

WHEY PROTEIN-BASED WATER-RESISTANT AND ENVIRONMENTALLY SAFE ADHESIVES FOR PLYWOOD

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Whey protein is a renewable and environmentally safe biomaterial, a by-product of cheese production. It can be utilized for non-food applications for value-added products. The substances glyoxal (GO), glutaraldehyde (GA), polymeric methylene biphenyl diisocyanate (p-MDI), urea-formaldehyde (UF) resin, and phenol-formaldehyde oligomer (PFO) that contain reactive groups were applied together with whey protein as modifier in order to increase crosslinking density and molecular weight for improving the bond strength and water resistance of whey protein. A water-resistant and environmentally safe whey protein-based wood adhesive for plywood was developed by evaluating the effects of these modifiers on the bond strength, bond durability, and free formaldehyde emission of the resulting plywood panels. Results of FTIR and SEM analyses and bond evaluation indicated that GO, GA, and p-MDI were not suitable to modify whey proteins due to their high reactivity with whey proteins, causing phase separation. UF resin was not a good modifier for whey proteins because of either its poor water-resistance or higher emission of hazardous formaldehyde. Whey protein adhesives modified with PFO had a dry shear bond strength of 1.98 MPa and a 28h-boiling-dry-boiling wet shear strength of 1.73 MPa, which were both much higher than the required values for structural use according to standard JIS K6806-2003, while its formaldehyde emission was 0.067mg/L, much lower than the required value for green plywood according to standard JIS A5908.

Keywords: Wood adhesive; Whey protein; Plywood; Water resistance; Environmental safety

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INTRODUCTION

Ever-increasing attention is being given to obtaining useful materials from renewable bio-based resources. Such attention is motivated by a decrease in availability and increase in cost of non-renewable fossil-based raw materials; therefore, research has focused on renewable resources such as biomass energy, green chemicals and materials, or developing substitutes for petroleum-based materials. A variety of bio-based materials, such as cellulose (Zhang 2003), lignin (Sarkar and Adhikari 2004), tannin (Santana *et al.* 1995), wood (Lee and Chen 2008), corn bran (Lee *et al.* 2000), starch (Yao *et al.* 1995), barks (Yuan *et al.* 2009), bamboo (Yip *et al.* 2009), waste paper (Lee *et al.* 2002), and soybean protein (Kumar *et al.* 2002; Wang *et al.* 2007), have been characterized and

investigated with regard to the preparation of bio-based plastics, adhesive, foams, and other bio-polymers.

Whey protein is a by-product of cheese making. Generally, about 8 to 9 kg of whey is generated for every kilogram of cheese produced (Onwulata and Huth 2008). A large amount of whey is generated in Europe and North America annually. It was estimated by the USDA National Agricultural Statistics Service that more than 90 billion pounds (*ca.* 40 billion kg) of whey was produced in the US in 2008. Whey protein is one of the major components in whey; however, whey protein has not been fully utilized other than as a food ingredient, and more than 30% of whey production is directly disposed to the environment in the US, which results in waste of bio-resources and environmental pollution.

Whey protein comprises of β -lactoglobulin (50%), α -lactalbumin (20%), bovine serum albumin (6-7%), and immunoglobulin (12-13%) in cow's milk, which collectively account for about 18% of the total protein in milk (Smithers 2008; Walstra *et al.* 1999). Unlike soybean proteins or casein, whey proteins are generally compact globular proteins with much lower molecular weights and multiple components; thus whey proteins are often referred to as "waste proteins". Use of whey proteins in non-food applications such as adhesives might create value-added products in addition to applications in food (van der Leeden *et al.* 2000).

Commercial adhesives for bonding wood are predominantly UF resin and phenol-formaldehyde (PF) resin, which are derived from petroleum-based resources (Sellers 2001). In addition, wood products bonded with formaldehyde-based adhesives may release hazardous formaldehyde, which has been classified as a carcinogen by the World Health Organization (WHO Report 2004); therefore, studies have focused on the development of environmentally safe wood adhesives from renewable bio-resources, such as soybean protein-based adhesives (Hojilla-Evangelista 2002; Zhong *et al.* 2003), lignin (Sarkar and Adhikari 2004; Khan *et al.* 2004), and tannin (Vázquez *et al.* 2009; Kim 2009). Whey proteins have, however, seldom been studied for making wood adhesives. With this in mind, the aim of this study was to develop water-resistant and environmentally safe wood adhesives using whey protein with modifications for structure plywood manufacture.

EXPERIMENTAL

Materials

Whey protein isolate was provided by Fonterra Ltd. (New Zealand) with a protein content of 92.4%. A whey protein solution (40 wt%) was prepared before use. Polymeric methylene biphenyl diisocyanate with a free isocyanate group (NCO) weight content of 31.4% was obtained from Nippon Polyurethane. All chemicals were reagent grade. Commercial UF resin for plywood manufacture with a formaldehyde/urea molar ratio of 1.1, solid content of 53.2%, and a pH of 8.2 was supplied by a local adhesive company. Commercial PF resin for plywood manufacture with a formaldehyde/phenol molar ratio of 2.1, solid content of 40.8%, and a pH of 12.6 was supplied by a local adhesive

company. Birch veneers of dimensions 420 mm × 420 mm (1.6 mm in thickness) were obtained from a local plywood plant with moisture contents of about 2.5%.

Preparation and Pretreatment of PFO

A 1000 mL reaction kettle equipped with a mechanical stirrer, a thermostat, and a condenser for reflux was charged with 235 g of phenol, 513.7 g of a formalin solution with a formaldehyde concentration of 36.5 wt%, and 12.8 g of a NaOH solution (50 wt%). Then, the mixture was heated to 60°C and maintained at this temperature for 1 h. Thereafter, the reaction mixture was kept at 75°C for 1 h and then at 55°C for 4 h. The formaldehyde/phenol ratio and NaOH/phenol ratio for the PFO were 2.5 and 0.064, respectively. The reaction resultant had a pH between 9.0 and 9.3, a free formaldehyde content of 5.1%, and a solid content of 53.9%. Because free formaldehyde will react with whey protein and lead to the polymerization of whey proteins, ammonia and sodium sulfite were used to scavenge all free formaldehyde in PFO as follows: The PFO solution, 724.4 g, was transferred to a 1 L beaker with magnetic stirring, and formic acid was added gradually to reduce pH value to be about 6.0. Then 50 g of 28wt% ammonia was added with continued stirring for 10 min. After that, 56.3 g sodium sulfite was added into the mixture and kept stirring for another 10 min. Finally, formic acid was added gradually to reduce the pH of mixture to 6.5 to 7.0.

Adhesive Formulations

The whey protein solution (40 wt%) was heated to 60°C and held for 35 min. for thermal modification in order to improve its adhesion to the wood surface by adsorption via partially unfolding the globular structure of the whey protein and releasing the hidden or bonded polar groups (Gao *et al.* 2011). The treated whey protein solution was then blended with 5 modifiers, GO, GA, p-MDI, UF, and PFO, to obtain 5 modified whey protein-based wood adhesives. The formulations of each modified adhesive are shown in Table 1. The denatured whey protein solution was only used as a control adhesive.

Plywood Evaluation

Birch (*Betula platyphylla*) veneers were laminated into 3-ply plywood panels. The adhesive was applied at a spread rate of 300 g/m² in a double glue line. After applying the adhesive, the veneers were immediately assembled into panels and then hot-pressed at 140°C (for the adhesive modified by PFO) or 125 °C (for other adhesives) and 1.4 MPa for 4.5 min. The higher hot-pressed temperature was selected for PFO-modified adhesive because the curing reaction of PF resin or PFO requires higher temperature according to one of our previous study (Yuan *et al.* 2009). Two replicate panels were prepared with each adhesive. The plywood panels were sealed in independent PE plastic bags after cooling.

After the panels had been stored at room temperature for 24 h, specimens were cut to determine the dry-state shear bond strength, wet-state shear bond strength, and formaldehyde emission. A total of 30 specimens were cut from each panel for bond strength tests (15 for dry state and 15 for wet state) according to the JIS K6806-2004 standard. The specimens tested for wet-state bond strength were subjected to boiling water for 4 h, dried at 60 °C for 20 h, and further boiling in water for 4 h before testing.

Ten specimens were also cut from each panel to determine the formaldehyde emission according to JIS A1460-2003 standard (Building boards determination of formaldehyde emission -Desiccator method). As for the plywood panels bonded with finally optimized adhesive, its formaldehyde emission was also determined by ASTM D6007 (Standard Test Method for Determining Formaldehyde Concentration in Air from Wood Products Using a Small Scale Chamber) and ASTM D5197 (Standard test method for determination of formaldehyde and other carbonyl compounds in air).

Scanning Electron Microscope (SEM) Analysis

Samples of each adhesive, except the one modified by the UF resin, were placed in a Teflon pool sealed with a 1.5 mm-thick Teflon film, then cured at 140°C (for adhesive G modified by PFO) or 125 °C (for other adhesives) for 4.5 min to stimulate the plywood bonding under hot pressing. The whey protein-based adhesive after curing formed a transparent film with a thickness of about 1.2 mm. The cured adhesive film was fractured, and the fractured surface was examined with a QUANTA-200 SEM (FEI Co., USA).

Fourier Transform Infrared (FTIR) Analysis

Samples of each adhesive, except the one modified by the UF resin, were placed in a Teflon pool and then freeze dried at -50°C and at -25 Pa for 3 days. The freeze dried adhesive powder was mixed with potassium bromide (KBr) with a mass ratio about 1/150, ground into fine powder, then pressed in a special mold into a sample folium, and finally scanned using a Magna IR560 FTIR instrument (Nicolet Co., USA). The cured adhesive film at 125°C for 4.5 min for SEM analysis was also analyzed by FTIR.

RESULTS AND DISCUSSION

Whey proteins are generally composed of compact globular proteins. It has been reported that globular whey proteins without unfolding mostly formed compact layers or sometimes even rigid particles via adsorption (Norde and Favier 1992; Haynes and Norde 1995), which led to poor interfacial strength or bond strength during adhesion. Unfolding the structure by heating not only can release the hidden or bonded polar groups in whey proteins, but it also can offer additional cohesion strength of the adhesive due to the inherent intermolecular disulfide linkages, resulting in more efficient and firm attachment to the wood surfaces by adsorption. Parris and Baginski (1991) confirmed by reversed-phase HPLC that whey protein started denaturing at about 40°C, and denaturation became more rapid at 70°C. Qi and co-workers (1997) also indicated that the thermal denaturation of β -lactoglobulin at neutral and alkaline pH values showed a pronounced dependence on protein concentration. Previous work (Gao *et al.* 2011) also confirmed that thermal denaturation of whey protein at 60°C for 35 min at a neutral pH could partially unfold some of the globular structures of whey proteins and improve the bond strength of whey protein-based aqueous polymer-isocyanate (API) adhesives.

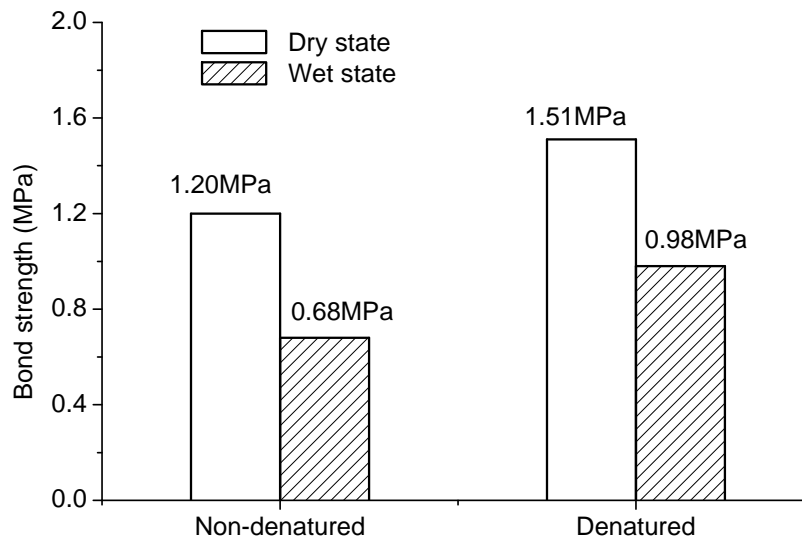


Fig. 1. Effect of thermal denaturation of whey proteins on bond properties of plywood panels

The results of plywood evaluation showed a positive effect of thermal denaturation on bond strength and durability of plywood bonded by the whey protein solution (40 wt%) alone as adhesive (Fig. 1). After thermal modification at 60°C and a neutral pH for 35 min, the whey protein solution produced a dry-state strength of 1.51 MPa and a wet-state strength of 0.98 MPa, which were respectively 25.8% and 44.1% more than that of the sample without heat treatment. The results also indicated that the whey protein solution alone (denatured or not) as an adhesive had a good dry bond strength, more than the required value (1.18 MPa) for structural use according to standard JIS K6806-2003. Though the bonded plywood could bear 4 h of boiling water, 20 h dry at 60°C, and an additional 4 h of boiling water, the bond durability and water resistance in terms of wet bond strength were not favourable. The wet bond strength of the whey protein after denaturing could marginally reach the required value (0.98 MPa) for structural use according to standard JIS K6806-2003.

Whey protein is soluble in water, but it clearly became water resistant after it was cured with hot pressing at 125°C. This observation is attributed to the heat-induced cross-linking of whey proteins resulting from disulfide bonding of sulfhydryl groups and sulfhydryl-bisulfide interchanges between cysteine and cystine (Shimada *et al.* 1989). After denaturation, the buried sulfhydryl groups within the globular structure were exposed and formed disulfide bonding, and thus increasing the wet strength of the plywood bonded with denatured whey protein from 0.68 MPa to 0.98 MPa; however, the total content of cysteine and cystine in whey proteins is about 2.4% according to the residual amino acids in whey proteins (McDonough *et al.* 1974). This indicated that the heat-induced crosslinking resulted from the cysteine and cystine was 2.4% at most, which was insufficient to give enough water resistance. Thus chemical modifications inducing crosslinking may be required to improve the water resistance of whey protein-based adhesives.

Whey proteins are rich in free hydroxyl groups (up to 0.1 mole per 100 g of whey protein) and residual amino groups (up to 0.13 mole per 100 g of whey protein) (Onwulata and Huth 2008; Tunick 2008), which readily react with active groups such as aldehyde groups (-CHO), isocyanate groups (-NCO), and hydromethyl groups (-CH₂OH); thus chemicals or synthetic resins containing two or more reactive groups, such as GO, GA, p-MDI, UF resin, or PF resin, can be used to crosslink whey proteins to form polymers with larger molecular weights and three-dimensional networks with good cohesive strength and water resistance. Because of this effect, GO, GA, p-MDI, UF resin, PF resin, and PFO were introduced separately into denatured whey proteins for chemical modifications. The formulas and properties of the modified whey protein-based adhesives are summarized in Table 1.

Table 1. Properties of Plywood Panels Bonded by Different Whey Protein-based Adhesives

Adhesive components	Dry strength (MPa)	Wet strength (MPa)	Formaldehyde emission (mg/L)
Whey protein (WP) only	1.51 (0.36)	0.98 (0.19)	0.042 (0.006)
WP + 25wt% UF	1.72 (0.24)	0.67 (0.26)	0.667 (0.030)
WP + 0.15wt% GA	1.98 (0.26)	0.83 (0.22)	0.078 (0.005)
WP + 1wt% GO	1.40 (0.36)	0 (N/A)	0.028 (0.003)
WP + 1wt% p-MDI	1.78 (0.35)	0.93 (0.17)	0.032 (0.005)
WP + 30wt% PFO	1.98 (0.37)	1.73(0.26)	0.067(0.005)
Standard value	>1.18	> 0.98	< 0.5

Note: values in parentheses are standard deviations; the levels used are the liquid modifier on the basis of liquid whey protein solution. Standard values of dry and wet bond strength are specified in JIS K6806-2003 standard for structural plywood; standard value of formaldehyde emission is specified in JAS JPIC-EW.SE00-01 standard for E₀-grade plywood.

UF and PF resins are predominantly used in the wood industry due to their low costs and acceptable bonding properties. In addition, whey proteins contain free amino groups (up to 0.13 mol per 100 g of whey protein), which could have been crosslinked by the free formaldehyde or methylol in the UF resins and the PF resins; therefore, PF and UF resins were used to modify the whey proteins. The whey protein solution, however, became gelled immediately after it was mixed directly with the thermosetting PF resin due to the higher pH value (12.6). When the pH of the PF resin was adjusted to neutral (6.8 to 7.0) using phosphoric acid or *para*-toluene sulfuric acid, it became too viscous (almost agglomerated) to blend with the whey protein solution. This should be attributed to the poor solubility of PF molecules under neutral condition. The condensation polymerization of hydroxymethylated phenols during resin synthesis generally resulted in PF molecules with the phenol rings linked by the -CH₂- or -CH₂-O-CH₂- bridges. For wood adhesive applications, PF resins are normally synthesized at a sodium hydroxide content of up to 0.8 mole per mole of phenol (Kin *et al.* 1994). With so much sodium hydroxide present, the phenol with poor solubility is converted into strongly hydrophilic sodium phenate. When acid was introduced, the hydrophilic sodium phenate formed phenol again and agglomerated. As a result, the PF resins after neutralized become very viscous due to the agglomeration of PF molecules. Because of this, the PF resin was unable to be used as a modifier.

The UF resin was neutral or slightly alkaline (pH value of 7.6) and blended well with whey protein solutions without a considerable increase in viscosity. The results in Table 1 indicate that using a 25% UF resin as a modifier increased the dry bond strength by 13.9% compared to that of the control whey protein alone; however, the adhesive modified with the UF resin resulted in poor water resistance, a 31.6% decrease in wet-state bond strength due to the poor water resistance of the UF resin itself. Additionally, this modified adhesive had a higher formaldehyde emission (0.67mg/L), which was much higher than the required value (<0.3mg/L) for green plywood according to JIS standard A5908-2003; therefore, the UF resin was also labeled as a poor modifier for whey protein-based adhesives.

Both GO and GA contain two active aldehyde groups that can react with the amino groups of whey proteins and crosslink whey protein molecules, as shown in Eq. (1). Every p-MDI molecule has 2.7 isocyno groups on average, and the active isocyno groups will react with amino groups to form polyurea, thus crosslinking the whey protein molecules, as shown in Eq.(2).

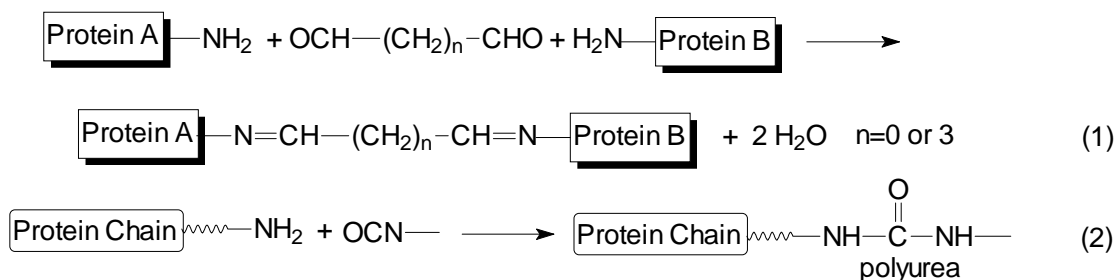


Fig. 2. Chemical reactions of whey proteins modified by dialdehyde and p-MDI

GO, GA, and p-MDI are very reactive to whey protein; however, they result in a rapid increase in viscosity of the adhesive immediately after mixing with the whey protein solution. The modifier levels must be reduced with consideration of acceptable spreading of the adhesives. As for GA and p-MDI as modifiers, the preferable levels were 0.2% and 1%, respectively. Otherwise, the mixtures would gel too quickly to be spread onto veneer because the aldehyde groups of GA and isocyno groups of p-MDI will immediately react with the amino groups of whey proteins. GO didn't clearly react with the protein at room temperature due to the steric hindrance of the two adjoining aldehyde groups, but the maximal level was 2% with 1% being the most optimal. The results in Table 1 indicate that whey protein adhesives modified with GA and p-MDI resulted in an increase of dry bond strength by 31.1% and 17.9%, respectively, compared with the control whey protein solution without modification, but their water resistance or wet-state bond strength slightly decreased. While plywood bonded with an adhesive modified by GO showed a lower dry bond strength, it could not bear water boiling treatment, indicating poor water resistance. Theoretically, whey proteins modified by dialdehyde and p-MDI could cause an increase in molecular weight and crosslinking density, preventing the adhesive molecules from slipping or even separating under wet or boiling conditions; therefore, the modified adhesives should have better water resistance. The bond evaluation in Table 1, however, indicates that plywood panels bonded by these whey protein-based adhesives modified by GO, GA, and p-MDI showed lower wet

strength or worse water resistance than those bonded by whey protein solutions without crosslinking modification. Because of this, the FTIR and SEM were used to investigate the effects of modifiers on the bond strength.

Because the contents of modifiers were low, ranging from 0.15% to 1%, FTIR could not effectively detect the variations of chemical structures related to the crosslinking reaction of these modifiers. Consequently, the FTIR spectra of the adhesives before and after cured were quite similar to each other although the modifiers were clearly different, as illustrated in Fig. 3.

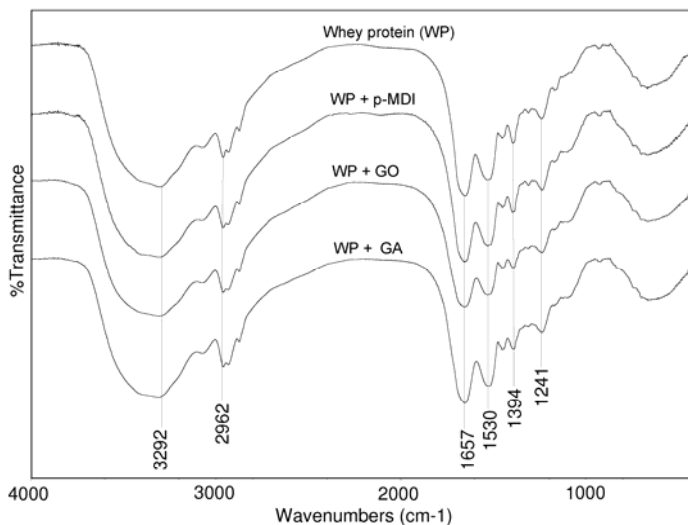


Fig. 3. FTIR spectra of whey protein based adhesives after curing at 125°C

SEM micrographs in Fig. 4 present the morphologies of the fracture surfaces of the whey protein-based adhesives after curing at 125°C for 4.5 min., similar to the hot-pressing conditions for plywood manufacture. The fracture surface of cured whey protein adhesives only appeared microscopically rough and corrugated like alternating ridges and grooves at a 500X magnification, as shown in Fig. 4A, suggesting that there was more than one fracture initiation point, indicating that crack propagation energy was high enough to allow the formation of additional fracture initiation points. Due to this effect, this adhesive showed better bond durability or wet-state bond strength than the other three adhesives modified by p-MDI, GA, and GO. Figures 4B and 4C show the fracture surfaces of adhesives modified by 1% p-MDI and 0.15% GA, respectively. Because the MDI and GA are so reactive towards the amino groups of whey proteins, the crosslinking reaction immediately started and formed some insoluble complexes in the adhesive when MDI or GA was mixed with whey protein solutions. During the curing reaction at higher temperatures, the insoluble resultants were separated from the cured whey protein matrix (phase separation), as shown apparently in Figs. 4B and 4D. Unfortunately, the insoluble resultant forming before curing resulted in porous structures with many pores as defects. The phase separation of insoluble resultants from the whey-protein matrix decreased the crack propagation energy when the adhesive was loaded because the stress concentrated at the defects and accelerated crack propagation. Consequently, the alternating ridges and grooves were not as evident near the insoluble-resultant phases, as represented by a lower

wet-state strength than the whey protein only as the adhesive. As for adhesives modified by 1% GO, the fracture surfaces appeared microscopically flat with lots of insoluble-resultant phases, as shown in Fig. 4D.

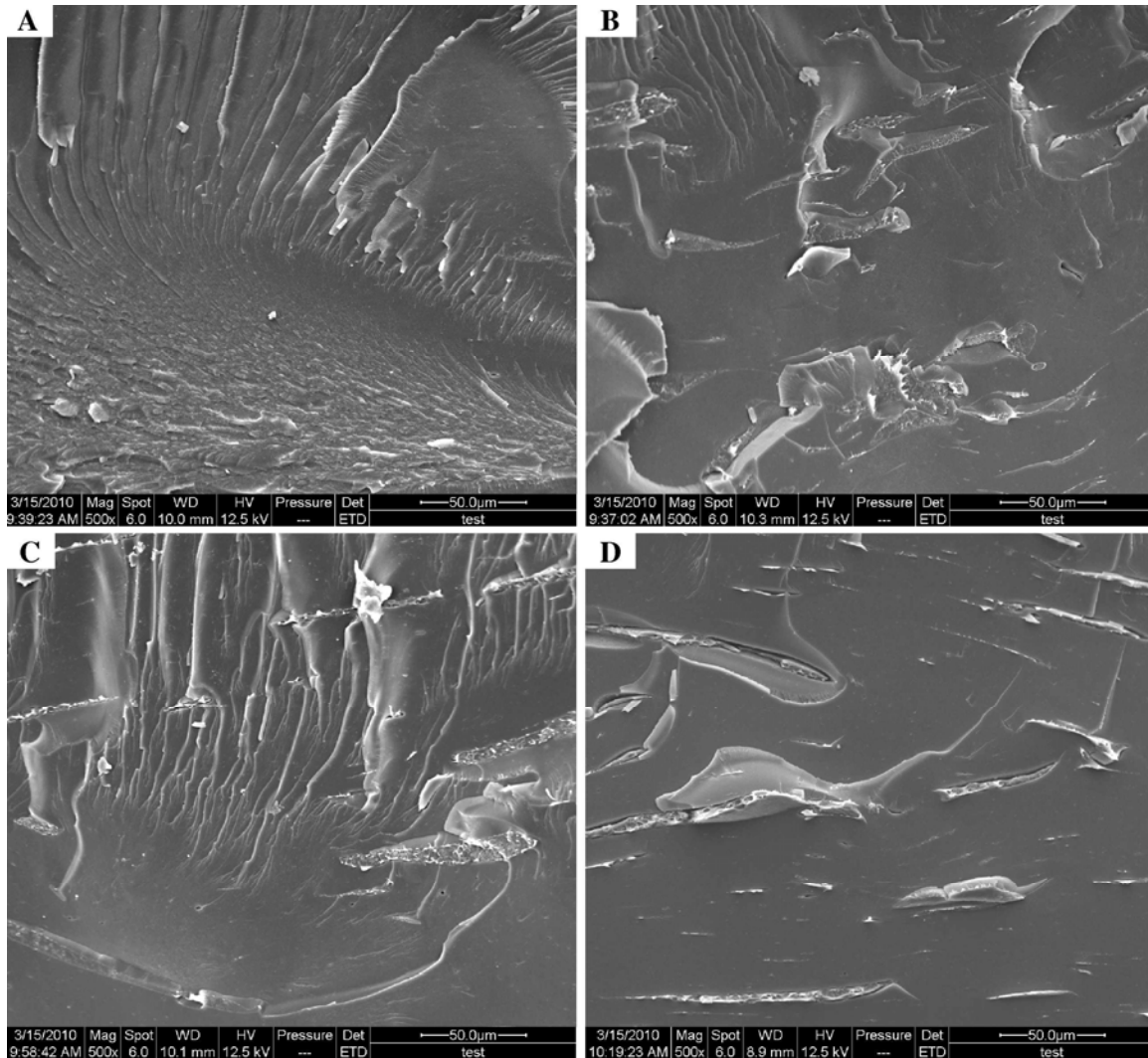


Fig. 4. SEM micrographs of whey protein based adhesives cured at 125°C
A: Whey protein (WP); B: WP + p-MDI; C: WP + GA; D: WP + GO

The flat fracture surfaces suggest that crack propagation energies were very low, meaning that the cracks could propagate quickly through the adhesive sample from a single fracture initiation point. In other words, the adhesive layer could not absorb high energy or high loads before fracture; therefore, when plywood specimens for bond evaluation were boiled in water, the different expanding coefficients between the wood and adhesive yielded a strong internal stress that was enough to break the bondline. In addition, there were many more insoluble-resultant phases in the whey protein matrix than that of the other adhesives, resulting in stronger stress concentrations at the insoluble-resultant phases or near areas that accelerated the breakage of bondlines. As a

result, the plywood specimens bonded by an adhesive modified by GO could not withstand the boiling water conditions for 4 h and led to an absence of wet strength.

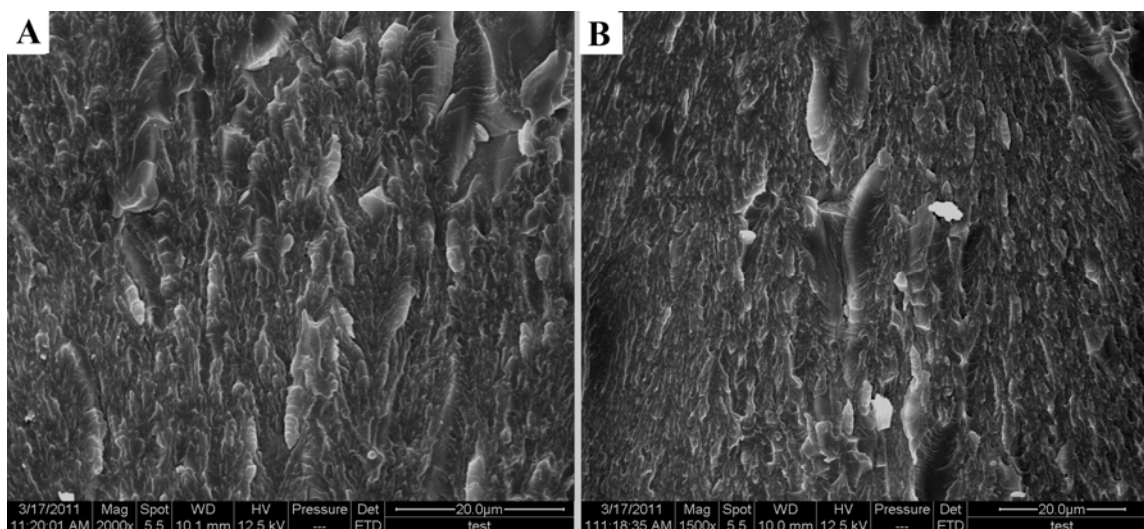


Fig. 5. SEM micrographs of PFO-modified whey protein based adhesives cured at 125°C

Based on these results, it may be concluded that the modifiers UF resin, PF resin, p-MDI, GA, and GO are not suitable to modify whey proteins to improve the water resistance of the resulting adhesives. Because of the poor solubility due to higher molecular weight and strong alkalinity of the thermosetting PF resin, it was proposed to substitute a PF oligomer for the PF resin for whey protein modification. Preliminary results indicated that a mixture of phenol and formaldehyde reacted at a lower temperature (60 to 75°C) with a low level of NaOH as a catalyst could result in a PFO suitable for whey protein modification. This PFO mainly composed of multi-hydroxy-methyl phenol and some low-molecular-weight condensation polymers. As a result, PFO still has good water solubility and lower viscosity after neutralization to a pH of 6.5 to 7.0, which were required for blending with the whey protein solution. When neutralized PFO was blended with the whey protein solution, however, the viscosity of the mixture increased very quickly or even gelled. This was attributed to the crosslinking reaction of whey protein by formaldehyde due to the high level of free formaldehyde content (5.1%) of PFO than that of the commercial PF resin (<0.1%). Selected amounts of ammonia and sodium sulphite, therefore, were used to scavenge the free formaldehyde in the neutralized PFO solution. After complete removal of free formaldehyde and pH neutralization, the treated PFO solution was well compatible with the whey protein solution without considerable increase in viscosity. As expected, the whey protein adhesive modified by 30 wt % of this PFO (liquid PFO on basis of liquid whey protein solution) resulted in an improvement in bond strength and water resistance. The dry-state and wet-state bond strengths were 1.98 MPa and 1.73 MPa, respectively, and increased 31.1% and 76.5% compared with that of the control whey protein solution as an adhesive. Both values were much higher than the required values (1.18 MPa and 0.98 MPa, respectively) for structural plywood according to standard JIS K6806-2003, indicating that the plywood panels can be used for structural purposes.

SEM micrographs shown in Fig. 5 indicated that the fracture surface of cured whey protein adhesives modified by PFO appeared considerably rough, suggesting very high crack propagation energy. This implied that PFO sufficiently crosslinked the whey proteins to form a strong network entity with good bond strength and water resistance. The PFO modified adhesive also had a very low formaldehyde emission (0.067 mg/L) that was comparable to the control whey protein solution (0.042 mg/L). This value was much lower than the required value (<0.3 mg/L) for green plywood according to JIS standard A5908-2003. The formaldehyde emission of plywood bonded by PFO modified adhesive was also measured according to ASTM D6007 and D5197, which was about 4.3 ppb (0.0043 ppm), much lower than required value (0.05 ppm) according to CARB (California Air Resources Board) Phase Two Emission Standards. This result indicated that the plywood bonded by PFO modified whey protein had almost no formaldehyde emission; therefore, the PFO modified whey protein-based adhesive has great potential for commercial application because of its excellent bond strength, water resistance, and environmentally safe characteristics.

CONCLUSIONS

1. The effects of five modifiers on the bond properties of adhesives for plywood were investigated.
2. A whey protein-based and environmentally safe wood adhesive was developed with good bond strength and water resistance that meets the requirements for structural wood applications and environmental standards.
3. Heat-induced polymerized whey proteins can be used to formulate environmentally safe wood adhesives for structural plywood manufacturing after modification by pre-treated of PFO free of formaldehyde at a neutral pH.
4. Due to the poor water resistance, high formaldehyde emission, and high reactivity, the modifiers UF resin, p-MDI, glutaraldehyde, and glyoxal are not suitable for modifying whey proteins as a green water-resistant plywood adhesive for structural use.

ACKNOWLEDGMENTS

The authors are grateful for the supports by a grant from USDA-NIFA and the Graduate Research Fund of the Northeast Forestry University (STIP10).

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Article submitted: May 31, 2011; Peer review completed: June 30, 2011; Revised version received: July 14, 2011; Accepted: July 17, 2011; Published: July 19, 2011.