup>c</sup>	1	0/20	0/20	0/20	2/20	1/4	0/4
		2	0/20	0/20	0/20	0/20	1/4	0/4
	5-py <sup>d</sup>	1	0/20	0/20	0/20	1/20	1/4	4/4
		2	1/20	1/20	0/20	1/20	4/4	3/4
55	7-p <sup>b</sup>	1	0/20	0/20	0/20	0/20	0/4	0/4
		2	0/20	0/20	0/20	0/20	0/4	0/4
	5-pa <sup>c</sup>	1	0/20	1/20	0/20	0/20	0/4	0/4
		2	0/20	0/20	0/20	0/20	0/4	0/4
	5-py <sup>d</sup>	1	0/20	0/20	0/20	0/20	3/4	1/4
		2	1/20	2/20	0/20	2/20	1/4	4/4
60	7-p <sup>b</sup>	1	0/20	0/20	2/20	2/20	0/4	1/4
		2	0/20	0/20	0/20	0/20	1/4	0/4
	5-pa <sup>c</sup>	1	0/20	0/20	0/20	0/20	0/4	1/4
		2	0/20	0/20	0/20	0/20	0/4	0/4
	5-py <sup>d</sup>	1	0/20	3/20	0/20	0/20	0/4	1/4
		2	1/20	1/20	0/20	0/20	4/4	0/4

<sup>a</sup> CAs were prepared by adding ECH and ammonium hydroxide to water all at once at the beginning of the reaction: <sup>b</sup> 7-p represents seven-ply panels: <sup>c</sup> 5-pa represents five-ply aspen panels: <sup>d</sup> 5-py represents five-ply yellow poplar panels.

When CAs were directly used with SF without a further heat treatment, the seven-ply panels, five-ply yellow poplar panels and five-ply aspen panels all passed the three-cycle soak test (Table 2.3). The seven-ply panels also passed the two-cycle boil test when the reaction temperature was at 50 °C or 55 °C, whereas one of the seven-ply panels had one specimen failed in the two-cycle boil test when the reaction temperature was at 45 °C or 60 °C. The reaction temperatures at 50 °C and 55 °C were better than those at 45 °C or 60 °C in terms of water resistance of the seven-ply panels. The five-ply aspen panels all passed the two-cycle boil test at all reaction temperatures studied except at 50 °C. For the five-ply yellow poplar panels, all but one panel at 60 °C failed in the two-cycle boil test. These results indicated that CAs prepared at 45 °C, 50 °C, 55 °C or 60 °C enabled all three types of plywood panels bonded with a SF-CA adhesive to meet the water-resistance requirement for interior application.

When the heat-treated CAs were used, all seven-ply panels except one panel at 60 °C, all five-ply yellow poplar panels and all five-ply aspen panels passed the three-cycle soak test (Table 2.3). The seven-ply panel at 60 °C had two specimens failed in the 1<sup>st</sup> cycle, thus being classified as failed. But it passed the 3<sup>rd</sup> cycle because only two out of 20 specimens failed after the 3<sup>rd</sup> cycle. These results revealed that the further heat treatment of CAs were not necessary for production of interior plywood panels. As a matter of fact, the heat treatment of the CA prepared at 60 °C reduced the water resistance of the resulting plywood panels in the three-cycle soak test.

When compared with the untreated CAs, the heat treatment of the CA prepared at 45 °C increased the number of specimens failed in the two-cycle boil test from 0 to

4 and 1 to 2 for the seven-ply panels, brought no change for the five-ply aspen panels (all panels passed the two-cycle boil test) and for one of the five-ply yellow poplar panels, and reduced the number from 3 to 1 for another five-ply yellow poplar panel (Table 2.3). The heat treatment did not enable the five-ply yellow panels to pass the two-cycle boil test. In summary, the heat treatment reduced the water resistance of the resulting seven-ply panels and had no significant effects on the water resistances of the resulting five-ply aspen panels and five-ply yellow poplar panels. Overall, the heat treatment of CAs prepared at 45 °C was not desirable and not necessary for plywood production.

For the CA prepared at 50 °C, the heat treatment resulted in one specimen from one of the seven-ply panels failed in the two-cycle boil test (Table 2.3). The heat-treatment of CAs prepared at 50 °C was not desirable for making the seven-ply panels. With the heat-treated CAs prepared at 50 °C, none of the specimens from the five-ply aspen panels failed in the two-cycle boil test. When compared with untreated CAs prepared at 50 °C, the heat treatment increased the water resistance of the five-ply aspen panels, thus being beneficial for making the aspen panels. Effects of the heat treatment of the CAs prepared at 50 °C on the water resistance of the resulting five-ply yellow poplar panels were mixed (the number of specimens failed in the two-cycle boil test increased for one panel and decreased for another) (Table 2.3). The heat treatment of the CAs prepared at 50 °C was thus not necessary for making yellow poplar panels.

For the CA prepared at 55 °C, the heat treatment did not affect the water resistance of the seven-ply panels and five-ply aspen panels and generated a mixed result for the five-ply yellow poplar panels (the number of specimens failed in the two-cycle boil test increased for one panel and decreased for another) in the two-cycle boil test (Table 2.3). The heat treatment of the CAs prepared at 55 °C was thus not necessary for making all plywood panels.

For the CA prepared at 60 °C, the heat treatment generated mixed results for both seven-ply panels and five-ply yellow poplar panels (the number of specimens failed in the two-cycle boil test increased for one panel and decreased for another) and resulted in one specimen from one of the five-ply aspen panels failed in the two-cycle boil test, thus reducing the water resistance of the five-ply aspen panels (Table 2.3). The heat treatment of the CAs prepared at 60 °C was thus not necessary.

In summary, heat-treatment of all CAs except those prepared at 50 °C for aspen panels were not beneficial in terms of improving water resistance of the resulting plywood panels. As mentioned previously, both azetidinium groups and chlorohydrin groups in CA could effectively crosslink SF. The heat treatment of a CA could indeed increase the amount of the azetidinium groups, but could also reduce the number of chlorohydrin groups through their conversion to the azetidinium groups and the hydrolysis of the chlorine in chlorohydrins. Results from this study suggested that it was not necessary to convert the chlorohydrins groups to the azetidinium groups for the effective crosslinking of SF.

### 2.5.5 The effect of addition order of reactants on the water resistance of plywood bonded with SF-CA adhesives

Table 2.4 Effect of different addition order of reactants on the water resistance of panels bonded with SF-CA adhesives

Addition order <sup>a</sup>	Structure of plywood	Panel #	Specimens failed in three-cycle Soak test				Specimens failed in two-cycle boil test	
			untreated		Heat-treated		untreated	Heat-treated
			1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle		
ECH to a mixture of ammonium hydroxide and water	7-p <sup>b</sup>	1	0/20	0/20	0/20	0/20	3/4	2/4
		2	0/20	0/20	0/20	0/20	1/4	2/4
	5-pa <sup>c</sup>	1	0/20	0/20	0/20	0/20	0/4	0/4
		2	0/20	0/20	0/20	0/20	0/4	0/4
	5-py <sup>d</sup>	1	0/20	0/20	0/20	0/20	1/4	2/4
		2	2/20	3/20	3/20	5/20	4/4	3/4
	7-pa <sup>b</sup>	1	0/20	1/20	0/20	0/20	2/4	1/4
		2	6/20	- <sup>e</sup>	2/20	5/20	1/4	3/4
Ammonium hydroxide to a mixture of ECH and water	5-pa <sup>c</sup>	1	0/20	1/20	0/20	1/20	0/4	1/4
		2	0/20	0/20	0/20	1/20	0/4	0/4
	5-py <sup>d</sup>	1	0/20	4/20	0/20	0/20	2/4	2/4
		2	0/20	0/20	0/20	0/20	4/4	4/4

<sup>a</sup> CAs were prepared at 55 °C: <sup>b</sup> 7-p represents seven-ply panels: <sup>c</sup> 5-pa represents five-ply aspen panels: <sup>d</sup> 5-py represents five-ply yellow poplar panels: <sup>e</sup> “-” means no test was performed.



CA prepared at 55 °C was used for this study due to its relatively better performance over other reaction temperatures (Table 2.3). When the CAs were prepared by adding ECH to a mixture of ammonia hydroxide and water, the seven-ply panels and five-ply aspen panels had no specimens delaminated, whereas one of the five-ply yellow poplar panels passed the three-cycle soak test and another one did not for both untreated and heat-treated CAs (Table 2.4). In other words, CAs prepared by adding ECH to ammonia hydroxide were effective curing agents for making the seven-ply panels and five-ply aspen panels for interior application, but were not effective for making five-ply yellow poplar panels. Both seven-ply panels and five-ply yellow poplar panels failed and the five-ply aspen panels passed in the two-cycle boil test for both untreated and heat-treated CAs prepared by adding ECH to ammonia hydroxide (Table 2.4). The seven-ply panels did not pass the two-cycle boil test for CAs prepared by adding ECH to ammonia hydroxide at 55 °C (Table 2.4), whereas the seven-ply panels passed the two-cycle boil test for CAs prepared by mixing ECH and ammonia hydroxide all at once (Table 2.3). These results implied that CAs prepared by mixing ECH and ammonia hydroxide all at once were superior to those prepared by adding ECH to ammonia hydroxide dropwise.

For both untreated and heat-treated CAs that were prepared by adding ammonium hydroxide to a mixture of ECH and water, the seven-ply panels had one panel passed and another panel failed in the three-cycle soak test and all failed in the two-cycle boil test (Table 2.4). For untreated CAs that were prepared by adding ammonium hydroxide to a mixture of ECH and water, the five-ply aspen panels

passed in the three-cycle soak test and the two-cycle boil test. For heat-treated CAs that were prepared by adding ammonium hydroxide to a mixture of ECH and water, both five-ply aspen panels passed in the three-cycle soak test, but one failed and one passed in the two-cycle boil test (Table 2.4).

For untreated CAs that were prepared by adding ammonium hydroxide to a mixture of ECH and water, one of the five-ply yellow poplar panels passed and another failed in the three-cycle soak test, and both panels failed in the two-cycle boil test (Table 2.4). For heat-treated CAs that were prepared by adding ammonium hydroxide to a mixture of ECH and water, both five-ply yellow poplar panels passed in the three-cycle soak test, but both failed in the two-cycle boil test (Table 2.4). Overall, CAs prepared by mixing ECH and ammonia hydroxide all at once were superior to those prepared by adding ammonia hydroxide to ECH dropwise.

### 2.5.6 The stability of the CAs at room temperature

Table 2.5 The water resistance of plywood panels bonded with SF-CA adhesives

CAs <sup>a</sup>	Structure of plywood	Panel#	Specimens failed in three-cycle Soak test		Specimens failed in two-cycle boil test
			1 <sup>st</sup> cycle	3 <sup>rd</sup> cycle	
	7-p <sup>b</sup>	1	0/20	0/20	0/4
		2	0/20	0/20	1/4
	5-py <sup>c</sup>	1	0/20	0/20	4/4
		2	1/20	3/20	4/4

<sup>a</sup> The CAs were prepared at 50 °C by adding ECH and ammonium hydroxide to water all at once at the beginning of the reaction. The CAs were not heat-treated and were stored at room temperature for two months: <sup>b</sup> 7-p represents seven-ply panels: <sup>c</sup> 5-py represents five-ply yellow poplar panels.

The storage time of the CAs is an important consideration on their commercial applications. The viscosities of untreated and heat-treated CAs prepared at 50 °C were fairly stable over two months of storage (Figure 2.3). The stable viscosities of both untreated and heat-treated CAs indicated that insignificant crosslinking reactions occurred in the CAs during the storage. When the untreated CAs were used after two months of storage, both the seven-ply and five-ply yellow poplar panels passed in the three-cycle soak test, but failed in the two-cycle boil test (Table 2.5), which indicated that the untreated CAs were still effective for making interior plywood panels even after they were stored at room temperature for two months. The two-month storage time is sufficiently long for commercial applications of the CAs.

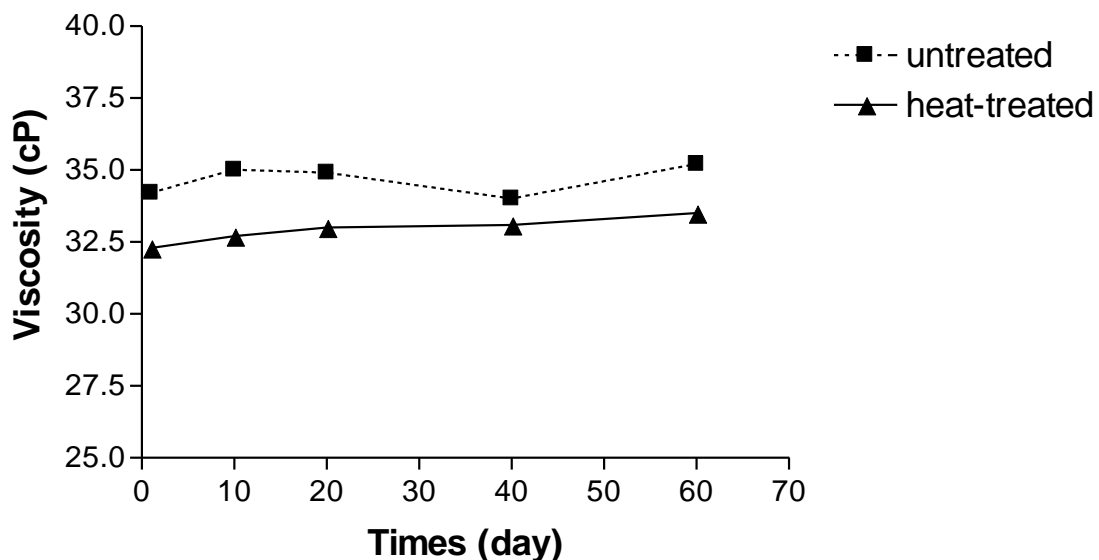


Figure 2.3 Viscosities of untreated and heat-treated CAs during storage (The CAs were prepared at 50 °C by adding ECH and ammonium hydroxide to water all at once at the beginning of the reaction).

## 2.6 Conclusions

The CAs could be prepared in a reasonably short time (less than four hours) when the reactions were carried out at 45-60 °C. Use of NaOH in the SF-CA adhesive improved the water resistance and dry shear strength of the resulting plywood panels. The CAs prepared by adding ECH and ammonium hydroxide all at once in water at the temperature ranging from 45 °C to 60 °C were all effective curing agents with SF for making all types of interior plywood panels. A further heat treatment of a CA before use with soy flour was not beneficial in terms of improving the water resistance of the resulting plywood panels with an exception for the CA prepared at 50 °C for five-ply aspen panels. The CAs prepared by adding ECH and ammonium hydroxide

all at once in water were superior to those prepared by either adding ECH to a mixture of ammonium hydroxide and water dropwise or adding ammonium hydroxide to a mixture of ECH and water dropwise. The CAs could be stored for at least two months without significant increase in their viscosities and negative effects on the water resistance of the resulting plywood panels.

### **2.7 Acknowledgements**

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### CHAPTER 3 GENERAL CONCLUSIONS

A new formaldehyde-free adhesive, consisting of soy flour (SF) and a new curing agent (CA), was developed and evaluated for making interior plywood. The CA was developed from the reaction of epichlorohydrin (ECH) and ammonium hydroxide in water. The weight ratio of SF/CA was 7/1 with a solids content of 36 wt% for the resulting adhesive. The reaction time, reaction temperature, and addition order of reactants in the preparation of the CA; the heat-treatment and storage time of the CA; and the NaOH usage in the SF-CA adhesive were investigated in terms of their effects on the water resistance of the resulting plywood panels. In this study, it was found that all the adhesives containing the CAs (prepared by adding ECH and ammonium hydroxide all at once in water at the temperature of 45 °C to 60 °C) enabled all types of plywood panels to meet the water-resistance requirements for interior applications. The heat-treatment of all CAs, except the CA prepared at 50 °C for five-ply aspen panels, had no effects on improving the water resistance. It was demonstrated that the storage time of the CAs within at least two months had no significant effects on the water resistance of the resulting plywood panels.



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