

**Protein-based phenolic wood adhesives for aspen/agricultural residue
blended medium density fiberboard**

by

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GENERAL INTRODUCTION

INTRODUCTION

Protein-based adhesives controlled a significant portion of the wood adhesives market share prior to World War II. Soybean-based wood adhesives peaked in 1956 consuming 100 million pounds (Lambuth, 1977). Utilizing roughly 50 million pounds of blood annually, blood-based glue in the plywood industry peaked in the 1960's (Detlefsen, 1989). The development of modern wood adhesives resulted from the post-war surplus of petrochemicals at low prices.

Newly developed synthetic adhesives far outperformed natural adhesives of the period with more effective moisture resistance properties, shorter press times at lower temperatures, and lower overall adhesive cost. Representing a combined total of 99.5% of the wood adhesives sold in the United States and Canada in 1999, urea formaldehyde (UF), phenol formaldehyde (PF) and polymeric diphenylmethane diisocyanate (pMDI) are the dominant synthetic wood adhesives in North America (Johnson, 2001). Strict regulations on toxic emissions and the foreseeable reduction of acceptable limits have made wood product industries reevaluate the potential of biorenewable adhesives. Price and performance similar to today's commercial synthetic resins will be required for successful implementation of biorenewable adhesives. Co-polymerization of modern synthetic adhesives with biorenewable materials, producing resins with sufficient performance standards, is one potential method of achieving this goal.

Sources such as lignins and tannins have gained significant research focus. Interest lies in the partial replacement of synthetically derived phenol with largely abundant natural phenols from lignins and tannins. Due to limited success with lignins and tannins, research turned to carbohydrates. Chemical structures of carbohydrates make cross-linking possible with synthetic resins developing a three-dimensional matrix upon curing. Combinations of wide varieties of hydrolyzed carbohydrates made the utilization of holocellulosic feedstocks extremely complex. Protein sources for adhesive formulations have reemerged with the most potential as a constituent in natural adhesives.

Sawmill residues, small, and low-quality logs are traditional raw material sources for medium density fiberboard (MDF) and particleboard production in the US. Due to growing global demand for wood products, utilization of agricultural residues have emerged as a potential alternative to wood fiber. This study focuses on the evaluation of protein-based phenolic adhesive resins cross-linked and co-polymerized with PF for manufacturing MDF containing an aspen/cornstalk fiber blend.

THESIS ORGANIZATION

This thesis is composed of a literature review, a manuscript to be submitted to the Forest Products Journal for publication, a general introduction and conclusion, and a references list. The manuscript is written in compliance with the journal requirements, containing an abstract, an introduction, a materials and methods section, a results and discussion section, a conclusion section, and a list of references.

LITERATURE REVIEW

Biorenewable adhesives historically had a strong foothold in the wood products industry prior to the 1960's. Sources of raw material for these adhesives were primarily protein or carbohydrate-based. There has been a resurgence of interest in natural adhesives, attempting to make them competitive with today's synthetic resins while maximizing additional advantages unattainable by synthetics. Potential resources for utilization in the formulation of these adhesives include previously significant sources, such as a variety of proteins and carbohydrates, as well as recent sources, such as lignins and tannins. Success will require examination of adhesive performance and modification to mimic that of today's commercial synthetic resins at a justifiable cost. One potential method to achieve this is to co-polymerize modern synthetic adhesives with adhesives of a biorenewable nature, yielding a resin of desired quality and performance.

Biorenewable adhesives have long played a role in the wood products industry, though their relative importance in today's marketplace has been dramatically reduced. Properties associated with natural adhesives based on materials, such as carbohydrates, casein protein, vegetable proteins, and blood albumin were sufficient to carry the industry

through World War II. Peaking in 1956 with an annual consumption of 100 million pounds, soybean-based glues played an integral role in the adhesives industry (Lambuth, 1977). Similarly, the use of blood-based glue in the plywood industry peaked in the 1960's, utilizing roughly 50 million pounds of blood annually (Detlefsen, 1989). As a result of post-war surplus of petrochemicals, low cost production of today's petrochemical-based commercial resins commenced. These synthetic resins far outperformed biorenewable adhesives of the time in both physical and economic aspects. Specific attributes responsible for dissolving the existing platform of natural adhesives included more effective moisture resistance properties, shorter press times at lower temperatures, and lower overall adhesive cost. Technology to produce resorcinol-formaldehyde (RF) and phenol-formaldehyde (PF) resins had long been established at that time, but production had been cost prohibitive on a large-scale basis (Lambuth, 1989).

Urea formaldehyde (UF), PF, and polymeric diphenylmethane diisocyanate (pMDI), the dominant synthetic wood adhesives in North America, constitute a combined total of 99.5% of the wood adhesives sold in the United States and Canada. Consumption of UF-based adhesives (wet basis) tops the list, utilizing 4.2 billion pounds (56.6% of total), followed by PF-based resins with 3.0 billion pounds (40.3%) and pMDI, with an estimated 196 million pounds (2.6%). The largest consumers of UF, PF and pMDI are particleboard, plywood, and oriented strand board (OSB) respectively. Over 7.4 billion pounds of adhesives were consumed in North America in 1999, with the largest consumer being the particleboard industry (2.7 billion lb), followed by medium-density fiberboard (MDF) (1.5 billion lb), plywood (1.4 billion lb), and OSB (1.3 billion lb) (Johnson, 2001). Unlike their natural adhesives counterparts, modern commercial adhesives, being of a petrochemical basis, are not renewable. Further justification for the development and utilization of biorenewable adhesives commonly originates from the uncertainty of crude oil supply. The "Energy Crisis" experienced by much of the world since 1974 further emphasizes this concern. Strict regulations on toxic emissions and the foreseeable reduction of acceptable limits have also stimulated the wood products industry to develop biorenewable adhesives. In addition to the further advancement of traditional natural adhesives, extensive research has focused on the development of new adhesive sources.

Lignins as an adhesive resource

Lignins, a natural feedstock high in polyphenolics, have been examined as a replacement for synthetic phenol. Lignin is present in a variety of natural sources, but wood is likely the primary source. Gillespie (1989) demonstrated that kraft lignin reacted with formaldehyde produced wood adhesives with adequate shear strength and water resistance. Press times of 10 minutes at 150 °C and 150 psi were required before adequate bonding could be achieved. Evaluation of shelf life demonstrated acceptable properties after 120 days. Calve et al. (1988) developed a low-cost lignin adhesive utilizing 50% replacement for waferboard and OSB derived from ammonium spent sulfite liquor and PF. With the addition of an acid catalyst, properties reflective of commercial PF were achieved. Low molecular weight fractions of ammonium spent sulfite liquor containing high proportions of carbohydrates resulted in slightly higher board properties. Additional testing in replacing ammonium spent sulfite liquor with glucose concluded that both lignin and carbohydrates contribute to overall bond strength. Sellers et al. (1994) formulated a PF-based resin utilizing a 30% acid hydrolyzed lignin substitution in which bonded panels were not significantly different from control panels when examined at a 4% resin application level. Panels were hot-pressed at 205°C for either four or five minutes. Unlike internal bond values for control resins, higher values were observed as a result of increasing press time with lignin-PF resins. Kuo et al. (1991) incorporated 50% alkali treated kraft lignin into flakeboard adhesives, but boards bonded with such resin resulted in compromised properties. Southern pine kraft lignin was hydrolyzed with NaOH, but NMR studies showed that alkaline hydrolysis failed to increase the reactivity of lignin with formaldehyde under the conditions used.

Tannins as an adhesive resource

Interest in utilizing tannins, primarily from bark, has sparked strong research and new advancements. The driving force behind this research is the partial replacement of synthetically derived phenol with largely abundant natural phenolics present in tannins. Tannins extracted from black wattle (*Acacia mearnsii*) bark have been successfully incorporated into adhesives in the South African wood products industry (Pizzi, 1989). Kriebich and Hemingway (1989) established that pine bark tannins replacing 50% of phenol

resorcinol-formaldehyde (PRF) for end-jointing lumber could successfully be used in conjunction with the honeymoon system. Samples demonstrated excellent moisture resistance with wood failures ranging from 70-90%. Within 5-10 minutes at ambient temperature, glue joints had set up enough to allow gentle handling. Nearly 50% of ultimate tensile strength was achieved after 20 minutes of cold setting. Santana et al. (1995) developed a tannin-incorporated plywood adhesive with a 33% replacement of synthetic PF for bonding loblolly pine (*Pinus taeda*) that exhibited comparable results to commercial PF. They liquefied tannins in phenol with 5% sulfuric acid inclusion, yielding a solution for adhesives upon addition of formaldehyde and NaOH. These solutions demonstrated increased pot-life and shelf life. Barbosa et al. (2000) demonstrated that tannin-based resins could be modified to reduce adhesive brittleness. Additional flexibility in plywood glue lines was achieved by partial esterification of the free hydroxyl groups within tannins with adipoyl chloride. Tannin-modified adhesives had significantly longer cure time compared to non-modified adhesive formulations. It was determined that partial esterification of tannin-based adhesives resulted in a more uniform distribution of forces throughout the glue line and improved adhesive performance.

Incorporation of biorenewable sources into adhesive formulations is not without limitations. The structural and chemical complexity of many of these substances or mixtures of substances can limit their potential use as adhesive constituents. A multitude of research efforts have concentrated on the chemical activation of lignin, making further manipulation feasible, yet lignin-based adhesives are virtually non-existent in the North American wood products industry. Limitations of lignin-based adhesives, such as longer press times, restrict the industrial applicability of such formulations. Contrary to the limited chemical reactivity of lignins, problems existing with the use of tannin-based adhesives stem from the over-reactivity of tannins. Unlike many other sources of natural adhesives, tannins are highly reactive and exhibit short pot life and drastically reduced shelf life. Though these properties can be advantageous under certain circumstances, such as tannin-based PRF adhesives in conjunction with the honeymoon system for finger jointing lumber, this is certainly a limitation for adaptation to other manufacturing systems. In addition, due to the linear chemical structure of tannins, brittleness associated with glue lines after curing is a concern.

Carbohydrates as an adhesive resource

After numerous years of research focused on the utilization of lignins and tannins as a viable adhesive resource, little industrial success has been achieved. Due to the chemical complexity associated with lignins and tannins, research continued to search for alternative materials for adhesive feedstocks. Numerous researchers focused on the utilization of readily available carbohydrate sources for adhesive formulation. The chemical structure of carbohydrates allows for the possibility of cross-linking reactions, resulting in a three-dimensional matrix capable of stable bonding.

Conner (1989) demonstrated that a wide variety of carbohydrates from both plant and animal sources could be used for adhesive purposes. Carbohydrates in the form of cellulose and hemicelluloses are abundant from a diversity of plant-based biorenewable resources. Upon hydrolysis, cellulose gives glucose, while hemicelluloses yield a variety of sugars. These products in particular can be used for adhesive formulations. Karchesy et al. (1989) confirmed that fast curing carbohydrate-based adhesives for gluing high moisture content veneers under hot press conditions could be formulated with satisfactory results. They synthesized a new carbohydrate-phenol-resorcinol (CPR) resin from glucose, urea, phenol and resorcinol that was completely waterproof when cured with formulation pH's ranging from 7.8-10.8. CPR adhesives also demonstrated excellent cold setting properties with above 98% wood failure for 2-hour boil specimens. Similarly, Conner et al. (1989) demonstrated that carbohydrate modified PF resins using a 50% substitution level formulated at neutral conditions could bond Douglas-fir veneer panels with acceptable dry and wet shear strength and wood failures. Xylose, a reducing sugar, as well as xylitol and methyl xyloside, both non-reducing sugars, were acceptable modifiers. Studies of IR spectroscopy, extractability, and reactions with model compounds concluded that the carbohydrate was incorporated into the resin. Additionally, Kuo et al. (1994) formulated starch-PF resins for exterior plywood application. They formulated resins by reacting PF prepolymers with cornstarch-derived maltodextrins under neutral conditions. Cornstarch is a readily available carbohydrate in a relatively pure form; therefore, it may have distinctive advantages over other potential carbohydrate feedstocks. Press times of 12 minutes at 170°C were required for proper

adhesive curing. Results show up to 1.04 mole of maltodextrin per mole of phenol incorporated into adhesives formulations does not harm glue bond integrity.

Proteins as an adhesive resource

Combinations with wide varieties of hydrolyzed carbohydrates after hydrolysis make utilization of holocellulosic feedstocks extremely complex. Separation and purification of active ingredients from these mixtures are cost prohibitive. Furthermore, the utilization of carbohydrates encountered similar inactivity issues as experienced with lignin, sending researchers on a quest to find materials more easily incorporated into adhesives.

Resulting from the established history of protein-based adhesives in the wood products industry, significant research efforts have been devoted to this area. Utilizing the underlying technology of soy and blood-based adhesives of the 1960's, further development has been devoted to the transformation of these systems into competitive alternatives. The alteration of past performance to be more reflective of modern synthetics has been a focus of these advancements. Extensive concentration has been devoted to utilizing soy protein as an adhesive constituent. Lorenz et al. (1999) modified UF resins with soy protein isolates and soy flour in order to reduce formaldehyde emissions. It was concluded that increasing the percentage of protein used to modify the resin did not decrease formaldehyde emissions. The addition of up to 30% soy protein isolates could be added to UF resins; consequently, reactivity of UF decreased with increasing protein percentage, resulting in compromised strength properties. Kuo et al. (1998; 2001) successfully manufactured wood/agricultural fiberboards by reacting soy protein isolates with commercial PF resins. Due to the high molecular weight of protein isolates, sprayable adhesives for fiberboard could not be formulated under neutral conditions. Formulation with NaOH into an aqueous solution composed of 30% solids overcame this issue but severely compromised moisture resistant properties. In an additional study, Kuo and Stokke (2001) evaluated wood/agricultural fiber MDF and hybrid poplar OSB containing soy-based adhesives. Laboratory prepared PF combined with soy flour hydrolyzates in a 3:7 weight ratio, respectively, met product performance standards. This soy-PF adhesive formulation was suitable for spray application for both MDF and OSB production. Manufactured OSB exhibited excellent bending strength

but reduced internal bond (IB) and moisture resistance compared to commercial PF. A similar study carried out by Hse et al. (2001) showed that a phenol-soy flour hydrolyzate resin with a 7:3 weight ratio had highly comparable IB strength with OSB control boards prepared with commercial PF. Soy PF adhesives demonstrated lower moisture resistance than that of PF counterparts. Riebel et al. (1997) describes a method of preparing a soy-based thermosetting adhesive cross-linked with MDI. Molded biocomposite materials were formed by mixing resin and newspaper fibers in a 4:6 ratio.

Current uses of blood proteins within the forest products industry have narrowed to a very limited scope compared to their historical significance. Blood protein is presently being added to commercial plywood adhesives in very low percentages to increase foaming properties associated with the extrusion of adhesive onto plys. This not only adds integrity to the extruded bead of adhesive but also provides increased resin efficiency by reducing the amount of wasted adhesive.

Due to the strong historical importance of protein based adhesives, numerous improvements to preexisting formulations have already occurred, placing these resins at a slight advantage. Protein adhesives also have disadvantages associated with their implementation as adhesives sources. Increased press times and temperatures are typically associated with renewable adhesives; protein is no exception though blood and casein-based resins can fully cure under cold-setting conditions. Much of the protein-based adhesive research has focused on the utilization of soy protein due to the prolific abundance of soybean crops in the US. Soy isolates tend to be the focus of most formulations yet use of these food grade isolates is cost prohibitive, compared to synthetic components, when alternative forms of soy protein are examined.

Agricultural fiber as a raw material

Traditional raw materials for MDF and particleboard production in the US forest products industry include sawmill residues, small, and low quality logs. Environmental interests have led to alterations in typical forest management practices, resulting in regional supply concerns. Bowyer (2001) demonstrates the growing global demand for wood products along with the potential of utilizing agricultural residues as a raw material for the

panel industry. Bowyer concludes that based on current available volumes of agricultural residues, the panel industry in North America has the potential to grow to approximately $\frac{2}{3}$ the size of the present wood-based panel industry. Sellers (2001) reports that during 1998 and 1999 six agricultural fiber panel mills were reportedly in operation in North America, with seven additional particleboard and MDF mills scheduled for startup in 2000-2001. Total industrial capacity of these mills would result in an additional 1.564 million cubic meters of product made primarily out of wheat straw. Kuo et al. (1998) successfully manufactured agricultural-based fiberboard utilizing soy-based adhesives with results showing wood fiber was superior to cornstalk and switchgrass fibers, with corn fiber providing better results than switchgrass. They found that the properties most directly affected by fiber type were dimensional stability followed by IB. Mechanical properties and dimensional stability decreased with additional agricultural fiber percentages. Boards composed of 50% corn or switchgrass residues demonstrated an 18% and 29% lower modulus of rupture (MOR) and a 3% and 21% weaker IB respectively compared to 100% wood fiber. Utilization of agricultural residues within the forest products industry imposes limitations due to their unique biological differences compared to wood. Agricultural residue supply is a concern because they are typically harvested over a one to three month period annually. Storage of adequate supplies for mill production must therefore be obtained within a relatively narrow window of opportunity and stored in a manner to avoid biological degradation. Due to the need for isocyanate resins rather than PF or UF to provide sufficient board properties, additional costs and concerns are associated with agricultural fiber composites. Kuo et al. (1998) pointed out that cell surfaces covered with waxy cuticle layers might be associated with decreased properties of agricultural fiber composite products bonded with UF and PF.

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Protein-based phenolic wood adhesives for aspen/agricultural residue blended medium density fiberboard

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ABSTRACT

Petrochemical-based adhesives dominate today's wood products industry. Biorenewable adhesives once commanded a strong market share prior to World War II. Post-war synthetic adhesives were capable of exceeding biorenewable resins of the era in both physical and economic aspects. Biorenewable-based adhesives have seen a resurgence of research interest attempting to formulate resins competitive with today's synthetics. The objectives of this study were to evaluate the adhesive properties of soybean flour, whole animal blood meal, and feather meal, as well as evaluate the effects of melamine-formaldehyde (MF) and polymeric diphenylmethane diisocyanate (pMDI) as cross-linking agents. Alkaline hydrolysis of proteins was done followed by treatment with either 2% MF powder or 2% pMDI. Pretreated hydrolyzates were co-polymerized with 28% laboratory prepared PF. MDF was manufactured using a 1:1 mix of aspen and corn fiber. In general, blood-based phenolic resin performed better than soy-based resins, and soy-based resins, in turn, were better than feather-based resin. Differences in protein content and protein structure significantly affected properties of boards bonded with protein-based resins. High viscosities of blood-based phenolic resins caused problems during spraying, but can be overcome with appropriate amounts of ammonium hydroxide. Few differences were exhibited in properties of boards bonded with blood-based phenolic resins compared to boards bonded with resins containing blood/feather and blood/soy mixtures. There was no effect of using cross-linking agents to enhance properties of boards bonded with protein-based phenolic resins. The possible inactivity of cross-linking agents used may be responsible for the results obtained. Presence of propylene carbonate may provide sufficient cross-linking, deeming pretreatment of protein hydrolyzates with cross-linking agents unnecessary under the reaction conditions used. Results of this study show all boards bonded with protein-based resins except those formulated with feather protein alone meet the ANSI

standard requirement for interior use. This study also clearly indicated the advantage of mixing different proteins in formulating protein-based resins.

INTRODUCTION

Petrochemical-based adhesives are the mainstay of today's wood products industry. Urea formaldehyde (UF), phenol formaldehyde (PF), and polymeric diphenylmethane diisocyanate (pMDI), the dominant synthetic wood adhesives in North America, constitute a combined total of 99.5% of the wood adhesives sold in the United States and Canada. Over 7.4 billion pounds of adhesives (wet basis) were consumed in North America in 1999, with the largest consumer being the particleboard industry (2.7 billion lb), followed by medium-density fiberboard (MDF) (1.5 billion lb), plywood (1.4 billion lb), and oriented strand board (OSB) (1.26 billion lb) (Johnson, 2001). Physical properties and moisture resistance achieved from these adhesives, coupled with low costs, drive the consumption of synthetic resins. Unlike their natural adhesive counterparts, modern commercial adhesives being petroleum-based are non-renewable. Additional rationalization for the development and utilization of biorenewable adhesives commonly originates from the uncertainty of the crude oil supply. Further emphasizing this concern is the "Energy Crisis" experienced by much of the world since 1974. Motivation for the wood products industry to develop adhesives of a biorenewable nature is also stimulated by stringent toxic emissions regulations and foreseeable reductions of acceptable limits.

In the years preceding the 1960's, biorenewable adhesives had a strong foothold in the wood products industry. Properties associated with natural adhesives derived from materials, such as carbohydrates, casein protein, vegetable proteins, and blood albumin, were sufficient to carry the industry through World War II. Proteins and carbohydrates were primary sources of raw material for these adhesives. Peaking in 1956 with an annual consumption of 100 million pounds, soybean glues played an integral role in the adhesives industry (Lambuth, 1977). Heat cured blood albumin glues in the plywood industry peaked in the 1960's, utilizing roughly 50 million pounds of blood annually (Detlefsen, 1989).

The production of today's petrochemical-based commercial resins resulted from a post-war surplus of low-cost petrochemicals. Production of resorcinol-formaldehyde (RF)

and PF resins had been cost prohibitive on a large-scale basis though the technology had long been established at that time (Lambuth, 1989). Synthetic resins far outperformed biorenewable resins of the era in both physical and economic aspects. More effective moisture resistance properties, shorter press times at lower temperatures, and lower overall adhesive cost were specific attributes responsible for capturing large portions of the market.

There has been a resurgence of interest in natural adhesives, attempting to make them competitive with today's synthetic resins while capturing additional advantages unattainable by synthetics. Potential resources for utilization in the formulation of these adhesives include previously significant sources, such as a variety of proteins and carbohydrates, as well as modern adhesive sources, such as lignins and tannins. Extensive research efforts have been devoted to the formulation of proteins into inexpensive adhesives. Success will require examination of adhesive performance and modifications to mimic that of today's commercial synthetic resins at a competitive cost. One potential method to achieve this is to co-polymerize modern synthetic adhesives with biorenewable materials, yielding resins of desired quality and performance. This study focuses on the evaluation of biorenewable protein-based adhesives cross-linked and co-polymerized with PF for manufacturing MDF containing an aspen fiber/cornstalk fiber blend. Three proteinacious materials, low-fat soybean flour, ring-dried whole animal blood meal, and feather meal, were the main components in formulation of protein-based phenolic resins.

MATERIALS AND METHODS

Fiber Processing

Bales of freshly harvested cornstalks obtained from central Iowa and commercial aspen wood flakes obtained from northern Minnesota were further processed. Initial refining of materials was done with a hammer mill. After processing with the hammer mill, the materials were soaked in hot water (140°F) prior to fiberization with a Sprout-Bauer single disc atmospheric grinder. Soaked material was hand fed with hot running water (140°F) through grinding plates set with 0.005 inches of clearance. After sufficient air drying, the fibers were further oven dried at 180°C to about two percent moisture content.

Pretreatment of Proteins

Low-fat soybean flour obtained from Kerry Ingredients, ring-dried whole animal blood meal obtained from Animal Protein Corporation, and feather meal acquired from Consumer Supply Distributing Company, were the three proteinaceous materials evaluated. Compositions of the three protein sources used in the formulation of protein-based adhesive resins are summarized in Table 1. Alkaline dispersion of proteins was conducted in a three-gallon Fluitron pressure reactor. Hydrolysis was accomplished with the addition of NaOH and Na₂CO₃ in protein specific percentages and H₂O to form a solution of ~35% solids. The conditions for protein hydrolysis are summarized in Table 2. The resulting hydrolyzates typically had pH's of 9.5-10.0 and required a simple evaporation to reach target solid contents of 35~37%. Following protein hydrolysis, hydrolyzates were treated with either 2% melamine-formaldehyde (MF) powder (BTLM 806, BTL SR Toledo Inc.) or 2% pMDI (RUBINATE® 1840, Huntsman). Reactions were carried out in a 1000 ml beaker with vigorous stirring. MF powder was added to preheated hydrolyzates (70°C) and reacted for one hour. MDI was added to preheated hydrolyzates (50°C) and reacted for 25 minutes.

Phenol Formaldehyde Resin Synthesis

Laboratory prepared PF for co-polymerization was formulated in a 3000 ml resin kettle under the following conditions: F/P molar ratio=2.4 and NaOH/P molar ratio=0.1. The initial hydroxymethylation reaction was carried out at 65°C for one hour, followed by a subsequent condensation reaction at 95°C for 45 minutes. The resulting PF resin typically has a solid content of 50~55%, a viscosity of 40-80 centipoise, and a pH of 9.5~10.

Formulation of Protein-Based Phenolic Resins

Formulated protein-based resins are composed of 70% protein, 2% cross-linking agent, and 28% laboratory prepared PF resins. Formulations consisting of protein combinations contained two distinct proteins in a 1:1 mixture. Protein hydrolyzates treated with cross-linking agents were heated to 50°C, followed by the addition of PF resin and allowed a 30-minute reaction time with vigorous stirring. If blood was a constituent of the adhesive formulation, appropriate amounts (~25-75 ml) of ammonium hydroxide (NH₄OH)

were added prior to PF addition to prevent gelling from occurring. After completion of the reaction, adhesives were cooled to room temperature followed by an addition of 1% wax emulsion (Cascowax EW-403HS, Borden Chemical Inc) based on dry fiber weight. If deemed necessary, viscosity was adjusted with additional amounts of NH_4OH to allow spraying. Immediately before spraying, propylene carbonate was added at 1% of the total resin solids.

Fiberboard Fabrication and Evaluation

MDF was manufactured using a 1:1 mix of corn and aspen fiber based on oven-dry fiber weight. Enough furnish to make three 15"x15"x½" MDF boards at a target density of 0.75 g/cm³ was placed into a tumbler. Resins were atomized and sprayed onto the fiber furnish at a 12% application rate based on dry fiber weight. Following the completion of adhesive spraying, furnish was removed from the tumbler with the aid of a vacuum/blower. Furnish was hand-felted into a 15"x15" forming box, followed by prepressing. Boards were pressed with a 150-ton hydraulic press with sufficient pressure to allow closing within 30 seconds. All boards were pressed with an eight-minute press cycle at 200°C. Post curing of fiberboards was done overnight in an oven at 100°C. Prior to trimming specimens to 14"x14" to determine densities, fiberboards were conditioned under ambient conditions in the laboratory. Static bending (MOE and MOR) and strength perpendicular to surface (IB) were determined in accordance to ASTM Standard D 1037-96a (ASTM 1998). Dimensional stability samples (3"x4"), conditioned in an environment of 21°C and 65% relative humidity for three days prior to testing, were obtained from bending specimens after failure. Following 2-hour boil measurements, samples were dried and residual IB specimens were obtained.

Experimental Design and Analysis

Experimental design allowed for the examination of three pure protein formulations and two mixtures. Protein hydrolyzates were subjected to three pretreatment regimes, no cross-linking agent, MF, and MDI. In addition to protein-based phenolic resins, laboratory prepared PF and commercial UF controls were also manufactured. Each treatment was

replicated three times. Statistical Analysis System (SAS) programming package was used to analyze data. LSD tests were used to determine differences among means ($p < 0.05$), and controls were done to compare effectiveness of treatments.

RESULTS AND DISCUSSION

Effects of Protein Sources

Properties of MDF bonded with protein-based resins are shown in Table 3. Results show that blood protein-based resins performed superior to soy and feather-based resins in all properties except in MOE and 24-hr TS. Soy-based resin formulations performed better than feather-based resins in all properties examined. As indicated in Table 1, blood meal contains about 16% more protein than low fat soy flour. Protein-PF interactions on the molecular level are anticipated to be predominantly responsible for the development of a three dimensional matrix during adhesive curing. The presence of the additional protein found in blood meal promotes and further enhances co-polymerization. The globulin structure of blood and soy proteins compared to the fibrin structure of feather proteins could explain the fact that properties of boards bonded with resins formulated from feathers were inferior. Feather protein also contains a large quantity of sulfur containing amino acids unlike blood or soy proteins.

Performances of protein-based resins were greatly influenced by different protein sources, and the effect of protein source was highly significant at the 5% level (Table 4). MOE was not affected by resin formulations. Boards bonded with resins containing blood protein had significantly greater MOR and residual IB, while there were no differences in these same properties for boards bonded with soy and feather based resins. For IB and 2-hr boiling TS, blood-based resins were significantly superior to soy-based and soy-based were better than feather-based resins. However, 24-hr TS for soy-based resins were significantly lower than that of blood-based resins, which was better than feather-based resins.

In general, blood-based phenolic resin performed better than soy-based resins, and soy-based resins were better than feather-based resin. However, blood-based phenolic resins characteristically have a high viscosity, which causes problems during spraying. This problem can be overcome by the use of appropriate amounts of NH_4OH , but this is an

additional step in resin formulation. Furthermore, NH_4OH is subject to evaporation, raising the issue regarding pot life and emission of NH_3 .

Phenolic resins formulated with blood/feather mixtures outperformed feather-based resins and resins containing blood/soy mixtures outperformed soy-based resins in most board properties. In fact, there were few differences in properties of boards bonded with blood-based phenolic resins compared to those boards bonded with resins containing blood/feather and blood/soy mixtures (Table 3). When comparing the resin containing blood/soy mixtures and the resin containing blood/feather mixtures, they were not significantly different. Again, the former resin had a similar problem with high viscosity, which needed NH_4OH for viscosity adjustments.

With raw material costs being a significant input into resin formulation, selecting proteinaceous raw materials is an important consideration. Results of this study clearly indicate the advantage of mixing different proteins in formulating protein-based resins. For example, blood meal costs roughly \$0.25 per pound compared to \$0.05 per pound for feather meal. The formulation of a 50/50 mixture by weight significantly reduces overall adhesive costs without compromising board properties. Furthermore, feather hydrolyzate had a much lower viscosity than blood or soy hydrolyzates; therefore formulations containing feather hydrolyzate reduce overall viscosity of the resins, thus eliminating NH_4OH in the formulations.

Effect of Cross-linking Agents

The results in Table 4 show that there was no effect of using cross-linking agents to enhance properties of boards bonded with protein based phenolic resins. This result is contrary to previous studies conducted in our laboratory, which indicated that the use of cross-linking agents enhanced most board properties. Similar results in past experiments were attributed to the inactivity of the cross-linking agent used and corrected by replacement with freshly formulated material. The only difference between this study and the previous ones in resin formulation was that propylene carbonate was used as a polymerization accelerator. Presence of propylene carbonate in protein-based phenolic resins may provide

sufficient cross-linking making pretreatment of protein hydrolyzates with cross-linking agents unnecessary under the reaction conditions used.

Comparison with PF and UF Resins

The MOR of all boards bonded with protein-based phenolic resins, except feather-based resins, were comparable to PF-bonded boards, surpassed those bonded with UF resin, and met the ANSI standard requirements for interior applications (MDF 130). MOE of all boards bonded with protein-based phenolic resins, except feather-based resins, were significantly better than PF and UF-bonded boards and met the ANSI requirements. Boards bonded with PF resin had superior IB, dimensional stability, and residual IB. The best protein-based resin, blood-based resin, was 34% lower in IB, 61% higher in 24-hr soaking TS, 102% higher in 2-hr boiling TS, and 52% lower in residual IB compared to that of PF-bonded boards. All boards bonded with protein-based resins, except those bonded with feather-based resins, had IB's meeting ANSI standards. Most boards bonded with protein-based phenolic resins outperformed UF-bonded boards but had 24-hr soaking TS about 2% above the ANSI standard. Boards bonded with protein-based resins containing only feather protein do not meet ANSI standards for most properties other than MOE and MOR.

CONCLUSIONS

In general, blood-based phenolic resin performed better than soy-based resins and soy-based resins were better than feather-based resin. Differences in protein content and protein structure significantly affected properties of boards bonded with protein-based resins. Minimal differences were exhibited in properties of boards bonded with blood-based phenolic resins compared to those boards bonded with resins containing blood/feather and blood/soy mixtures. Results showed that there was no effect of using cross-linking agents to enhance properties of boards bonded with protein based phenolic resins. MOR of all boards bonded with protein-based phenolic resins, except those bonded with feather-based resins, were comparable to PF-bonded boards, surpassing those bonded with UF resin, and met the ANSI standard requirements for interior applications. Results of this study clearly indicate the advantage of mixing blood protein with other proteins in formulating protein-based

resins. Based on these results, further research should be conducted into different protein mix compositions to find the lowest blood protein content needed in mixtures without seriously compromising performance. Additionally, it is recommended that an investigation of propylene carbonate be conducted to determine the role of cross-linking agents.

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Table 1. General composition of protein sources (%).

	LF soybean flour	Whole blood meal	Feather meal
Protein	49.00	85.00	80.00
Fat	6.00	0.50	1.00
Fiber	3.50	1.00	4.00
Ash	7.00	---	6.00
Carbohydrates	34.50	---	9.00

Table 2. Chemical percentages and reaction conditions of protein hydrolysis.

Protein	NaOH	Na ₂ CO ₃	Temp (°C)	Duration (hrs)
Feather	6	2	130	2
Soy	8	2	140	2
Blood	6	2	130	2

Table 3. Properties of MDF bonded with protein-based phenolic adhesives.^a

Resin properties ^b		Fiberboard properties						
Protein	Cross-linker	Dry strength			24-hr soak		2-hr boil	
		MOR (psi)	MOE (1000 psi)	IB (psi)	TS (%)	TS (%)	R-IB (psi)	
Blood	None	5349	546	124	12.2	27.7	74	
Blood	MF	4972	533	97	12.3	27.1	58	
Blood	MDI	5186	537	109	12.7	27.2	73	
(AVG)		5169 A ^c	539 A	110 BC	12.4 B	27.3 B	68 B	
Feather	None	5470	560	109	13.2	26.9	58	
Feather	MF	4947	520	115	14.4	30.2	58	
Feather	MDI	4930	516	116	11.4	28.5	51	
(AVG)		5116 C	532 AB	113 E	13.0 C	28.5 D	56 D	
Soy	None	5004	520	101	9.5	26.4	61	
Soy	MF	5006	514	111	10.5	26.0	82	
Soy	MDI	5404	540	97	10.6	26.1	60	
(AVG)		5138 BC	525 A	103 D	10.2 AB	26.2 C	68 CD	
Blood/Feather	None	4380	487	49	13.3	34.2	17	
Blood/Feather	MF	4654	545	68	17.2	39.6	16	
Blood/Feather	MDI	3898	474	46	17.9	41.4	5	
(AVG)		4311 AB	502 A	54 B	16.1 B	38.4 BC	13 BC	
Blood/soy	None	4526	519	66	12.1	33.6	22	
Blood/soy	MF	4682	529	89	9.5	30.2	38	
Blood/soy	MDI	4498	548	88	9.0	31.0	31	
(AVG)		4569 A	532 A	81 BCD	10.2 AB	31.6 B	30 B	
PF	--	4981 AB	465 BC	167 A	7.7 A	13.5 A	144 A	
UF	--	3741 D	444 C	83 CD	19.7 D	---	---	
ANSI Standard ^d MDF 130		3481	348	87	10.0	---	---	

^aEach value is the average of 9 boards (3-board batches replicated 3 times); target density = 0.75 g/cm³.

^bResin solid content = 12%, based on dry fiber; PF = phenol-formaldehyde; UF = urea-formaldehyde; MF = melamine-formaldehyde; MDI = polymeric diphenylmethane diisocyanate.

^cMeans in columns with common letters are not significantly different at the 5% level (LSD test).

^dAmerican National Standard Institute (ANSI); MDF for interior applications ANSI A208.2-2002.

Table 4. P values from the analysis of protein, cross-linking agent, and interaction on MDF properties.^a

Resin properties ^b	Fiberboard properties					
	Dry strength			24-hr soak	2-hr boil	
	MOR (psi)	MOE (psi)	IB (psi)	TS (%)	TS (%)	Residual IB (psi)
Protein	<0.001	0.633	<0.001	<0.001	<0.001	<0.001
Cross-linker	0.276	0.702	0.627	0.806	0.608	0.730
Protein*Cross-linker	0.136	0.269	0.611	0.328	0.225	0.887

^aProbability > F^bResin solid content =12%, based on dry fiber.

GENERAL CONCLUSIONS

In general, blood-based phenolic resin performed better than soy-based resins and soy-based resins were better than feather-based resin. High protein content in blood meal could be responsible for boards bonded with blood-based resins exceeding soy in most properties. The presence of the additional protein found in blood meal promotes protein-PF interactions and further enhances co-polymerization. The structure of globulins compared to that of fibrin could explain the fact that properties of boards bonded with resins formulated from feathers were inferior. Performance of protein-based resins is greatly influenced by different protein sources, the effects of protein source is significant at the 5% level.

High viscosities of blood-based phenolic resins caused problems during spraying, but can be overcome with addition of appropriate amounts of NH_4OH . Due to NH_4OH 's tendency for evaporation, questions regarding pot life and emission of NH_3 arise.

Phenolic resins formulated with blood protein in combination with soy or feather proteins typically outperformed soy-based and feather-based resins alone. In fact, few differences were exhibited in properties of boards bonded with blood-based phenolic resins compared to those boards bonded with resins containing blood/feather and blood/soy mixtures. Comparison of resins containing blood/soy mixtures and resins containing blood/feather mixtures shows that there were no significant differences in board properties. Blood/soy mixtures had a similar problem as blood-based resins concerning high viscosity, which required the addition of NH_4OH for viscosity correction. Results of this study clearly indicate the advantage of mixing blood protein with other proteins in formulating protein-based resins.

Contrary to previously conducted research within our laboratory, results showed that there was no effect of using cross-linking agents to enhance properties of boards bonded with protein based phenolic resins. Similar results in past experiments were attributed to the inactivity of the cross-linking agent used and corrected by replacement with freshly formulated material. The addition of propylene carbonate as a phenolic resin polymerization accelerator was the only difference between the present study and the previous ones.

Therefore, pretreatment of protein hydrolyzates with cross-linking agents may be unnecessary with the addition of propylene carbonate.

MOR properties of all boards bonded with protein-based phenolic resins were comparable to PF-bonded boards, surpassing those bonded with UF resin, and met the ANSI standard requirements for interior applications. Boards bonded with PF resin had superior IB, dimensional stability, and residual IB. All boards bonded with protein-based resins, except those bonded with feather-based resins, had IB properties meeting ANSI standards. Boards bonded with blood-based resin were lower in IB, higher in 24-hr soaking TS, higher in 2-hr boiling TS, and lower in residual IB compared to PF-bonded boards. The 24-hr soaking TS of boards bonded with protein-based resins were only about 2% above the ANSI standard requirement. Board properties of most protein-based phenolic resins outperformed UF-bonded boards.

Based on the present study, two recommendations are put forth for further investigations:

- I. Investigate different blood/feather protein mix compositions to find the lowest blood protein content needed without seriously compromising performance. Currently, protein mixture formulations are based on 35% blood hydrolyzates, 35% feather hydrolyzates, and 28% PF and are as good as formulations containing 70% blood hydrolyzates and 28% PF. Future formulations of protein-based resins could include formulations containing lower amounts of blood proteins. Findings have the potential to further reduce overall adhesive costs as well as overcome viscosity problems.
- II. Investigate the role of propylene carbonate to determine whether it definitely replaces the role of cross-linkers.

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