IOWA STATE UNIVERSITY
Digital Repository

1992

Influence of extractives on bonding properties of white oak

Ying-Shen Wang
Iowa State University

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Influence of extractives on bonding properties of white oak

Wang, Ying-Shen, Ph.D.

Iowa State University, 1992

Influence of extractives on bonding
properties of white oak

by

Ying-Shen Wang

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Forestry
Major: Forestry (Forest Biology-Wood Science)

Approved: Members of the Committee:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department   Signature was redacted for privacy.

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa
1992

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

CHAPTER 1. INTRODUCTION

Because of its hardness, high resistance to abrasion, easiness to be finished smoothly, and attractive figure, oak lumber is used extensively in furniture, interior paneling, and flooring. Oaks are a very important part of the United States hardwood resources. The oak species constitute about 40% and 20% of the total hardwood volume grown in the Appalachian region and on southern pine sites, respectively (U.S. Forest Service, 1982). According to a recent U.S. Forest Service inventory (Brand and Walkowiak, 1992), the oak species also dominate in Iowa, accounting for 37% of the growing-stock volume. These resources have not been utilized to their full potential because of their small size and low quality. Furthermore, industrial use of low quality oak species for composite products has been inhibited by a technical difficulty in forming durable adhesive bonds. As future demand for wood products rises, the need for developing reliable gluing processes for oak will become important.

The technical difficulty in forming durable oak adhesive bonds may be caused by two possible factors. The first one is the effect of high wood density on gluing. Infiltration of resin adhesives into cell walls has been considered essential for durable adhesive bonds (Nearn, 1974; Wellons, 1976). A high wood density may cause insufficient resin penetration into the cell wall and thus limit the bond strength. In addition, a high wood density requires a higher specific pressure to

bring the bonding surfaces into close contact to form good bond. The second factor is the effect of extractives on bonding. Hse and Kuo (1988) have pointed out that wood extractives may affect gluing in the following ways: (1) heavy deposits of extractives on the gluing surfaces block the reaction sites; (2) chemical incompatibility between the extractives and adhesives results in inferior glue bonds; (3) extractives influence the wettability and polarity of the wood surface so that the wettability-permeability relationship of a particular adhesive is changed; and (4) extractives affect the curing and setting characteristics of adhesives.

Craft (1970) found that white oak grown in the Appalachian region was very difficult to glue with phenolic resins as indicated by low wood failure values of plywood panels. Roffael and Rauch (1974) found that phenolic bonded particleboard made from old growth white oak was inferior to boards made from young oaks. Kuo et al. (1984) also found that white oak grown on southern pine sites were very difficult to glue with phenolic resins. They attributed the difficulty to migration of water-soluble extractives to veneer surfaces during veneer drying. All these studies indicate that gluing difficulty of white oak plywood is related to extractives.

The overall objective of this study was to improve the adhesive bond quality of white oak composite products. Specific objectives were:

    (1) To study the influence of extractives on adhesive bond properties, and

    (2) To formulate phenolic resin adhesives for improving adhesive bonds.

CHAPTER 2. LITERATURE REVIEW

White Oak Extractive Content and Distribution

The extractive content of white oak is quite variable, depending upon the age of trees and specific location in the stem, and sometimes also depending upon growing sites. According to results obtained at the U. S. Forest Products Laboratory, the average hot water, alcohol-benzene, and ether solubility of white oak wood were 4.0, 5.0, and 0.9%, respectively (Pettersen, 1984). The average alcohol-benzene solubles for white oaks grown on southern pine sites is 4.99% (Koch, 1985). Kuo et al. (1984) reported an average of 8.7% of hot water-solubles with a subsequent alcohol solubility of 0.8% for white oak heartwood grown on southern pine sites. Most of these reports on white oak wood extractive content made no reference to the age of trees being studied. Roffael and Rauch (1974) found that 20- to 30-year old white oak wood contained about 5% hot water solubles, while the corresponding value for old-growth trees was about 12%.

Wood extractives, although being the non-skeletal components of wood and sometimes representing only a few percent of the oven-dry weight of wood, consist of a complex mixture of compounds. For example, Seikel et al. (1971) reported that *Quercus rubra* L. (northern red oak) contained 6.2% and 8.2% of total extractives in sapwood and heartwood, respectively, which included sixteen phenolic compounds.

C.-L Chen (1970) found that the heartwood of white oak contained scopoletin, gallic and ellagicacids, gallotannins and ellagitannins, sitosterol, stigmasterol, campesterol, stigmastanol, lignoceryl ferulate and related esters, triglycerides of linoleic, oleic, and palmitic acids, and coniferaldehyde. Rowe and Conner (1979) reported that oak wood contained 2.7% tannins.

The extractive content of sapwood is generally much lower than that of heartwood. For most species, the gross distribution of extractives within trees generally follows a pattern that the amount of extractives decreases with increasing height in a tree and increases from the pith to the heartwood-sapwood boundary. The gross distribution of extractives in white oak trees, however, is not available in the literature.

Extractives in the sapwood are almost entirely located in the ray parenchyma cells (Hillis, 1968). In heartwood, extractives are found in ray and vertical parenchyma cells, tracheids of conifers, and fibers and vessels in hardwoods. In addition, extractives are present in large quantities in normal and traumatic resin canals of conifers and gum canals in hardwoods. In the heartwood region, extractives also may exist in the cell wall, and whether extractives are present in the cell wall or not depends upon the species. In some species, polymerization of water-soluble extractives proceeds very slowly so that these substances are able to spread to the entire woody tissue and into the cell wall (Bosshard, 1966, 1968). Because of the bulking effect, species with extractives in the cell wall are more dimensionally stable. For example, Kuo and Arganbright (1980) found that a large amount of heartwood extractives of redwood existed in the cell wall. Because of this characteristic, volume shrinkage of old-growth redwood from green to oven dry is 6.8%, the least among domestic softwoods (Wood Handbook, 1987). In white oak

wood, some extractives also are present in the cell wall, and therefore, these extractives are responsible for the dimensionable stability of the wood (Shim, 1954).

Distribution of extractives in wood products such as lumber and plywood veneer may be altered during processing. Anderson and Fearing (1961) found that the outer surface of kiln-dried redwood lumber had about five times the amount of water-soluble extractives as did the inner core, and that this outer layer accumulated over twice as much water-soluble extractives as compared with the corresponding region in the green lumber. Kuo et al. (1984) also found that mill drying of white oak veneers caused the surface to accumulate about twice as much water-soluble extractives as those in the interior portion due to extractive migration during drying. In addition, nonpolar extractives can also migrate to surface in the vapor form during drying at high temperatures. Swanson and Cordingly (1959) showed that vapor migration of resinous materials in wood pulps changes the fiber surface to a less polar and more of a hydrocarbon-like chemical nature. Hancock (1963) also found that the removal of extractives in Douglas-fir veneer prior to drying prevented vapor migration of nonpolar extractives. Migration of extractives to wood surfaces often causes deleterious effects on gluing.

Influence of Extractives on Bonding Properties of Wood

Extractives often change the surface characteristics of wood, affecting adhesion properties in many ways. Hse and Kuo (1988) summarized influences of extractives on wood gluing as follows: First of all, extractives may influence the wettability and polarity of the wood surface, changing the wettability-permeability of a particular adhesive. Heavy deposits of extractives on the gluing surface form a

physical barrier which often prevents the anchoring of adhesives. Finally, chemical incompatibility between extractives and adhesives affects the normal flow, curing, and setting characteristics of adhesives. In addition, these gluing interferences caused by extractives may act individually or in combinations.

Thomas (1959) studied the gluing characteristics of determa (*Ocotea rubra* Mez.), a tropical hardwood, and found that removal of the ether- and benzene-solubles caused a considerable increase in the gluebond quality obtained with a phenolic resin. The result indicated chemical incompatibility between the nonpolar extractives and the phenolic resin, resulting in the inability of the adhesive to wet the wood and to secure adequate penetration. C.-M Chen (1970) reported that wettability of many tropical woods could be improved by removing extractives from wood surfaces with various solvents. Hemingway (1969) also showed that the poor wettability of yellow birch wood was attributed to oxidation of linoleic acids and related esters on the wood surface. Hillis (1968) summarized the influence of nonpolar extractives on gluing by pointing out that water-repellent extractives affect the surface tension of wood surfaces and the application and penetration of adhesives, which subsequently affects bond strength.

Plomley et al. (1976) found that dipping of hoop pine (*Araucaria cunninghamii* Hook) veneer into solutions of commercial tannins, crude wood extracts, and model compounds significantly reduced the bond quality of a phenol-formaldehyde resin adhesive. They attributed the reduced bond quality mainly to the formation of a physical barrier by the added compounds which prevented a good contact of the adhesive to the wood surface, resulting in a reduced cohesive strength of the adhesive. Wellons et al. (1977) examined delaminated kapur (*Dryobalanops* spp.) and keruing (*Dipterocarpus* spp.) plywood and found that the gluelines failed to

adhere to the wood surface. They attributed the "unanchored" gluelines to both physical blockage of extractives coated on the wood surface and to premature gelation of the phenolic resin caused by the extractives on the wood surface. Kuo et al. (1984) also found that heavy deposition of extractives on the fiber walls on white oak veneer surfaces was the main reason causing the failure of gluelines to adhere to the cell wall.

In a detailed study of effects of kapur extractives on phenolic resin, Nguyen (1975) found that alcohol-, ether-, and water-soluble extractives added to a phenolic resin caused premature gelation of the resin and that the added extractives also caused a substantial increase in the water solubility of the cured resin. Wellons et al. (1977) confirmed such effects of kapur extractives on phenolic resins and concluded that premature gelation of resins altered the flow property of phenolic resins and hindered their penetration into wood and that the extractives caused an incomplete curing of the resins resulting in a weak glue bond.

Nguyen (1975) found that extractives in kapur made the wood sufficiently acidic to decrease glueline pH from 11 to 9.5 immediately after spreading of the adhesive, and this reduction in pH caused phenolic solids to precipitate and required a significant increase in press time to cure. Therefore, low acidity due to extractives may precipitate phenolic solids and cause the adhesive to be substantially less crosslinked and lower in strength. Albritton and Short (1979) found that water-soluble extractives of most southern hardwoods lengthened and the ethanol-soluble extractives shortened gel time of a urea-formaldehyde resin. Roffael and Rauch (1974) reported that old-growth white oak wood had a pH value of about 3.5 and the corresponding pH value for young-growth wood was 4.5. These authors attributed the difficulty of gluing old-growth white oak particles to its

high acidity due to the presence of extractives. Abe and Akimoto (1976) reported that a phenolic resin was changed from basic to neutral in the presence of acidic extractives, resulting in the formation of a large quantity of dimethylene ether linkages and thus requiring a prolonged curing time. Abe and Ono (1980) also demonstrated that the acidity of extractives reduced glueline pH and this reduction in pH required a significant increase in press time to properly cure the phenolic resins.

Methods of Minimizing the Influence of Extractives on Wood Adhesion

Influences of extractives on wood adhesion can be minimized or reduced by mechanical or chemical means. Hse and Kuo (1988) have pointed out that a light sanding immediately before gluing is a rapid and economical method for removing almost all types of surface contamination, but planing is even more effective. Jokerst and Stewart (1976) found that plywood made from abrasive- and knife-planed veneers were similiar in dry shear strength, but plywood made from abrasive-planed veneer had inferior durability. Dougal et al. (1980) showed that a light knife-planing of bonding surfaces removed surface contaminants and simultaneously exposed the highly polar secondary cell walls to which adhesives bonded most effectively. Caster et al. (1985) compared the surface quality of abrasive- and knife-planed wood surfaces and found that abrasive-planing of wood produced rougher surfaces and caused more cellular damages than the knife-planed surfaces. Although mechanical damages to the cell walls on the wood surfaces may increase percentage of wood failure, the rough surfaces obtained

during abrasive-sanding often produce discontinuous gluelines and thus reduce the durability.

A surface treatment with sodium hydroxide (NaOH) or neutral organic solvents to remove surface contaminants is also effective in improving glue bond quality. Hancock (1963) showed that the glue bond quality of Douglas-fir plywood could be improved by extracting the veneers with methanol-benzene before drying and gluing. C.-M Chen (1970) also found that surface treatments of veneers of eight tropical species with NaOH solution improved urea-formaldehyde and resorcinol-formaldehyde adhesive joint strength. He attributed the improvement in bond quality to the increased pH and wettability of treated surfaces as a result of extractives removal. Chen (1975) improved the glue bond quality of fire-retardant-treated plywood by treating the surfaces with an alcohol solution of NaOH and by pressing at a higher press temperature and longer press time. Wellons et al. (1977) and Dougal et al. (1980) also found that removal of water-, alcohol-, and 1% NaOH-solubles from kapur veneer greatly improved the bond quality with phenol-formaldehyde.

Roffael and Rauch (1974) attributed the difficulty in bonding white oak particles with phenol-formaldehyde resins to low pH caused by extractives. They found that extraction of white oak wood particles with hot water had only a marginal improvement on bonding quality and that an extraction with 1N sodium carbonate solution greatly improved the bond quality. In addition, they found that adding extra amounts of NaOH to the phenolic resin also was effective in improving the bond quality, especially the durability, of white oak particleboard. Kuo et al. (1984) also reported that glue bond quality of white oak plywood could be significantly improved by soaking the veneers in 1% NaOH aqueous solution for 5 minutes. They

attributed this improvement to the removal of extractives on veneer surfaces and to the increase in pH as a result of the treatment.

According to Anderson and Fearing (1960, 1961), solvent seasoning is a possible method of drying wood and simultaneously removing a large quantity of extractives. The cost of solvent seasoning, however, has been estimated to be at least three times more expensive than conventional drying methods, thus limiting its economical application to improve gluability of species rich in extractives.

Summary

White oak heartwood may contain more than 10% extractives. The heartwood of older trees contain a higher extractive content than that of younger trees. The major extractives in white oak wood are tannins, fatty acids, and sterols. Water-soluble extractives tend to migrate to wood surfaces during drying, and nonpolar extractives also can migrate to surfaces when the wood is dried at high temperatures.

Accumulation of extractives on white oak wood surfaces changes the physical and chemical characteristics of the wood surface and adversely affects adhesion properties. Extractives, especially the nonpolar components, may influence the wettability and polarity of the wood surface, changing the wettability-permeability relationship of a particular adhesive. Heavy deposits of extractives form a physical barrier which often prevents the anchoring of adhesives. Chemical incompatibility between extractives and adhesives affects the normal flow and curing and setting characteristics of adhesives. Effects of extractives on wood adhesion can be minimized or reduced by mechanical or chemical treatments. Light planing is an

effective method to remove surface contaminants, and surface treatments with NaOH solution or neutral solvents has also been proven to remove surface contaminants and improve glue bond quality.

CHAPTER 3. MATERIALS AND METHODS

Materials and Test Specimen Preparation

One white oak (*Quercus alba* L.) and one hard maple (*Acer saccharum* L.) butt logs without apparent defects such as spiral grain and biological deterioration were purchased from Buttermore Saw Mill near Ames, Iowa. The white oak log was 20 inches in diameter at the butt end with a growth ring count of 106, and the hard maple log was 15 inches in diameter at the butt end with a growth ring count of 102. These two logs were converted at the saw mill into 1-1/2 inches thick lumber and shipped to the laboratory. The white oak and hard maple lumber were air-dried in the laboratory to an average moisture content of 8%. After air-drying, white oak and hard maple lumber were machined into test specimens 1-1/8 inches in width, 1/2 inch in thickness, and 10 inches in length. To test the effect of grain orientation on glue bond quality, a total of 516 pieces of white oak heartwood test specimens were obtained in 3 different grain orientations, radial-grained, tangential-grained, and mix-grained. Radial- and tangential-grained specimens were prepared to test radial plane to radial plane and tangential plane to tangential plane bond strength, respectively. The mix-grained specimens were prepared so that the adhesive bonding occurred neither between radial nor tangential planes. A total of 168

pieces of hard maple test specimens were obtained, and prepared as mix-grained pieces.

Solvent Extraction of Test Specimens

A large glass extractor capable of extracting 9 pieces of test specimens at the same time was made for this study to remove certain fractions of white oak heartwood extractives. A schematic of this extractor is shown in Figure 1. Because the extractor was so large, it was necessary to use a hot plate to maintain the solvent extraction of test specimens at 50°C. Hexane, 95% ethanol, and water were used as extraction solvents. Test specimens were subjected to single-, double-, and triple-solvent extractions. Extraction was done for 2 days in each solvent at a temperature of 50°C. After each extraction, specimens were air-dried before the subsequent extraction or further processing. No effort was made to determine the amount of extractives removed in each solvent extraction procedure. Hard maple test specimens were not subjected to any solvent extraction.

Collection of White Oak Wood Extracts

Four types of white oak heartwood extracts were collected. They were hexane extract, ethanol extract with hexane extract removed, hot-water extract with hexane extract removed, and hot-water extract with hexane and ethanol extracts removed. Extraction was done by boiling oak saw dust in a 3-liter round-bottom flask in the solvent for 4 hours with a reflux condenser. At the end of extraction, saw dust was filtered off with the aid of vacuum suction. To collect hexane extract, the solvent
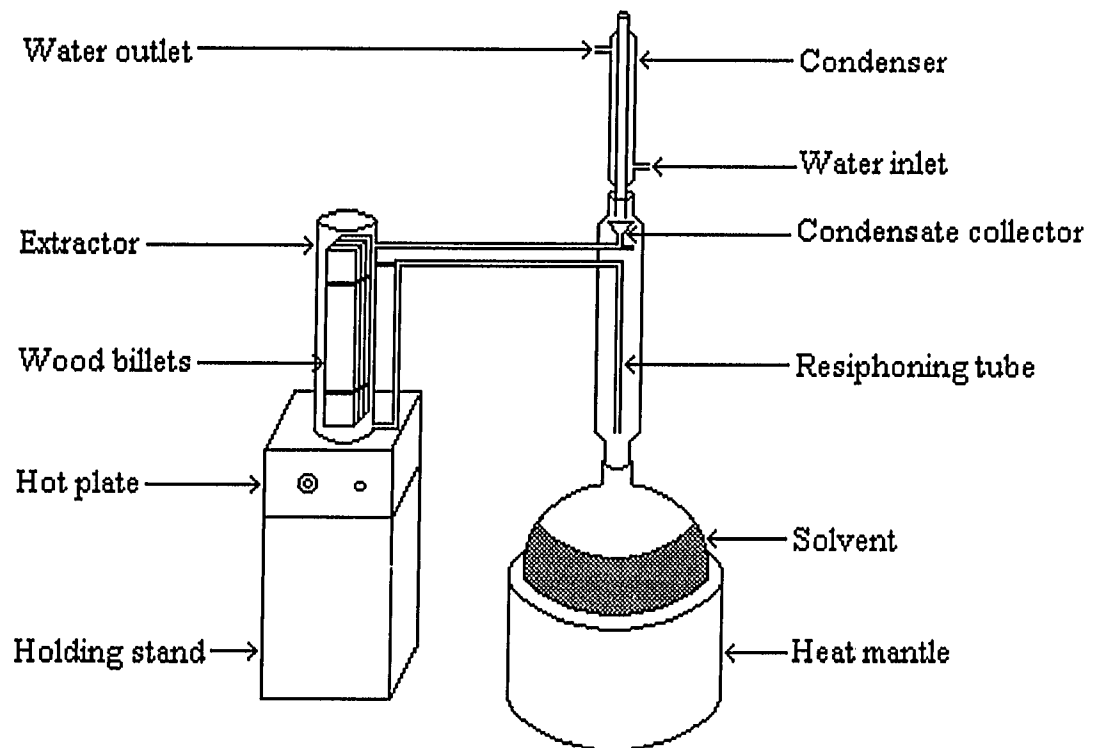
Figure 1. Schematics of the extraction apparatus

was removed by using a rotary vacuum evaporator operated at a temperature of 45°C. A yellowish and waxy hexane extract was obtained. The ethanol extract was collected by first removing the majority of the solvent with a rotary vacuum evaporator to obtain a brownish viscous material. The remaining solvent was evaporated off overnight in a vacuum oven at 45°C . To concentrate hot-water extract, the filtrate was poured into stainless steel pans and the solvent was evaporated off by placing these pans in an 80°C oven. The water extract so obtained was much darker than the ethanol extract. Because ethanol and water extracts were extremely hygroscopic, these dry extracts had to be stored over P_2O_5 in a desiccator.

Resin Adhesives

Three types of resole phenol-formaldehyde resin, were used in this study. The first type was a commercial resin (GP 92C22) manufactured by Georgia-Pacific Corporation, Atlanta, GA, having a solid content of 50 %, pH of 11, and viscosity of 300 centipoises (cps) at 25°C. The second phenolic resin was prepared in the laboratory, having a solid content of 50 %, pH of 11, and viscosity of 100 cps at 25°C. This phenolic resin was prepared using a NaOH/phenol molar ratio of 0.4 and a formaldehyde/phenol molar ratio of 1.8. In the synthesis of laboratory phenol-formaldehyde resin, 400 grams of industrial phenol were dissolved in 247 grams of water. After adding 613 grams of 37.5% formaldehyde and 72 grams of NaOH aqueous solutions, the mixture was heated to 70°C for 2 hours. During the reaction at 70°C, 3 16-gram portions of 50% NaOH solution were added at 30-minute intervals. At the end of reacting at 70°C, the mixture was quickly heated to 95°C,

and the viscosity of the mixture was closely monitored. When the mixture reached a viscosity of 100 cps at 25°C, 16 more grams of 50% NaOH solution was added and the mixture was quickly cooled to room temperature in 5 minutes. It typically took about 30 minutes of heating at 95°C to reach the desired viscosity of 100 cps. The third type of resin was prepared by mixing equal parts of the commercial resin and the laboratory made resin, resulting in a mixture with a pH of 11 and viscosity of 170 cps at 25°C.

Experimental Design

The experiment of studying the effect of solvent extraction on white oak specimens was designed with 3 experimental factors, solvent extraction treatment, grain orientation, and resin type. Factors considered were 8 levels of extraction treatment (control, hexane, ethanol, hot-water, hexane/ethanol, hexane/hot-water, ethanol/hot-water, and hexane/ethanol/hot-water), 3 types of grain orientation (radial, tangential and mixed grain), and 3 resin types (commercial phenol resin, lab-made resin, and the mixture of equal parts of commercial and lab resins). Therefore, the experiment had 72 treatment combinations, and each treatment combination was replicated 3 times.

Preparation of Shear Blocks and Evaluation of Adhesive Joints

All test shear blocks were prepared according to the standard method described in ASTM D905-49 (ASTM 1974) except that the dimension of shear blocks was reduced to that shown in Figure 2. The standard requires gluing two

pieces of wood samples of 2 inches in width, 3/4 inch in thickness, and in random length to obtain 2" (width) by 2" (length) by 1-1/2" (thickness) shear block test specimens. The modified shear block dimension was 1" (width) by 1-1/2" (length) by 5/8" (thickness), providing an effective joint of 1 square inch in each shear block. Reduction of shear block size was made to accommodate the evaluation of wet shear strength of the adhesive joints. Because white oak wood is impermeable, it was felt necessary to reduce the dimension of test shear blocks to ensure a thorough aging treatment of test shear blocks for the evaluation of durability of the adhesive joints.

The white oak wood specimens were conditioned to 6% moisture content and planed to a thickness of 5/16" just before the gluing operation. The resin adhesive was spread onto both surfaces of the paired wood specimens at a rate of 27 lbs. per thousand square feet. The glue-assemblies were hot pressed in the following conditions:

Assembly time:	10 minutes
Press time:	10 minutes
Specific pressure:	300 psi
Platen temperature:	350°F

After pressing, the glued assemblies were allowed to cool to room temperature and conditioned in an environmental chamber to 12% moisture content before cutting into test shear blocks as shown in Figure 2.

Adhesive joints were evaluated for both dry and wet shear strengths and percentages of wood failure. For the evaluation of dry shear strength and percentages of wood failure, test shear blocks were conditioned to 12% moisture content and tested in the ambient temperature. To evaluate glue bond durability,
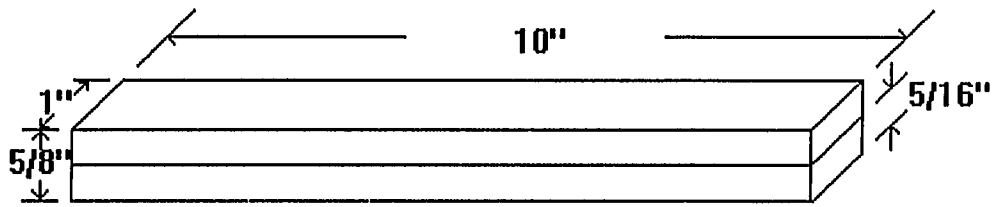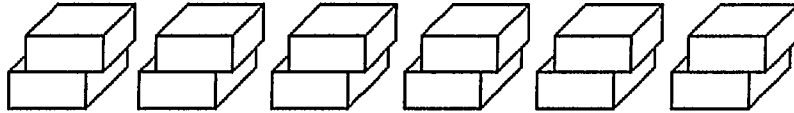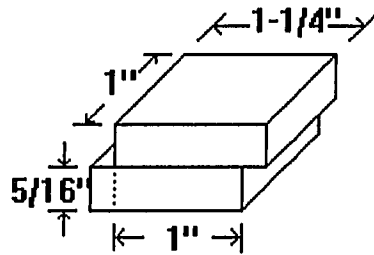
Figure 2. Assembly of wood specimens(a), preparation of shear blocks(b), and dimension of test shear block(c)

shear blocks were subjected to a 2-hour boiling in water, allowed to cool to room temperature, and tested wet. The shear strength was determined by compression loading as described in ASTM D-905-49 (ASTM 1974). To avoid sawing variation during shear block cutting, the critical dimension of the actual area of adhesive joint in each block was measured with a micrometer to obtain an accurate stress measurement. Percentage wood failure was visually evaluated with the aid of a transparent mesh grid. The percentage wood failure was determined after the test specimens were air-dried.

Effects of White Oak Extractives on Curing of Phenolic Resins

The inhibitory effect of white oak extractives on the curing of phenol-formaldehyde resins was measured by comparing the water solubility of the resins cured with and without white oak extractives. White oak heartwood hexane, ethanol, and water extracts, and the water extract without ethanol solubles in the amount of 0, 0.2, 2, and 10%, based on resin solids, were added to the commercial phenol-formaldehyde resin and cured at 100°C and 150°C. The cured resins were crushed and ground with a Wiley mill to a uniform particle size that passed through a 40 mesh screen and was retained on a 60 mesh screen. The resin particles were then extracted with water in a Soxhlet extractor to measure the water solubility of the cured resins.

Effects of White Oak Extractives on Bonding Hard Maple

Hard maple, a diffuse porous species containing very few extractives, is used in the ASTM method as a standard substrate for evaluating gluebond quality of different adhesives. In this experiment, hard maple test specimens were coated with various amounts of white oak heartwood extracts to verify the deleterious effect of extractives on bonding with phenolic resins. Types of extracts and amounts of these extracts applied on wood surfaces are listed as follows:

Extracts	Grams per 10 grams of PF solid
Hexane	0.1 and 0.5 grams
95% ethanol	0.1 and 0.5 grams
Hot-water	0.1 and 0.5 grams
Hot-water(ethanol extract removed)	0.1 and 0.5 grams

The extract was dissolved in respective solvent and applied to specimen surfaces with a brush. After conditioning to 6% moisture content, these hard maple test specimens containing white oak extractives were bonded with the commercial phenolic resins, and the adhesive bond quality was evaluated as previously indicated.

CHAPTER 4. RESULTS AND DISCUSSION

Extractive Content of White Oak Heartwood

Table 1 shows the extractive content of white oak heartwood. The average amount of hexane-solubles was 0.36%, and this fraction of extractives consisted of mostly fatty materials, waxes, oils, and resin acids (Sjöström, 1981). The 95% ethanol extractives of white oak heartwood was found to be 11.56%. Most of the materials that are soluble in hexane, except waxes, also are soluble in ethanol. But ethanol also can dissolve simple phenols, polymerized phenols such as tannins and phlobaphenes, and low molecular weight saccharides (Sjöström, 1981). Because there were only 0.36% hexane-solubles in white oak heartwood, most of the 11.56% of ethanol-solubles must be phenolics and saccharides. There was no increase in the 95% ethanol solubility proceeded by a hexane extraction.

The average hot water solubility of white oak heartwood was 13.69%. Materials that are soluble in water are simple phenols, tannins (but not phlobaphenes), and low molecular weight and polymeric carbohydrates such as arabinogalactans (Sjöström, 1981). Therefore, there was a large overlap between the ethanol and hot water solubility of white oak heartwood. The main difference is most likely that the hot water extract contains more polymeric carbohydrates than the ethanol extract.

Table 1. Average extractive content of white oak heartwood

Solvent	Extractive content (%)
Hexane	0.36
Ethanol	11.56
Water	13.69
Hexane/Ethanol	11.71
Ethanol/Water	14.67
Hexane/Ethanol/Water	15.03

The white oak tree contained a total of 15.03% heartwood extractives. This value is much higher than values reported by others (Pettersen, 1984; Kuo et al., 1984; and Koch, 1985). The water and 95% ethanol solubility of the heartwood of this tree is about 4% to 8% higher than those values reported elsewhere. A major reason for this difference is that a 24-hour extraction time was used in this study. Other factors such as the age of the tree and site differences also may influence the extractive content determination.

Influence of Extractives on Curing of Phenolic Resins

In the study of effects of extractives on resin curing, extractives were added to the resin in the form of solutions by dissolving in various solvents. Therefore the effect of solvent on resin curing was first studied. Table 2 shows the effect of diluting the phenol resin with water, 95% ethanol, and hexane. When the phenol resin was cured at 100°C, dilution of the resin with 40%, either ethanol or water, based on resin solids, had an effect on it's curing, whereas dilution of the resin with hexane did not affect the curing. Although water and ethanol only caused a slight increase in the solubility of cured resin, there was a significant inhibitory effect of these 2 solvents on curing the resin at 100°C. When the resin was cured at 150°C, however, dilution of the resin with solvents did not affect curing. In addition, the phenol resin was more efficiently cured at 150°C than at 100°C as indicated by a much lower water solubility of the 150°C-cured resin.

Table 3 also shows effects on curing of various amounts of different fractions of white oak heartwood extractives mixed in the resin. When the resin was cured at 100°C, the water solubility of cured resin increased with increasing amount

Table 2. Effect of solvents on curing of phenol-formaldehyde resin

Solvent(40%)[c]	Solubility(%)[a] of PF-resin[b] cured for 24 hrs.			
	None	Hexane	Ethanol	Water
Cured at 100°C	21.38(0.19)[d]	21.23(0.04)	24.17(0.52)	22.86(0.45)
Duncan grouping	C	C	A	B
Cured at 150°C	16.35(0.84)	17.25(0.45)	17.00(0.11)	17.06(0.22)
Duncan grouping	A	A	A	A

[a]Solubility of cured resin determined by a 2-hour water extraction.

[b]A commercial phenol-formaldehyde resin; 50% solid content, pH11, Viscosity 295 cps at 25°C.

[c]Percentage based on resin solids.

[d]Numbers in parentheses are standard deviations.

Table 3. Inhibitory effect of white oak heartwood extractives on curing of phenol-formaldehyde resin

Solubility(%)[a] of PF-resin[b] cured at 100°C for 24 hrs.				
Heartwood extractive	None	Hexane	Ethanol	Water	Wtr(w/o EtOH)
10%[c]	21.38(0.19)[d]	24.05(0.16)	24.21(0.04)	24.61(0.31)	24.40(0.26)
Duncan grouping	C[e]	B(A)[f]	AB(A)	A(A)	AB(A)
2%	21.38(0.19)	22.75(0.28)	21.75(0.75)	23.10(0.42)	21.92(0.06)
Duncan grouping	B	A(B)	B(B)	A(B)	B(B)
0.2%	21.38(0.19)	21.77(0.06)	21.58(0.19)	22.43(0.47)	21.92(0.45)
Duncan grouping	B	B(C)	B(B)	A(C)	AB(B)

Solubility(%) of PF-resin cured at 150°C for 24 hrs.				
Heartwood extractive	None	Hexane	Ethanol	Water	Wtr(w/o EtOH)
10%	16.35(0.84)	17.68(0.12)	21.07(0.10)	21.28(0.06)	21.54(0.30)
Duncan grouping	C	B(A)	A(A)	A(A)	A(A)
2%	16.35(0.84)	16.88(0.36)	19.67(0.14)	20.79(0.27)	21.32(0.19)
Duncan grouping	C	C(B)	B(B)	A(A)	A(A)
0.2%	16.35(0.84)	16.70(0.03)	19.43(0.09)	20.75(0.38)	21.15(0.29)
Duncan grouping	C	C(B)	B(B)	A(A)	A(A)

[a]Solubility of cured resin determined by a 2-hour water extraction.

[b]A commercial phenol-formaldehyde resin; 50% solid content, pH11, Viscosity 295 cps at 25°C.

[c]Extractive concentration (based on resin solids) added as solutions in various solvents.

[d]Numbers in parentheses are standard deviations.

[e]Letters represent Duncan's grouping at 0.05 level.

[f]Letters in parentheses are from Duncan group for effect of extractive concentration.

of extractives. The effect of the concentration of extractives on resin curing, however, was generally diminished when the resin was cured at 150°C. This result can be explained by the fact that phenolic resins are more efficiently cured at higher temperatures. When the effect of different fractions of white oak heartwood extractives on the curing of resin was examined, it was found that all extractives had some degree of inhibitory effect on resin curing. In general, ethanol and water extracts and water extracts without ethanol-solubles had about the same level of effect, but the hexane extract had the least but a significant effect at high concentrations. Because of relatively low concentrations of extractives added to the phenol resin, this experiment was not able to identify which fraction of white oak heartwood extractives had the most inhibitory effect on resin curing.

Effect of Solvent Extraction on White Oak Bond Quality

Table 4 summarizes the effects of solvent extraction on bond quality of mix-grained white oak specimens when a commercial phenol-formaldehyde resin is used. These results also are shown in Figures 3, and 4.

Results showed that, in general, various solvent extraction treatments of the test specimens gave no significant improvement in either dry or wet shear strengths. In fact, there is a tendency for solvent extraction of test specimens to decrease both dry and wet bond strengths. For example, water and hexane/ethanol/water extracted specimens showed significant deleterious effects on dry and wet bond shear strengths. Decrease in gluebond strength is unlikely due to the removal of extractives. Rather, decrease in gluebond strength is probably due to physical changes of test specimens such as warping as a result of solvent extraction. This

Table 4 Effect of solvent extraction of white oak mix-grained specimens on bonding quality using a commercial phenol-formaldehyde resin

Treatment[a]	C	H	E	W	HE	HW	EW	HEW
Dry shear strength	2910	2630	2746	2499	2826	2763	2731	2517
(psi)	(261)[b]	(355)	(341)	(210)	(179)	(312)	(169)	(251)
Duncan grouping	A[c]	AB	AB	B	A	AB	AB	B
Wet shear strength	1304	1247	1297	1239	1303	1182	1242	1142
(psi)	(176)	(123)	(95)	(166)	(94)	(153)	(122)	(214)
Duncan grouping	A	AB	AB	AB	A	AB	AB	B
Dry wood failure	61	69	72	77	73	78	73	58
(%)	(25)	(31)	(22)	(25)	(18)	(17)	(19)	(22)
Duncan grouping	A	A	A	A	A	A	A	A
Wet wood failure	31	40	47	60	49	50	50	38
(%)	(12)	(30)	(30)	(21)	(25)	(15)	(30)	(13)
Duncan grouping	B	AB	AB	A	AB	AB	AB	AB

[a]Treatment: C=Control; H=Hexane; E=Ethanol; W=Water; H/E=Hexane/Ethanol; H/W=Hexane/Water; E/W=Ethanol/Water; H/E/W=Hexane/Ethanol/Water.

[b]Numbers in parentheses are standard deviations.

[c]Letters represent Duncan's grouping at 0.05 level.
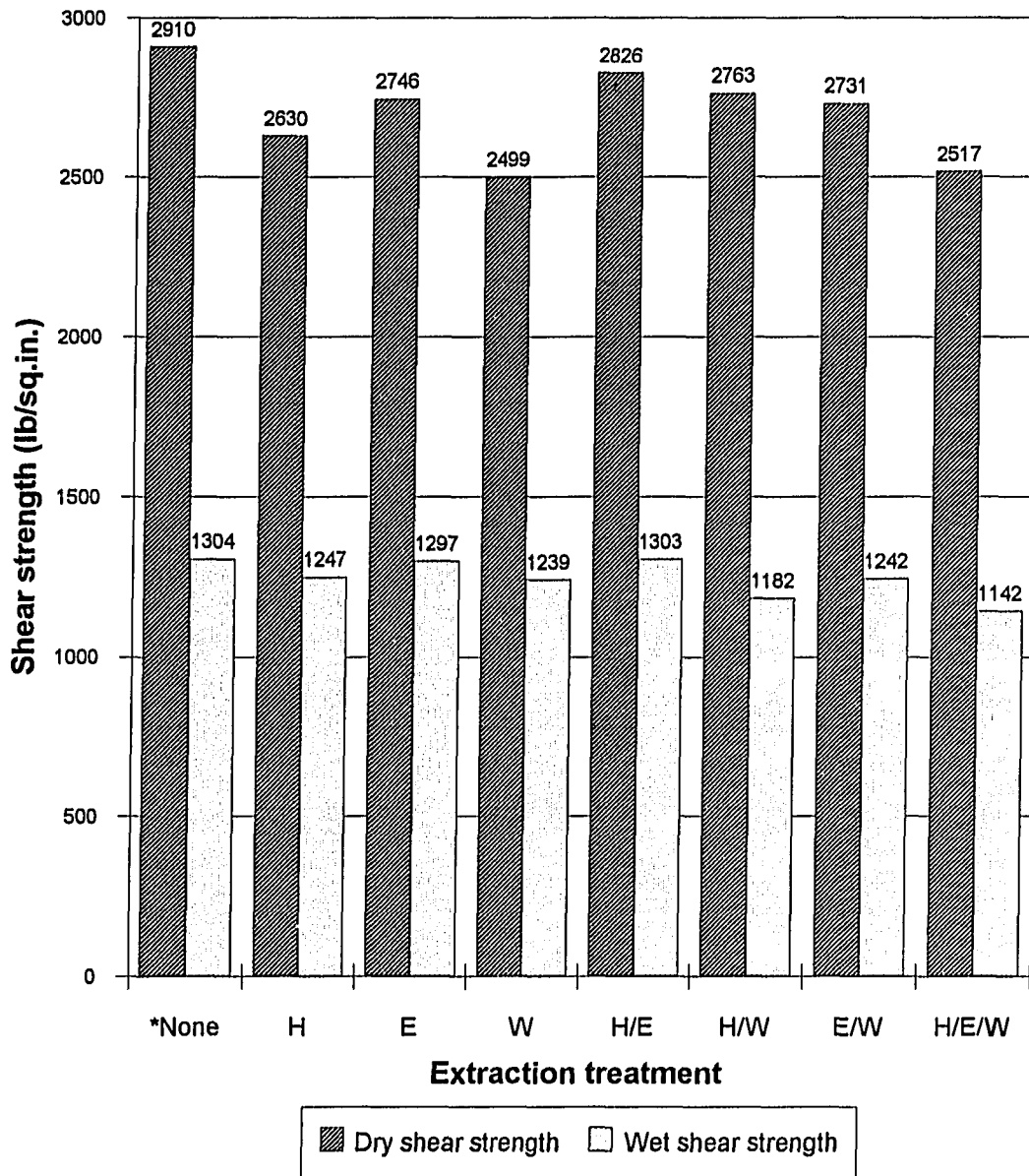
*None=Not extracted; H=Hexane; E=Ethanol; W=Water; H/E=Hexane/Ethanol;
H/W=Hexane/Water; E/W=Ethanol/Water; H/E/W=Hexane/Ethanol/Water

Figure 3. Effect of solvent extraction on shear strength of CPF-bonded, mix-grained white oak specimens

Figure 4. Effect of solvent extraction on wood failure of CPF-bonded, mix-grained white oak specimens

*None=Not extracted; H=Hexane; E=Ethanol; W=Water; H/E=Hexane/Ethanol; H/W=Hexane/Water; E/W=Ethanol/Water; H/E/W=Hexane/Ethanol/Water

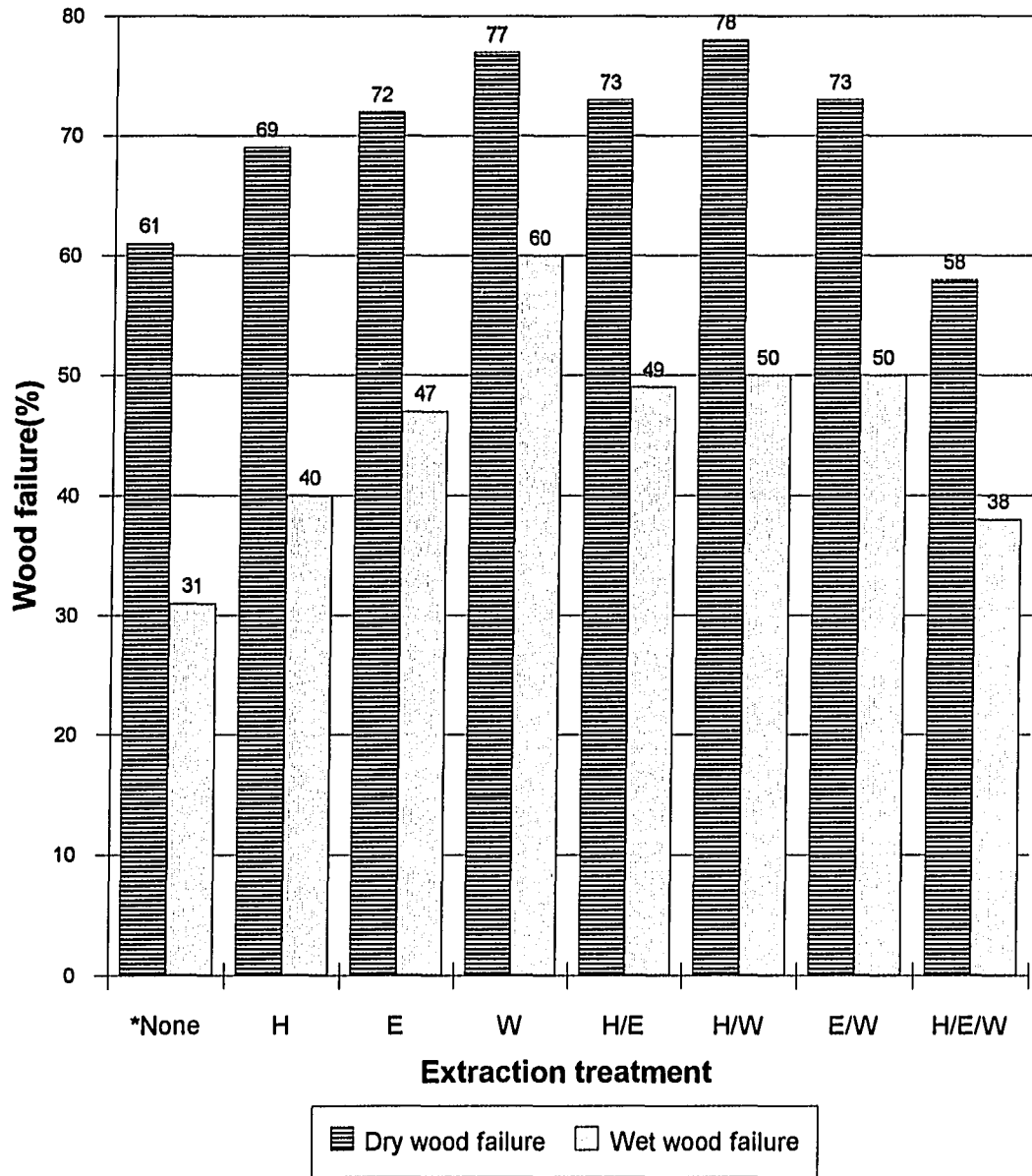rationale is supported by the fact that a specific pressure of 300 psi was not enough to bring some of the glue assemblies to a close during hot pressing.

Solvent extraction treatments of the test specimens, however, showed some improvement for both dry and wet wood failure. For example a hexane/water extraction of test specimens improved dry wood failure as much as 28% compared to the non-extracted specimens. Another example is that a hexane/water extraction of test specimens improved wet wood failure as much as 61%. These improvements, however, were not statistically significant because there was substantial variation of wood failure during tests. One possible source of this variation may come from warpage of test specimens during the drying process of the extracted specimens. Warping of the test specimens in turn causes a non-uniform contact between the two bonding wood surfaces.

In general, this experiment was not successful in measuring whether extraction of test specimens with various solvents improves the gluebond quality of white oak. These results, however, do not necessary imply that there is no deleterious effect of extractives on bonding. Kuo et al. (1984) showed that extractives migrating to veneer surfaces and that this was one of the factors causing white oak plywood to have a very low wood failure value. When the extractives which accumulated on the veneer surfaces were removed with a NaOH solution treatment, the wet wood failure was improved from below 20% to 35%. In the present study, the test specimens were prepared after the 2-inch thick lumber had been air-dried and, therefore, there was no extractive migration to the bond surfaces. In addition, planing of test specimens just before gluing exposed fresh cell wall materials which undoubtedly would enhance bonding. The combined effect of lack of extractive migration and planing of bond surfaces is reflected in a substantially higher average

dry and wet wood failure, 61% and 31%, respectively, as compared to below 20% for white oak plywood.

Effect of Applying White Oak Extracts on Wood Surfaces to Bonding Quality

Because the experiment of solvent extraction of white oak specimens failed to show the effect of extractives on bonding quality due to lack of extractive migration and to the manner the specimens were prepared, a different experimental approach was tried. In this experiment, the effect of white oak heartwood extractives was studied by applying different amounts of white oak extractives onto hard maple wood surfaces before gluing. Hard maple, a diffuse porous species containing very few extractives, is used in the ASTM method as a standard substrate for evaluating gluebond quality of different adhesives.

Table 5 shows results of the influence of applying 2% and 10% white oak extracts, based on resin solids, on the adhesive bond quality of hard maple. These results also are illustrated in Figures 5 and 6. Results clearly show the deleterious effect of all white oak heartwood extracts on hard maple adhesive bond quality, especially the aged gluebonds. Application onto hard maple surfaces of 2% ethanol and water extracts and the water extract with the ethanol fraction removed did not affect dry gluebond shear strength and dry wood failure. But an application of 10% of these extracts significantly reduced both dry shear strength and dry wood failure. The hexane extract reduced all dry and wet gluebond properties at both levels of extractive application.

Application of 2% of all white oak heartwood extracts, with the exception of the ethanol extract, significantly reduced wet gluebond shear strength and wet wood

Table 5. Effect of white oak extractives on adhesive bond quality of hard maple[a]

Treatment	Control	Hexane		Ethanol		Water		Water(w/o EtOH)	
Concentration[b]	0%	2%	10%	2%	10%	2%	10%	2%	10%
Dry shear strength	3514 A[c]	3065 E	2751 F	3446 AB	3351 BC	3431 ABC	3289 CD	3380 ABC	3211 D
Wet shear strength	1261 A	1112 B	820 D	1225 A	1009 C	978 C	346 E	796 D	0 F
Dry wood failure	93 A	72 BCD	46 E	92 A	86 ABC	89 AB	68 CD	83 ABCD	65 D
Wet wood failure	63 A	37 B	3 E	26 C	11 DE	15 CD	0 E	14 CD	0 E

[a]Hard maple specimens were bonded with a commercial PF resin.

[b]Concentration of extractives based on resin solids.

[c]Letters represent Duncan's grouping at 0.05 level.
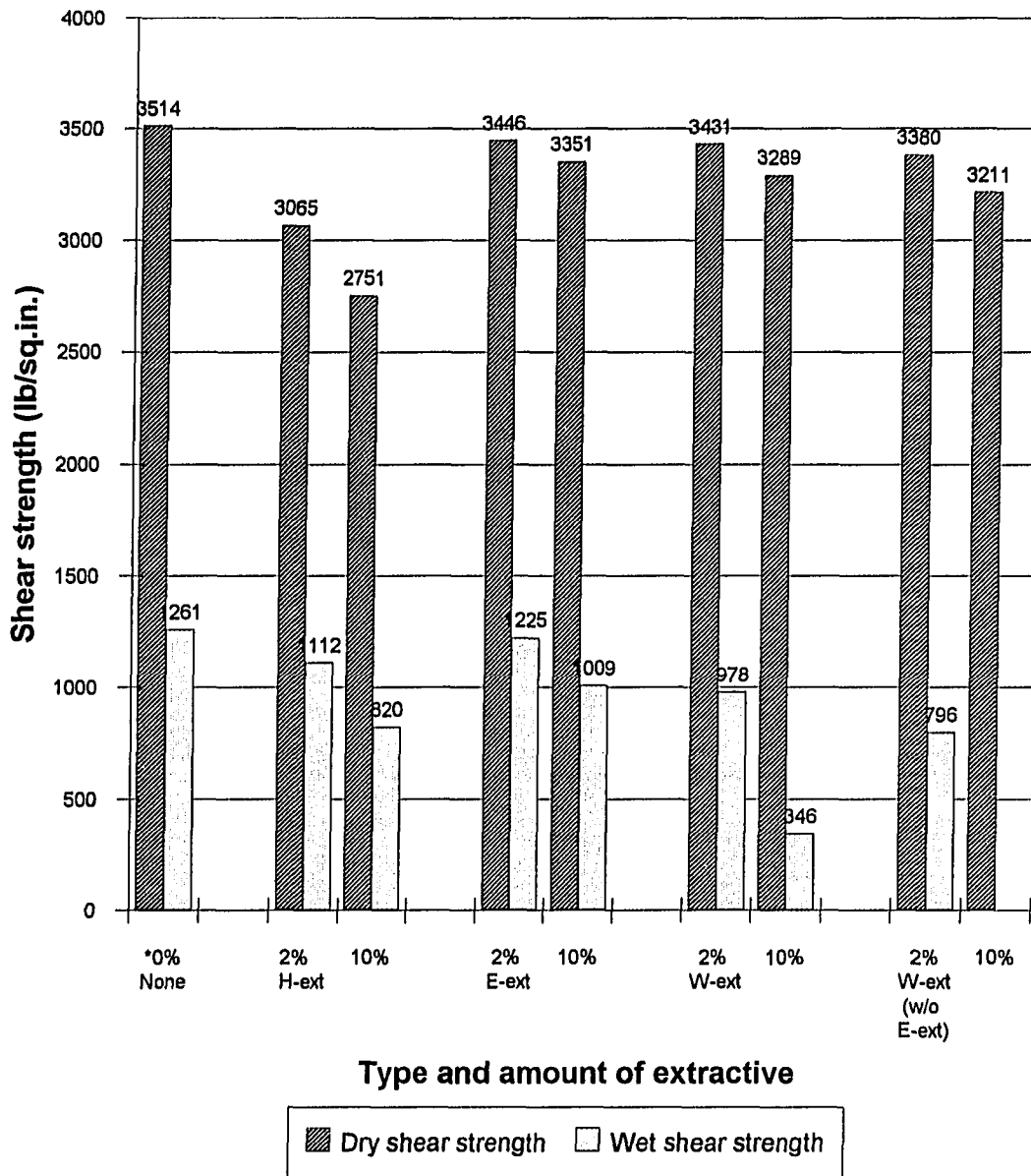
Shear strength (lb/sq.in.)

4000

3500

3000

2500

2000

1500

1000

500

0

3514

3065

2751

3446

3351

3431

3289

3380

3211

261

112

820

225

1009

978

346

796

*0%
None

2%
H-ext

10%

2%
E-ext

10%

2%
W-ext

10%

2%
W-ext
(w/o
E-ext)

10%

Type and amount of extractive

Dry shear strength ☐ Wet shear strength

*% of various extractives was based on the resin solid of CPF-resin used for bonding;
None=Control; H-ext=Hexane extract; E-ext=Ethanol extract; W-ext=Water extract;
W-ext(w/o E-ext)=Water extract(Ethanol extract removed)

Figure 5. Effect of applying white oak heartwood extractives on shear strength of
CPF-bonded hard maple
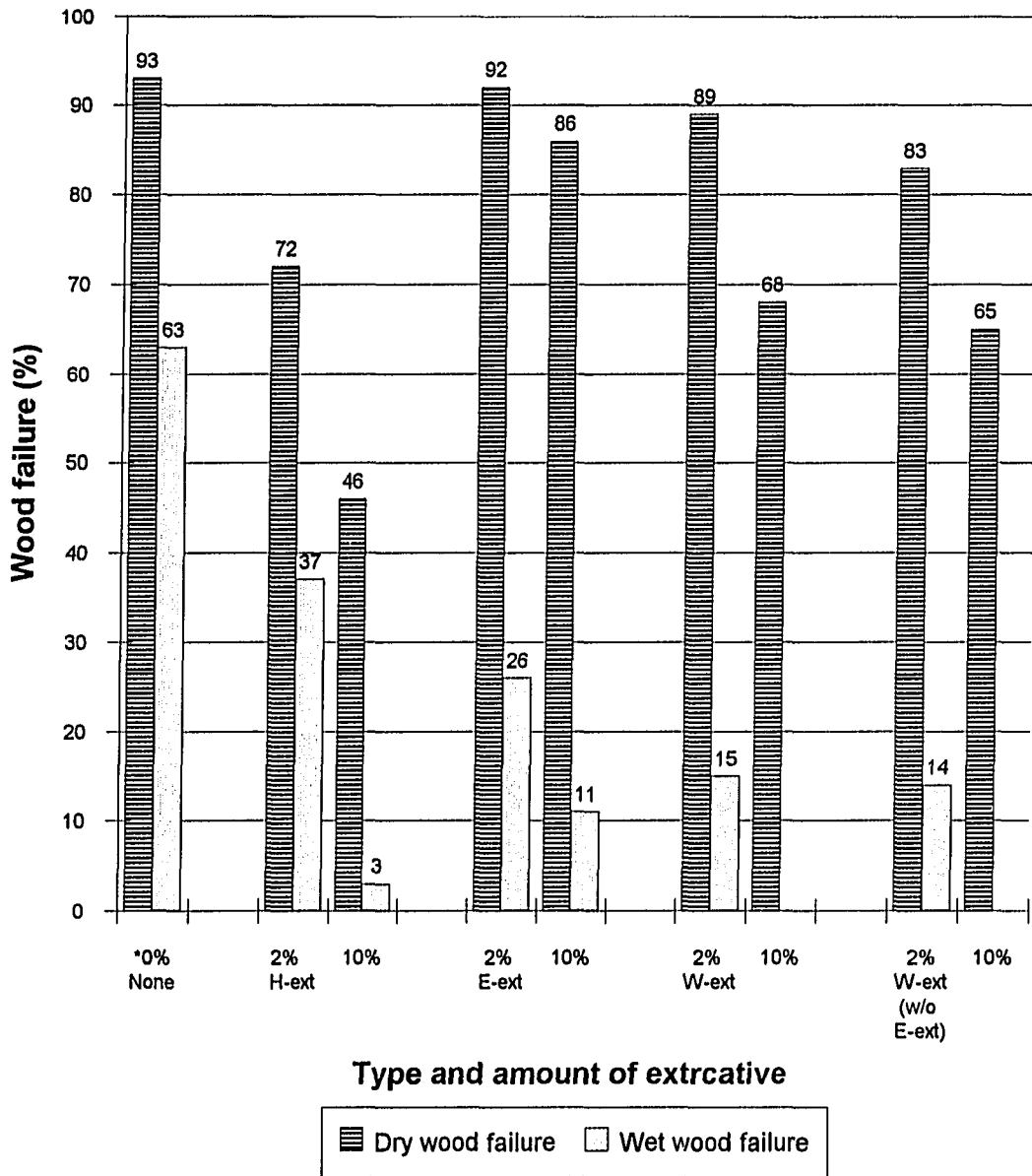
*% of various extractives was based on the resin solid of CPF-resin used for bonding;
None=Control; H-ext=Hexane extract; E-ext=Ethanol extract; W-ext=Water extract;
W-ext(w/o E-ext)=Water extract(Ethanol extract removed)

Figure 6. Effect of applying white oak heartwood extractives on wood failure of
CPF-bonded hard maple

failure. Application of 10% of these extracts reduced the aged gluebond quality even further. These results suggest that the presence of white oak heartwood extractives interfered with the proper curing of the resin. When the specimens were tested in the dry condition, the adhesive bond quality was reduced only to a limited extent. The aged adhesive bonds, however, were drastically weakened due to dissolution of uncured phenolic resin.

Of all the white oak heartwood extracts, water extract with the ethanol fraction removed showed the most deleterious effect on gluebond quality, followed by the water extract, the ethanol extract, and finally the hexane extract. The earlier study of white oak extractives indicated that there is a large overlap in the ethanol and water solubility of white oak heartwood and that the main difference between the ethanol and water extracts is that the latter contains polymeric carbohydrates such as arabinogalactans. In a study that attempted to incorporate simple sugars and oligosaccharides into phenolic resins, Conner et al. (1986) found that reducing sugars and oligosaccharides with reducing ends were rapidly transformed under a basic condition to acidic components, especially saccharinic acids. These acidic reaction products in turn neutralized the base catalyst in the phenolic resin, causing a detrimental effect on the curing of the resin. Therefore, it is possible that water-soluble polymeric carbohydrates and other reducing sugars in white oak heartwood interfere with the curing of phenolic resins.

The deleterious effect of white oak hexane extract on adhesive bond quality is most likely due to the reduction of wettability of hard maple surfaces with the PF-resin. As shown previously, white oak heartwood contains only 0.36% of hexane solubles, and therefore such a smaller amount of hexane-solubles is probably not enough to cause any significant effect on bonding of white oak.

Effects of Grain Orientation on Adhesive Bond Quality

Effects of grain orientation on the adhesive bonding quality of white oak using a commercial phenol-formaldehyde resin are summarized in Table 6. Results indicate that radial-grained specimens had lower dry shear strength values than those of the mix- and tangential-grained specimens. Okkonen and River (1989) also showed lower dry gluebond shear strengths in bonded radial-grained white oak specimens compared to those of tangential-graineded specimens. A weaker dry gluebond shear strength in the radial plane can be attributed to an inherently lower shear strength between the ray tissue and vertical elements of the wood. This explanation is in agreement with the result of dry wood failure evaluations, in which radial-grained specimens consistently had higher dry wood failure values than those of either the mix- or tangential-grained specimens. Differences in dry gluebond shear strength between radial-grained specimens and mix- and tangential-grained specimens gradually diminished as the specimens were subjected to more solvent extraction. This, again, is attributed to warping of specimens during drying after each solvent extraction. Warp in turn caused an incomplete closure of glue assemblies during hot pressing. Very little difference in dry gluebond shear strength between the mix-grained and tangential-grained specimens was observed.

After boiling the specimens in water for 2 hours, the adhesive bonds were considerably weakened, and no difference in wet gluebond shear strength among radial-, mix-, and tangential-grained specimens was observed. Because the aging process weakens both the gluebond and the wood, the effect of grain orientation on the wet gluebond shear strength was not as pronounced as that in the

Table 6. Effect of grain orientation on bonding quality of white oak using a commercial phenol-formaldehyde resin

Bonding properties	Dry shear strength (psi)			Wet shear strength (psi)			Dry wood failure (%)			Wet wood failure (%)		
Grain orientation[a]	Mix	Tan	Rad	Mix	Tan	Rad	Mix	Tan	Rad	Mix	Tan	Rad
Not extracted	2910	2810	2411	1304	1290	1238	61	58	80	31	26	54
	(261)[b]	(371)	(197)	(176)	(116)	(95)	(25)	(11)	(21)	(12)	(13)	(22)
Duncan grouping	A[c]	A	B	A	A	A	AB	B	A	B	B	A
Hexane extracted	2630	2749	2408	1247	1354	1259	69	59	75	40	30	53
	(355)	(173)	(241)	(123)	(152)	(139)	(31)	(21)	(25)	(30)	(12)	(26)
Duncan grouping	AB	A	B	A	A	A	A	A	A	A	A	A
Ethanol extracted	2746	2626	2576	1297	1220	1229	72	49	87	47	26	62
	(341)	(146)	(56)	(95)	(111)	(159)	(22)	(15)	(12)	(30)	(7)	(16)
Duncan grouping	A	B	B	A	A	A	A	B	A	A	B	A
Water extracted	2499	2643	2543	1239	1121	1099	77	44	64	60	21	40
	(210)	(256)	(330)	(166)	(161)	(90)	(25)	(15)	(25)	((21)	(3)	(21)
Duncan grouping	A	A	A	A	A	A	A	B	AB	A	C	B
Hexane/Ethanol extracted	2826	2694	2374	1303	1333	1220	73	53	71	49	27	44
	(179)	(174)	(194)	(94)	(152)	(71)	(18)	(12)	(18)	(25)	(9)	(18)
Duncan grouping	A	A	B	AB	A	B	A	B	A	A	B	AB
Hexane/Water extracted	2763	2353	2256	1182	1189	1136	78	43	62	50	21	42
	(312)	(332)	(186)	(153)	(65)	(122)	(17)	(14)	(13)	(15)	(11)	(12)
Duncan grouping	A	B	B	A	A	A	A	C	B	A	B	A
Ethanol/Water extracted	2731	2546	2309	1242	1170	1203	73	51	59	50	19	38
	(169)	(273)	(309)	(122)	(169)	(181)	(19)	(18)	(25)	(30)	(8)	(26)
Duncan grouping	A	AB	B	A	A	A	A	B	AB	A	B	AB
Hexane/Ethanol/Water extracted	2517	2340	2467	1142	1103	1140	58	36	72	38	16	50
	(251)	(232)	(209)	(214)	(123)	(123)	(22)	(11)	(24)	(13)	(5)	(24)
Duncan grouping	A	A	A	A	A	A	A	B	A	A	B	A

[a]Grain orientation: Mix = Mix-grained; Tan = Tangential-grained; Rad = Radial-grained.

[b]Numbers in parentheses are standard deviations.

[c]Letters represent Duncan's grouping At 0.05 level.

dry gluebond shear strength. In other words, wet shear strength is probably a better parameter to evaluate adhesive bond strength because wet shear strength is not as much affected by grain orientation as dry shear strength.

In general, radially bonded specimens showed both higher dry and wet wood failure values than those of mix-grained specimens, and tangentially bonded specimens had the least dry and wet wood failure. These differences obviously are due to the orthotropic nature of wood. In the bonding of rotary peeled veneers into plywood, adhesive bonds are formed mostly in the tangential plane. In the preparation of finger or scarf joints, pieces of wood are glued on transverse surfaces. Adhesive bond quality on the transverse plane was not evaluated in this study.

Effects of Resin Type on Adhesive Bond Quality

Three types of phenol-formaldehyde resin were used in this experiment: they were a commercial phenol-formaldehyde resin (CPF); a laboratory-prepared phenol-formaldehyde resin (LPF); a resin prepared by mixing equal parts of the commercial and lab-made resins (MPF). The molecular weight distribution of these three resins is shown in Figure 7. Molecular distribution was determined by gel permeation chromatography using a Sephadex G 100-120 gel in a 1.2 meter and 1.0 cm diameter column. The rate of elution was adjusted to 20 ml per hour by using 0.1 N NaOH aqueous solution. As shown in Figure 7, the CPF contained a higher amount of high-molecular-weight fraction than the low-molecular-weight fraction. The LPF had a normal molecular weight distribution, but in general had a lower
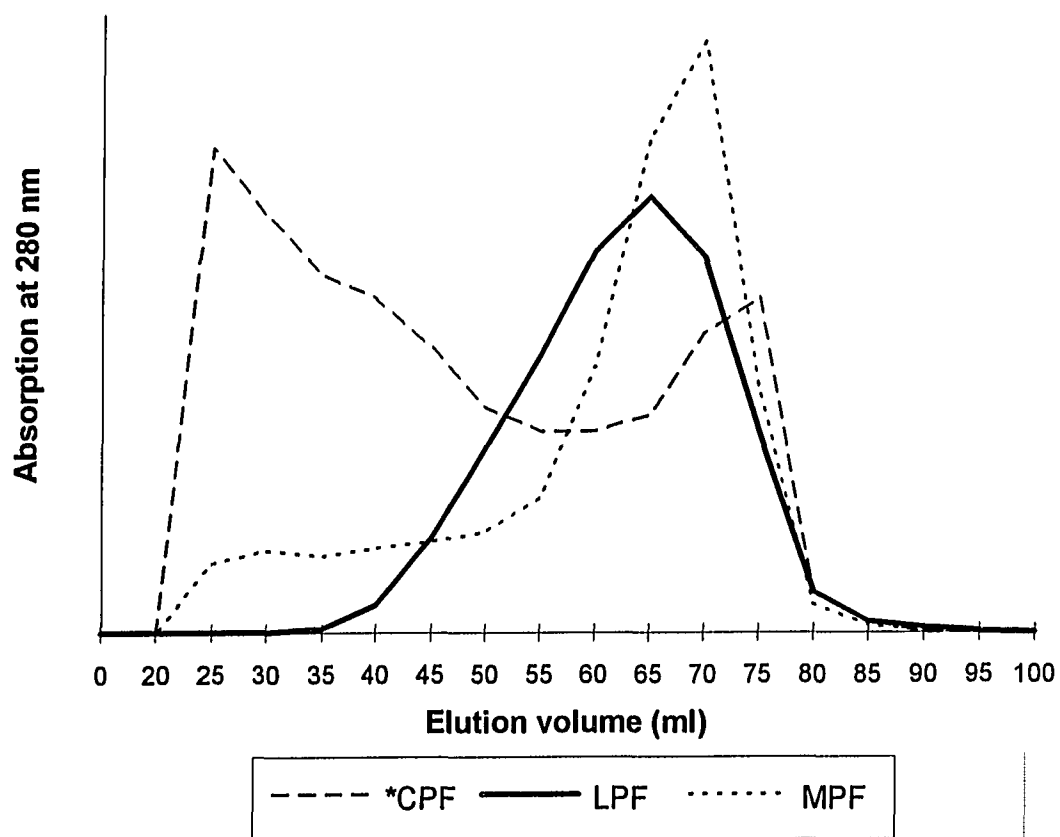
*CPF=Commercial phenol-fomaldehyde; LPF=Lab made phenol-fomaldehyde; MPF=Mixture of CPF and LPF by 1:1 ratio

Figure 7. Molecular weight distribution of three types of phenol-formaldehyde resin

average molecular weight than that of the commercial resin. As a result, the MPF had a strong peak toward the low molecular weight side, and the high-molecular-weight fraction was relatively reduced.

Table 7 shows effects of resin type and grain orientation on white oak adhesive bond quality. These results also are illustrated in Figures 8 and 9. In the radial-grained specimens, the low-viscosity LPF resin clearly gave the strongest and the CPF provided the lowest dry shear bond strength. Therefore, there is a strong correlation between resin viscosity and the dry shear bond strength in the radially bonded specimens. In the mix- and tangential- grained specimens, the LPF also provided significantly stronger dry gluebonds than those provided by MPF and CPF. But the difference between the MPF and CPF bond strengths in the mix- and tangential-grained specimens was not as pronounced as that in the radially bonded specimens. In the mix-grained specimens, MPF bonds were inferior to CPF bonds. Because wood is weakest in the radial direction, an improved resin penetration by the use of low viscosity resins can increase the strength properties in that direction, hence the gluebond shear strength.

The effect of resin type on dry gluebond shear strength is also reflected in dry wood failure, in that LPF-bonded specimens consistently showed higher dry wood failure values regardless of whether gluebonds were made on the radial plane, between radial and tangential plane, or on the tangential plane. Just as with dry gluebond strength, MPF-bonded specimens had the lowest percentage of wood failure. In examining the interaction of effects of resin type and grain orientation, it is found that percentage of wood failure is strongly correlated to grain orientation when the specimens were bonded with the LPF and MPF, i.e., radially bonded specimens had the highest and the tangentially bonded specimens the lowest

Table 7. Effects of grain orientation and PF-resin type on bonding quality of white oak specimens
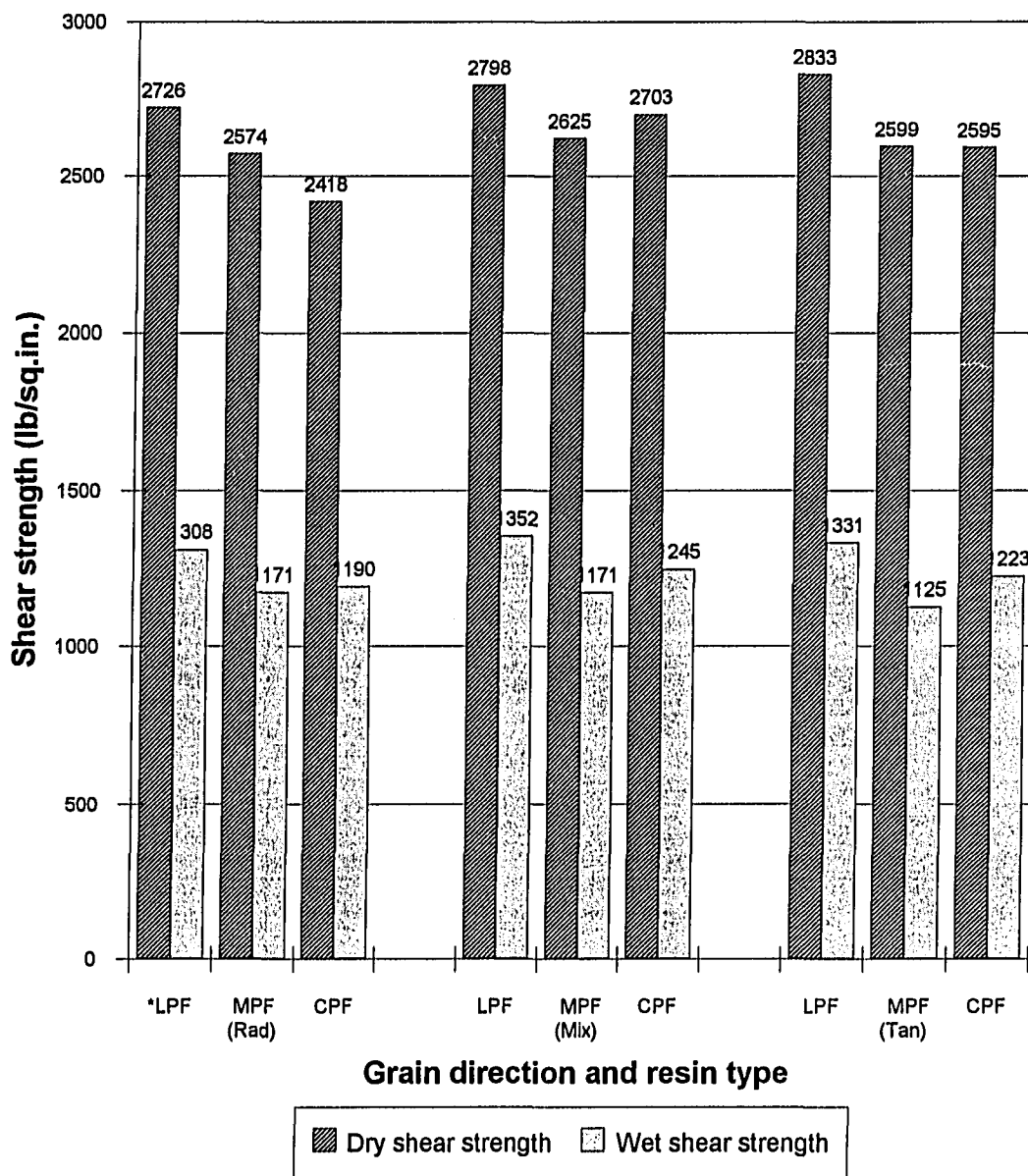
Bonding properties	Dry shear strength (psi)			Wet shear strength (psi)			Dry wood failure (%)			Wet wood failure (%)		
PF-resin type[a]	LPF	MPF	CPF	LPF	MPF	CPF	LPF	MPF	CPF	LPF	MPF	CPF
Radial-grained	2726	2574	2418	1308	1171	1190	78	63	71	56	38	48
	(97)[b]	(150)	(109)	(34)	(52)	(58)	(8)	(6)	(9)	(8)	(5)	(8)
Duncan grouping	A[c](A)[d]	B(A)	C(B)	A(A)	B(A)	B(A)	A(A)	B(A)	B(A)	A(A)	C(A)	B(A)
Mix-grained	2798	2625	2703	1352	1171	1245	65	51	70	45	26	46
	(130)	(166)	(144)	(64)	(64)	(59)	(12)	(5)	(7)	(8)	(4)	(9)
Duncan grouping	A(A)	B(A)	AB(A)	A(A)	C(A)	B(A)	A(B)	B(B)	A(A)	A(B)	B(B)	A(A)
Tangential-grained	2833	2599	2595	1331	1125	1223	48	39	49	26	19	23
	(155)	(189)	(173)	(52)	(99)	(95)	(12)	(7)	(8)	(9)	(4)	(5)
Duncan grouping	A(A)	B(A)	B(A)	A(A)	C(A)	B(A)	A(C)	B(C)	A(B)	A(C)	A(C)	A(B)

[a]PF-resin type: LPF = Lab-made phenol-formaldehyde resin; CPF = Commercial phenol-formaldehyde resin; MPF = Mixed phenol-formaldehyde resin.
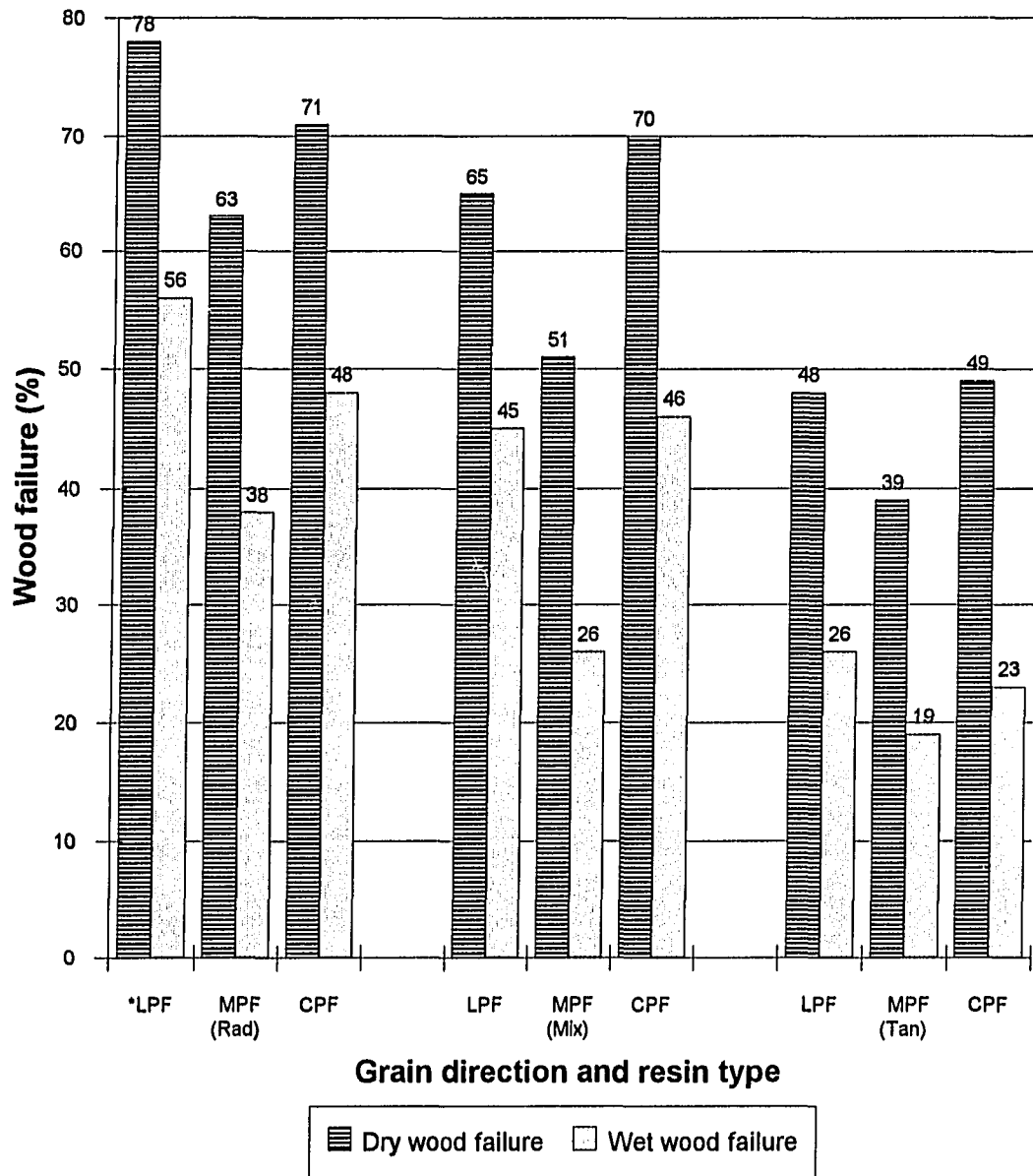
[b]Numbers in parentheses are standard vediations.

[c]Letters represent Duncan's grouping at 0.05 level for effect of PF-resin type.

[d]Letters in parentheses represent Duncan's grouping at 0.05 level for effect of grain orientation.

Figure 8. Effect of grain direction and resin type on shear strength of white oak specimens. Rad=radial-grained; Mix=Mix-grained; Tan=tangential-grained

Figure 9. Effect of grain direction and resin type on wood failure of white oak specimens. Rad=radial-grained; Mix=Mix-grained; Tan=tangential-grained

percentage of wood failure. When the CPF was used, tangentially bonded specimens had a lower wood failure value than radial-grained and mix-grained specimens did, and there was significant difference in wood failure between the latter two.

When the specimens were aged by boiling in water for 2 hours, the LPF gluebonds also showed superiority over the MPF and CPF bonds. On the average, LPF-bonded specimens had a significant 10% increase in wet gluebond shear strength from that of the CPF-bonded specimens. The MPF-bonded specimens had the weakest wet gluebond shear strength. Just like for the dry bond shear strength, there was no difference in wet bond shear strength in different grain orientations when a particular type of resin was used. The LPF also showed a significant improvement of radial plane wet wood failure from that of the CPF-bonded specimens. But differences in wet wood failure between LPF- and CPF-bonded specimens was not observed in mix- and tangential-grained specimens. Once again, the MPF gave the lowest wet wood failure regardless of which plane the wood was adhesive bonded.

In conclusion, the low viscosity, laboratory-prepared phenol-formaldehyde resin produced better white oak adhesive bond quality than did the commercial phenolic resin. The superiority of the LPF can be attributed to an improved resin penetration. The phenolic resin prepared by mixing equal parts of laboratory-prepared and commercial resins produced the worst white oak bond quality. No explanation can be offered as to why MPF performed worse than CPF even though the former has a lower viscosity than the latter.

CHAPTER 5. SUMMARY AND CONCLUSIONS

Previous studies showed that white oak plywood bonded with resole type of phenol-formaldehyde resins had low bond strength and wood failure. Studies also showed that white oak flakeboards bonded with phenol-formaldehyde resins were inferior to boards made from pine species. It is believed that difficulty in bonding white oak with phenol-formaldehyde resins is due to interference of extractives with the formation of a good adhesive bond.

The white oak butt log selected for this study had a ring count of 106 and a diameter of 20 inches. The heartwood had a total extractive content of 15.03%. Based on a successive solvent extraction of white oak heartwood, there was 0.36% hexane-solubles, 11.56% ethanol-solubles, and 2.96% hot water-solubles. The total average heartwood extractive content of this white oak tree is relatively high probably because the extractive content was determined based on a 24-hour extraction.

Solvent extraction of white oak heartwood specimens with hexane, 95% ethanol, hot water, and combinations of these solvents did not improve the adhesive bond quality. This is attributed to the fact that specimens were machined to thickness prior to bonding, removing possible extractive contaminants and exposing fresh cell wall surfaces for good adhesive bonding. In addition, solvent extractions caused warping of test specimens, preventing a complete closure of the gluelines during hot pressing, and resulting in inferior gluebond strength.

Applying white oak heartwood extracts onto freshly planed hard maple wood surfaces significantly reduced adhesive bond quality, especially the gluebond durability. Results indicated that water-soluble polymeric saccharides had the most deleterious effect on adhesive bond quality. Previous studies have shown that reducing sugars and polysaccharides with reducing ends under alkaline conditions can be transformed to acidic components, especially saccharinic acids. Therefore, these acidic components can neutralize the base catalyst in the phenolic resin and prevent proper setting and curing of the resin. Although white oak heartwood hexane-solubles can potentially interfere with proper wetting of wood surfaces with resin adhesives, their roles in influencing the gluebond quality of white oak is questionable because white oak contains only a small quantity of these extractives.

This study also found that bonding of radial-grained white oak specimens had a low bond strength but a high percentage of wood failure. This is most likely due to a high volume of ray tissues in white oak wood. Adhesive bonds between mix-grained and between tangential-grained white oak specimens showed higher bond strengths but low values of wood failure.

A phenol-formaldehyde resin with a viscosity of 100 centipoises at 25°C, a pH of 11, and a solid content of 50% prepared in the laboratory provided a better white oak adhesive bond quality than did a commercial phenolic resin with a viscosity of 300 centipoises. Improvement in adhesive bond quality with the low-viscosity resin was more apparent for the radial-grained specimens than in the mix- and tangential-grained specimens. Improvement of the adhesive bond quality of white oak with the low-viscosity resin is attributed to better resin penetration.

Although it has been demonstrated that white oak extractives have deleterious effects on adhesive bonding, it is impractical to efficiently remove extractives during

the industrial processes to manufacture PF-bonded products. Results of this study also indicated that a low-viscosity PF resin significantly improved the adhesive bond quality due to a better resin penetration. More research in the direction of formulating low-viscosity PF resins is needed to further improve the white oak adhesive bond quality. If a deep-penetrating PF resin that can overcome the deleterious effects of extractives can be developed, a large volume of PF-bonded products can be produced from lumber, veneer, flakes and particles, and fibers from low-quality oaks.

LITERATURE CITED

Abe I. and N. Akimoto. 1976. The inhibitory effect of kapur wood extractives on the curing reaction of the resol. Journal of the Japan Wood Research Society. 22(3):191-196.

Abe I. and K. Ono. 1980. Effect of the acidity of some tropical wood extractives on the curing of the resol. Journal of the Japan Wood Research Society. 26(10):686-692.

Albritton, R. O. and P. H. Short. 1979. Effects of extractives from pressure-refined hardwood fiber on the gel time of urea-formaldehyde resin. Forest Products Journal. 29(2):40-41.

Anderson, A. B. and W. B. Fearing., Jr. 1960. Solvent seasoning of tanoak. Forest Products Journal. 10(5):234-238.

Anderson, A. B. and W. B. Fearing., Jr. 1961. Distribution of extractives in solvent seasoned redwood lumber. Forest Products Journal. 11(5):240-242.

ASTM (American Society for Testing and Materials). 1974. D-905-49. Standard method of test for strength properties of adhesive bonds in shear by compression loading. ASTM, Philadephia, PA.

Bosshard, H. H. 1966. Notes on the biology of heartwood formation. IAWA News Bulletin No. 1, Utrecht, Netherlands.

Bosshard, H. H. 1968. On the formation of facultatively colored heartwood in *Beilschmidia tawa*. Wood Science & Technology. 2(1):1-12.

Brand, G. J., and J. T. Walkowiak. 1992. Forest Statistics for Iowa, 1990. USDA Forest Serv, North Central Forest. Experimental. Station., Resource Bulletin NC-136.

Caster D., N. Kutscha, and G. Leick. 1985. Gluability of sanded lumber. Forest Products Journal. 35(4):45-52.

Chen, C.-L. 1970. Constituents of *Quercus alba*. Phytochemistry. 9:1149.

Chen, C.-M. 1970. Effect of extractive removal on adhesion and wettability of some tropical woods. Forest Products Journal. 20(1):36-40.

Chen, C.-M. 1975. Gluing study of presote-treated fire-retardant plywoods - Part I. Forest Products Journal. 25(2):33-37.

Conner, A. H., B. H. River, and L. F. Lorenz. 1986. Carbohydrate modified phenol-formaldehyde resins. Journal of Wood Chemistry Technology. 6(4):591-613.

Craft, E. P. 1970. Construction-grade plywood from grade 3 Appalachian oak. USDA Forest Service Research Paper NE-163. USDA, Washington, DC.

Dougal, E. F., J. D. Wellons, R. L. Krahmer and P. Kanarek.1980. Gluline characteristics and bond durability of Southeast Asian species after solvent extraction and planing of veneers. Forest Products Journal. 30(1):48-53.

Hancock, W. V. 1963. Effect of heat treatment on the surface of Douglas-fir veneer. Forest Products Journal. 13(2):81-88.

Hemingway, R. W. 1969. Thermal instability of fats relative to surface wettability of yellow birchwood (*Betula lutea*). Tappi 52(11):2149-2155.

Hillis, W. E. 1968. Chemical aspects of heartwood formation. Wood Science and Technology. 2(3):241-259.

Hse, C. Y., and M. L. Kuo. 1988. Influence of extractives on wood gluing and finishing - A review. Forest Products Journal. 38(1):52-56.

Jokerst, R. W., and H. A. Stewart. 1976. Knife- versus abrasive-planed wood: quality of adhesive bonds. Wood and Fiber. 8(2):107-113.

Koch, P. 1985. Utilization of Hardwoods Growing on Southern Pine Sites. Vol. 1. The Raw Material. Agriculture Handbook No. 605. USDA, Forest Service Washington DC.

Kuo, M. L., D. DeCarlo, and C. Y. Hse. 1984. Influence of extractives on bonding properties of white and southern red oak. Journal of Adhesion. 16:257-278.

Kuo, M. L., and D. G. Arganbright. 1980. Cellular distribution of extractives in redwood and incense cedar. Part I. Radial variation in cell-wall extractive content. Holzforschung. 34(1):17-22.

Nearn, W. T. 1974. Application of the ultrastructure concept in industrial wood products research. Wood Science. 6(3):285-293.

Nguyen, D. 1975. Effect of wood extractives on cure of phenolic resin. M. S. thesis. Oregon State Univ., Corvallis. OR.

Okkonen, E. A., and B. H. River. 1989. Factors affecting the strength of block-shear specimens. Forest Products Journal. 39(1):43-50.

Pettersen, R. C. 1984. The chemical composition of wood. In "The Chemistry of Solid Wood," R. M. Rowell, ed., Advance in Chemistry Series 207, American. Chemistry Society, Washington DC.

Plomley, K. F., W. E. Hillis, and K. Hirst. 1976. The influence of wood extractives on the glue-wood bond. I. The effect of kind and amount of commercial tannins and crude wood extracts on phenolic bonding. Holzforschung. 30(1):14-19.

Roffael, E., and W. Rauch. 1974. Extractives of oak and their influence on the gluing with alkaline phenolic-formaldehyde resins. Holz als Rol- und Werkstoff. 32(5):182-187.

Rowe, J. W. and A. H. Conner. 1979. Extractives in eastern hardwoods-A review. USDA Forest Service General Technical Report. FPL 18. Washington DC.

Shim, C. S. 1954. A study on the effect of water-soluble extractives upon physical properties of wood. College Theseon. (Sci. Nat.), University Seoul No.1:117-162.

Seikel, M. K., F. D. Hostettler, and G. J. Niemann. 1971. Phenolics of *Quercus rubra* wood. Phytochemistry. 10:2249-2251.

Sjöström E. 1981. Wood Chemistry Fundamentals and Applications. Academic Press, Inc. Orlando, Florida.

Swanson, J. W., and S. Cordingly. 1959. Surface chemical studies on pitch. II. The mechanism of the loss of absorbency and development of self-sizing in papers made from wood pulps. Tappi. 42(10):812-819.

Thomas, R. J. 1959. Gluing characteristics on determa. Forest Products Journal. 9(8):266-271.

U. S. Forest Service 1982. An analysis of the timber situation in the United States, 1952-2030. USDA For. Serv., Forest Resource Report No.23. Washington DC.

Wellons, J. D. 1976. Adhesion to wood substrates. In "Wood Technology: Chemical Aspects, " I. S. Goldstein ed., ACS Symposium Series 43, American Chemistry Society, Washington DC.

Wellons, J. D., R. L. Krahmer, R. Raymond, and G. Sleet. 1977. Durability of exterior siding plywood with southeast Asian Hardwood Veneers. Forest Products Journal. 27(2):38-44.

Wood Handbook. 1987. Wood as An Engineering Material. USDA Forest Service Agriculture Handbook 72. Washington DC.