WATER-RESISTANT WHEY PROTEIN BASED WOOD ADHESIVE MODIFIED BY POST-TREATED PHENOL-FORMALDEHYDE OLIGOMERS (PFO)

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With the attempt to develop an environmentally safe whey protein-based adhesive with good water resistance, a low-molecular-weight PFO was used as a modifier, and the effects of scavengers on the formaldehyde emission and bond properties were investigated. Plywood evaluation and HPLC analysis indicated that the PFO synthesized with a low content of sodium hydroxide as a catalyst (NaOH/phenol mole ratio = 0.064) at a low reaction temperature (60-75^{o}C) had good water solubility and very low viscosity that was preferable to the modification of whey protein-based adhesives. Combinations of ammonia and sodium sulfite as formaldehyde scavengers had positive effects on the formaldehyde emissions of plywood panels bonded by the PFO-modified whey protein adhesives and had slight effects on bond properties. A necessary stoichiometric excess of ammonia-sulfite combination during PFO post-treatment is critical to effectively reduce formaldehyde emission. The whey protein-based adhesive modified with the most preferable post-treated PFO is water-resistant and environmentally safe, which had a dry shear bond strength of 1.98 MPa and a 28 hour-boiling-dry-boiling wet shear strength of 1.73 MPa according to standard JIS K6806-2003, a formaldehyde emission of 0.067mg/L according to standard JIS A5908, and undetectable level of free phenol by HPLC.

Keywords: Wood adhesive; Whey protein; Phenol-formaldehyde oligomer; Formulation; Water resistance; Environmentally safe

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INTRODUCTION

There is a growing demand to reduce the use of petroleum and minimize environmental pollution associated with the burning of fossil fuels by adopting renewable and environmentally safe alternatives. Biomass is an important alternative for both energy and chemical production that meets these requirements (Coleman *et al*. 2006). Biomass is considered an abundant carbon-neutral renewable resource for the production of bioenergy and biomaterials, and its use would address several societal needs (Ragauskas *et al*. 2006). Though adhesives for bonding wood are predominantly petroleum-derived resins, such as urea-formaldehyde, phenol-formaldehyde, polyvinyl acetate, and polyurethane, biomass-based adhesives intrigue many researchers. Different biomass stocks, such as soy flour (Huang *et al*. 2007), lignin (Mansouri *et al*. 2006), tannin (Kim 2009; Moubarik *et al*. 2009), and animal blood (Lin *et al*. 2010) have been studied for manufacturing adhesives.

Whey protein, derived from a by-product of cheese making, is a type of biomass that is widely used as a food ingredient, but it is rarely applied for wood adhesive formulations. About 1 kg of cheese and 8 to 9 kg of whey are generated from every 10 kg of cow's milk (Onwulata *et al*. 2008). As a result, a large amount of whey is generated annually in Europe and North America, where cheese production is prevalent. It was estimated by the USDA National Agricultural Statistics Service that more than 90 billion pounds (about 40 billion kg) of whey was produced in the US in 2008. However, more than 30% of whey is disposed to the environment directly in the US, resulting in waste of bio-resources and environmental pollution. Therefore, there is an increasing economic and environmental need for developing new applications for whey products, especially whey proteins. However, whey proteins are often so-called "waste proteins" for they are generally composed of multiple components with compact globular structure and low molecular weight, commonly 50-53% β-lactoglobulin, 19-20% α-lactalbumin, 6-7% bovine serum albumin, and 12-13% immunoglobulin in bovine milk (van der Leeden *et al*., 2000; Gao *et al*., 2011a; Wang *et al*., 2011). As a result, whey proteins are considered somewhat unsuitable for preparing adhesives. However, whey protein can be used to prepare wood adhesive by reason of the following facts: Whey protein is readily soluble in water, able to form gels or crosslinks by heating, and capable of attaching firmly to a wood surface by the absorption of its abundant polar groups (van der Leeden *et al*. 2000; Gao *et al*. 2011b).

Because the use of whey proteins in adhesives is expected to have higher added value than the application in food, some studies have focused on whey protein-based adhesives. Based on the fact that whey proteins are rich in hydroxyl groups and excessive amino groups that can react with polyisocyanates, an aqueous polymer-isocyanate (API) adhesive was developed by blending 100 parts of water based glue from whey protein with 15 parts of p-MDI as a crosslinker. This API adhesive had a 28 hour boiling-dry-boiling wet strength of 6.81 MPa, and a dry strength of 14.34 MPa, according to the test procedures in JIS K6806-2003 standard, showing good potential for commercial applications for Glulam by cold-press technology (Gao *et al*. 2011a,b). High-concentration whey protein solutions may become gel when the temperature is more than 60°C, due to both disulfide bonding of sulfhydryl groups and sulfhydryl-bisulfide interchanges between cysteine and cystine (Shimada *et al*. 1989; Parris *et al*. 1991; Qi *et al*. 1997). The characteristic of heat-induced gelation is especially advantageous in the preparation of adhesives that are cured under hot-press conditions. However, whey protein solution alone cannot be a good wood adhesive, because whey protein contains only about 2.4% of cysteine and cystine, which play a critical role in disulfide bonding interaction and sulfhydryl-bisulfide interchanges (McDonough *et al*. 1974; Barone *et al*. 2006). As a result, modifiers, including glyoxal, glutaraldehyde, p-MDI, urea-formaldehyde resin, and PFO, were applied to improve the bond strength and bond durability of whey protein-based adhesives (Wang *et al*. 2010; 2011). Of them, the whey protein based adhesive, modified by 30% PFO, showed good bond properties that are much higher than the required value according to the commercial standard and have almost no formaldehyde emission (Wang *et al*. 2011).

However, PFO for modifying whey protein adhesives should be synthesized under gentle conditions (NaOH/phenol mole ratio of about 0.06 and reaction temperature

of 60-75°C) in order to reduce its viscosity and improve the water solubility. This leads to an incomplete reaction between phenol and formaldehyde, and the obtained PFO will have a much higher content of free formaldehyde. The free formaldehyde can crosslink whey proteins by reacting with the residual amino groups and consequently results in quick gelation of the modified whey protein adhesive, which may also increase the formaldehyde emission of wood composites bonded by the resulting adhesive. Therefore, the purpose of this study was to investigate the effects of PFO post-treatments on the formaldehyde emissions and bond properties of the modified whey protein adhesives.

EXPERIMENTAL

Materials and Preparations

Whey protein isolate (WPI) was provided by Fonterra Ltd. (New Zealand) with protein content 92.4%. WPI was gradually dissolved in distilled water at 40 to 50°C to form a solution at 40wt% before use. Other reagent-grade chemicals, such as phenol, paraformaldehyde (95.7%), sodium hydroxyl (NaOH), formic acid, ammonia, sodium bisulfite ($NaHSO_3$), and sodium sulfite (Na_2SO_3), were all purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (China) and used as received. A commercial phenol-formaldehyde resin, supplied by a local plywood mill with solid content of 42.1%, was used as control. Birch veneers of dimensions 420 mm × 420 mm (1.6 mm in thickness) were obtained from a local plywood plant with moisture content of about 2.5%.

PFO Synthesis and Characterization

Paraformaldehyde was dissolved in water at 90 to 95°C to form a formaldehyde solution of 36.5wt% before use. In a 1000 mL reaction kettle equipped with a mechanical stirrer, a thermometer, a thermostat, and a condenser as reflux, 235 g of phenol, 513.7 g formaldehyde solution, and 12.8 g of NaOH solution (50wt%) were charged. Then, the mixture was heated to 60 °C and remained at this temperature for 1 hour. Thereafter, the reaction mixture was kept at 75 °C for 1 hour, then at 55 °C for 4 hours. The formaldehyde/phenol ratio and NaOH/phenol ratio for the PFO were 2.5 and 0.064, respectively.

The PFO was kept in a thermostatted water bath at 25 °C for half an hour before being tested for pH (using Sartorius PB-10 pH meter) and viscosity (using a Brookfield rotational viscometer, DV-II Pro, with No.1 spindle at 60 rpm. rotation rate). The solid content was obtained by weighing the mass in an analytical balance (± 0.0001 g) before and after oven drying an adhesive sample of about 2 g (accurate to 0.0001 g) at 120 °C for 3 hours. The free formaldehyde content was determined according to the standard ISO 9397: 1995. The reaction resultant had a pH value of 9.29, a viscosity of 13.5 mPa·s, a free formaldehyde content of 4.4%, and a solid content of 51.2%.

The un-reacted free phenol was determined by a HPLC method. PFO was diluted by water to about 0.5wt% and then adjusted pH value to 10.5. Each sample solution was measured by HPLC on an Agilent 1100 apparatus equipped with a C18 alkaline column. Water was used as the mobile phase at a flow rate of 1.0 mL/min. The wavelength of the UV detector was set at 270 nm. A series of phenol solutions of known concentrations

(0.1%, 0.2%, 0.3%, 0.4%, 0.5%, and 0.6%, pH also adjusted to 10.5) were used as standards to calculate the free phenol content. It was determined to be 1.75wt% on the liquid basis of PFO.

PFO Post-Treatment

Because free formaldehyde will react with whey protein and lead to the crosslinking of whey proteins, combinations of ammonia and Na_2SO_3 with various ratios were used to scavenge free formaldehyde of PFO as follows: 150 g of PFO solution was transferred to a 250 mL beaker with magnetic stirring, then formic acid was added gradually to reduce pH value to 6.0. Ammonia was added and kept stirring for 10 minutes. After that, proper sodium sulfite was added into the mixture and kept stirring for another 10 minutes. Finally, formic acid was added gradually to reduce the pH of mixture to 6.5-7.0. The mole ratios of ammonia/Na_2SO_3 were 4:3, 3:3, 2:3, and 1:3. The total moles of ammonia plus Na_2SO_3 were 5, 12, 19, 26, and 33% more than the stoichiometric number to scavenger all free formaldehyde remained in PFO, respectively.

Formulation of Adhesive

The whey protein solution (40wt%) was held at 60°C for 35 min for thermal denaturation. The 100 parts of denatured whey protein solution was then mixed with 30 parts of various post-treated PFO (on liquid basis), and the PFO-modified whey protein adhesives were obtained.

Free Phenol Content of PFO-modified Adhesive by HPLC

The free phenol contents of PFO-modified whey protein adhesives before and after cured were measured. In order to stimulate the curing condition of adhesive in the plywood by hot pressing, proper PFO-modified adhesive was transferred into a sealed Teflon pool (cavity depth of 1.5 mm) and then cured at 140°C for 4.5 min. As for the adhesive sample before curing, proper fresh PFO-modified adhesive was freeze dried at 50°C and 125 Pa for 3 days. Both the cured and the freeze-dried adhesive samples were ground into powder passed through 100-mesh sieve. About 2 g of powder (accurate to 0.0001g) was kept in boiling water and stirred for 2 hours in order to extract the remained free phenol. The cooled extracting mixture was filtrated and the residue on glass-fiber filter was rinsed with distilled water (2 × 50 mL). The pH of filtrate was adjusted to 10.5 and then diluted to 250 mL in a volumetric flask and finally subjected to HPLC analyses, as described above.

Evaluation of Plywood

Birch veneers with dimensions of 420 mm×420 mm×1.6 mm were used to prepare 3-ply plywood panels. Whey protein-based adhesive was applied to two sides of a veneer at a spread rate of 300 $g \cdot m^{-2}$ (for double gluelines). The adhesive-coated veneer was then stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. Thereafter, the assembled veneers were hot-pressed at 140°C for 4.5 min. 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 hours, specimens were cut to determine the dry-state shear bond strength, wet-state shear bond strength, and formaldehyde emission, as presented in Fig. 1. 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 JIS K6806-2004 standard. The specimens tested for wet-state bond strength were subjected to boiling water for 4 hours, dried at 60 °C for 20 hours, and further boiled in water for 4 hours 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).

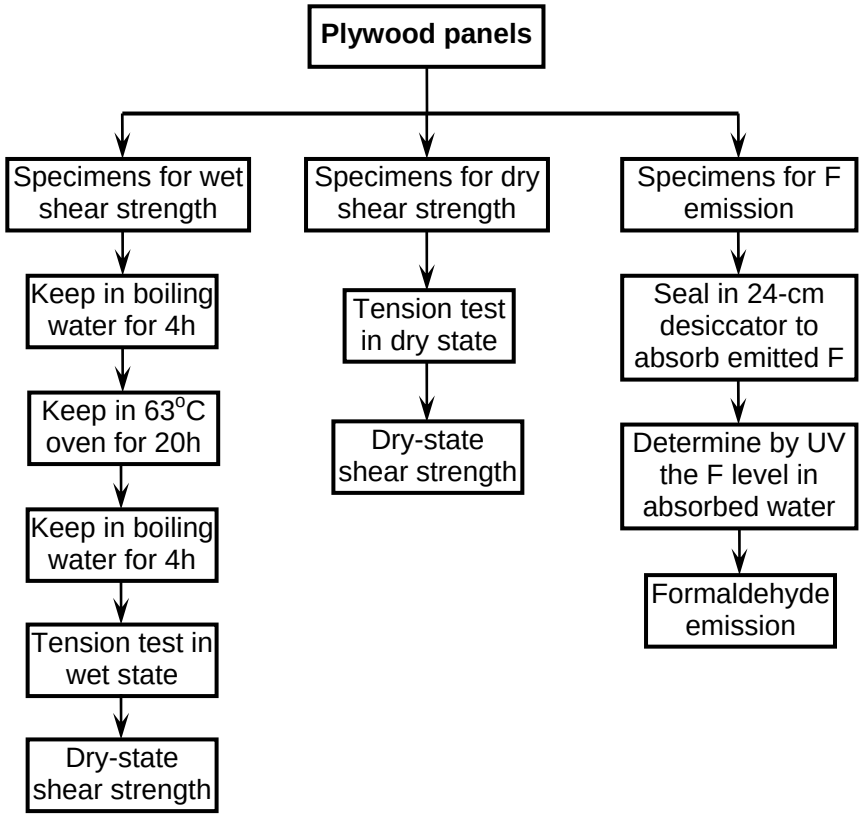


Fig.1. The scheme of plywood evaluations

RESULTS AND DISCUSSION

A good adhesive is expected to consist of relatively large, flexible, and interwoven polymer chains in order to firmly attach to the solid surface by adsorption (van de Leeden *et al*. 2000). However, whey proteins are generally composed of compact globular proteins with low molecular weight. As a result, the globular whey proteins mostly adsorb as a compact layer or sometimes even as a more or less rigid particle (Haynes *et al*. 1995, Norde *et al*. 1992), which is not able to effectively transfer stresses from the interface to the bulk and thus, the bond strength is poor during adhesion. Partly unfolding the native structure by proper denaturation condition could release the

embedded polar groups situated in the interior and turn the compact globular whey proteins into stretched conformations. Attributing to these transformations, more efficient and firm adhesion to wood substrate can be obtained, as shown in Table 1. After thermally denatured at 60°C at neutral pH for 35 min, whey protein solution obtained 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 one without thermal denaturation. This confirmed that partly unfolding the globular structure of whey proteins could effectively improve the bond strength and durability of whey protein adhesive.

Table 1. Bond Properties of Plywood Bonded by Whey Protein Solutions Only

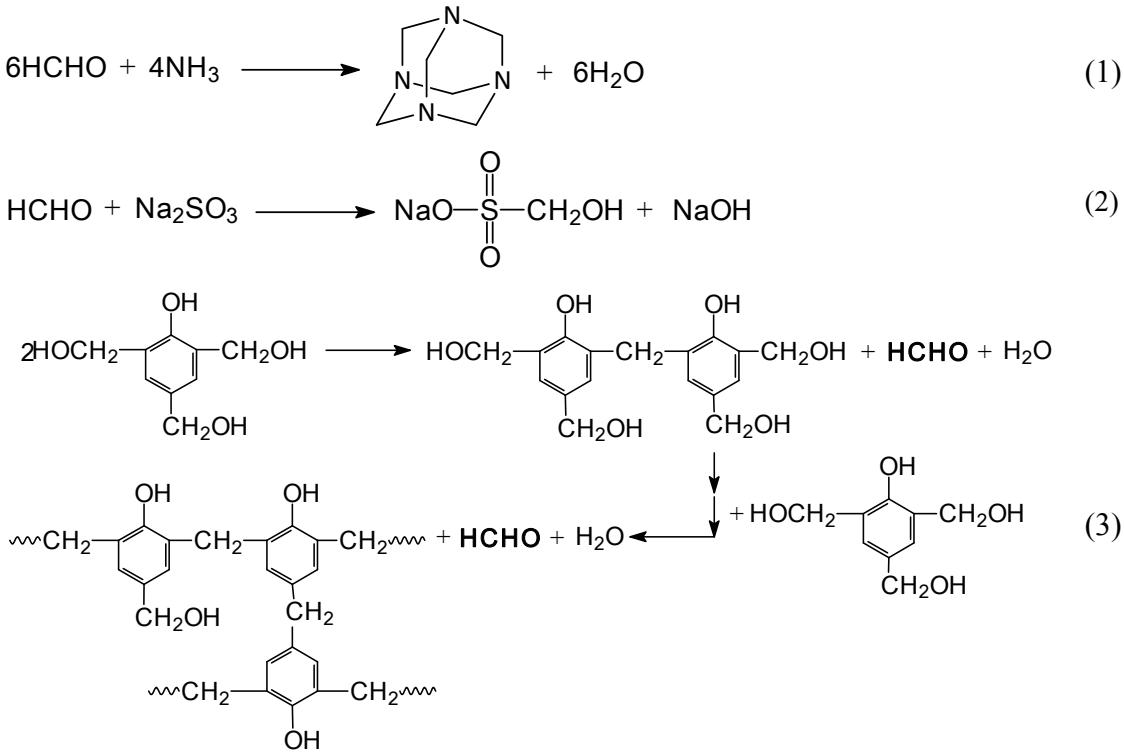
Adhesive	Shear strength (Dry-state, MPa)	Shear strength (Wet-state, MPa)
Non-denatured Whey protein	1.20 (0.25)	0.68 (0.28)
Denatured Whey protein	1.51 (0.29)	0.98 (0.18)
PF resin (control)	2.34(0.24)	1.75(0.14)
Note: the value in the parentheses refers to the standard deviation.		

The results in Table 1 also indicate that the plywood panels bonded by the two whey protein solutions could withstand two 4 hour boiling and one 20 hour of drying at 63°C, showing some water resistance as with whey protein only as adhesive. Water resistance must be attributed to the heat-induced gelation of whey protein, resulting from disulfide bonding of sulfhydryl groups and sulfhydryl-bisulfide interchanges between cysteine and cystine (Barone *et al*. 2006; Wang *et al*. 2010). 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), indicating that the heat-induced crosslinking via disulfide linkage was insufficient to yield good water resistance. Therefore, the dry strength of denatured whey protein as adhesive was higher than the required value (1.18 MPa) for structural use, according to standard JIS K6806-2003, but its wet bond strength that reflects the bond durability of the bondline only marginally reached the required value (0.98 MPa), implying that the adhesive may not be strong enough for use in structural wood products, because the commercial PF resin has much higher dry strength and wet strength. Thus, the water resistance and bond durability of whey protein adhesive needs to be improved for its safe application in structural wood products.

Phenol-formaldehyde (PF) resins are still the popular wood adhesive for both interior and exterior applications. Due to its excellent water resistance, using of PF resin for modifying wood adhesive, derived from biomass such as soy flour (Wescott *et al*. 2004), tannin (Moubarik et al. 2009), and lignin (Ma *et al*. 2011), had been investigated. Likewise, use of PF resin as a modifier may improve the water resistance of whey protein-based adhesives. PF resins used for wood adhesive are generally resol with sodium hydroxyl as a catalyst, resulting in high pH of the resin (>10). However, whey proteins tend to gel under alkaline conditions (Monahan *et al*. 1995). Our preliminary results also indicated that addition of 20% alkaline PF resin (pH 12.6) would lead to the quick increase in viscosity of whey protein solution and then immediate gelation. When the pH of the PF resin was adjusted to neutral (6.8 to 7.0) using phosphoric acid or *para*-toluene sulfonic acid, it became too viscous (almost agglomerated) to blend with the

whey protein solution. This should be attributed to the poor solubility of PF resin under neutral conditions due to its higher molecular weight. Thus, PF resin was not suitable to be used as a modifier of whey proteins. Alternatively, use of phenol-formaldehyde oligomer as a crosslinker may avoid this problem due to its excellent water solubility and much lower viscosity.

Hydroxymethylation is the first step of phenol-formaldehyde polycondensation, resulting in the mixture of hydroxylmethylphenol, dihydroxymethylphenol, trihydroxy-methylphenol, and very few low-molecular-weight condensation resultants (Higuchi *et al*. 1999; Kamo *et al*. 2002), known as PFO, having good water solubility and low viscosity. Due to the mild synthetic conditions in the present study compared with that of PF resin (Moubarik *et al.* 2009; Yuan *et al.* 2009), i.e., much lower NaOH level and lower reaction temperature, the reaction between phenol and formaldehyde was incomplete. As a result, the obtained PFO had much higher contents of free formaldehyde (4.4%) and free phenol (1.75%). Common commercial PF resins for wood adhesive should not have free formaldehyde more than 0.1% (Yuan *et al.* 2009).



When the PFOs were neutralized by formic acid to pH values from 6.5 to 7.0, the mixture of 100 parts of whey protein solution with 30 parts of PFO (on liquid basis) would be gelled quickly due to the high content of formaldehyde by reacting with the residual amino groups of whey proteins. Based on the fact that free formaldehyde can quickly and completely react with ammonia and sodium sulfite, as shown in Eqs.(1) and (2), both of them are able to scavenge the free formaldehyde of PFO. However, our results indicated that sodium sulfite, alone as formaldehyde scavenger, would result in separation of the obtained PFO into two layers. Ammonia alone as a scavenger would

avoid separation, but the mixture of ammonia-treated PFO and whey protein solution would gel very quickly. However, the combination of ammonia and sodium sulfite could result in a treated PFO that will not lead to the gelation of the whey protein. Therefore, the combinations with Ammonia/Na_2SO_3 mole ratios of 1:3, 2:3, 3:3, and 4:3 were investigated as formaldehyde scavengers. The total moles of ammonia and Na_2SO_3 were 5% more than the stoichiometric number to scavenge all free formaldehyde remaining in the PFO.

After mixing with these scavengers separately, the obtained post-treated PFOs had very low viscosity at 25°C (ranging from 18.2 to 20 mPa·s) and very low free formaldehyde content (below 0.2%). As a result, the modified whey protein adhesives by these post-treated PFOs did not gel after mixing and had pot lives of more than 8 hours. Plywood evaluation in Table 2 also indicated that the plywood panels bonded with these PFO-modified whey protein adhesives had much better bond strength and water resistance than that without PFO modification, as shown in Table 1. Both their dry-state and wet-state bond strengths were much higher than the required values specified in the commercial standard, JIS K6806-2003, for structural uses (1.18 MPa and 0.98 MPa, respectively). And the wet strength was comparable to that of commercial PF resin (1.75 MPa). This was attributed to the introduction of PFO that can crosslink itself and whey protein to form a strong three-dimensional network during hot pressing. However, their formaldehyde emissions were higher to some extent than the required value for environmentally safe wood composites (0.3 mg/L, grade $F_{4\text{-star}}$) according to JIS standard A5908-2003. Though the free formaldehyde in PFO has been scavenged by the combinations of ammonia and Na_2SO_3, the curing or crosslinking reactions of PFO will also release some formaldehyde (Pizzi and Mittal 2003), as illustrated in Eq. (3), which accounts for the higher formaldehyde emission of plywood panels. On the other hand, if more ammonia and Na_2SO_3 introduces, the free formaldehyde released from PFO curing can be further scavenged. Therefore, the excessive total moles of ammonia and Na_2SO_3 were increased from 5% to 32% more than the stoichiometric number to scavenge all free formaldehyde remained in PFO. In addition, results in Table 2 also indicated that the formaldehyde emission of plywood panels slightly decreased as the moles of ammonia in the combination scavenger were increased. However, further increase of ammonia content was not a good way to reduce formaldehyde emission because it would sharply reduce the pot life of modified whey protein adhesive. As a result, the mole ratio of ammonia to Na_2SO_3 was chosen as 4:3 for further investigations.

Table 2. Effects of Ammonia/Na_2SO_3 Ratios on Plywood Properties

Ammonia/Na_2SO_3 mole ratio	Dry-state strength (MPa)	Wet-state strength (MPa)	Formaldehyde Emission (mg/L)
1:3	1.83 (0.35)	1.61 (0.43)	0.407 (0.012)
2:3	1.78 (0.30)	1.63 (0.32)	0.394 (0.004)
3:3	1.85 (0.28)	1.61 (0.31)	0.370 (0.006)
4:3	1.80 (0.36)	1.76 (0.28)	0.332 (0.008)
PF control	2.34(0.24)	1.75(0.14)	0.119(0.006)
Note: the value in the parentheses refers to the standard deviation			

As expected, the formaldehyde emission of plywood panels were effectively reduced to 0.067 mg/L when the level of combination scavenger was increased. When the stoichiometric moles of ammonia and Na_2SO_3 were more than 12% over the free formaldehyde of PFO, the formaldehyde emission was not further decreased, but varied slightly between 0.067 mg/L and 0.134 mg/L, which were all much lower than the required value for environmentally safe wood composites (0.3 mg/L, grade $F_{4\text{-star}}$) according to JIS standard A5908-2003. This indicated that 12% stoichiometric moles of scavenger could sufficiently capture the formaldehyde released from the crosslinking reaction from PFO, and to produce plywood panels with very low formaldehyde emission. The formaldehyde emission of plywood panel bonded by PFO-modified whey protein adhesives with 19% stoichiometrically excessive scavenger was also measured according to ASTM D6007 and D5197, which was about 4.3 ppb (0.0043 ppm), much lower that required value (0.05 ppm) according to CARB (California Air Resources Board) Phase Two Emission Standards. The results indicated that the plywood bonded by PFO modified whey protein had almost no formaldehyde emission. Table 3 also showed that stoichiometric excesses of scavenger had slight impacts on the bond strength and durability of plywood panels because the dry-state strengths were varied between 1.68 MPa and 1.98 MPa and wet-state strengths were varied between 1.46 MPa and 1.81 MPa. The plywood panels bonded with the most preferable whey protein adhesive (modified by 19% stoichiometric excesses of scavenger) had dry strength and wet strength comparable to those of plywood panels bonded by commercial PF resin.

Table 3. Effects of Stoichiometric Excesses of Combination Scavenger on Plywood Properties

Stoichiometric excess	Dry-state strength (MPa)	Wet-state strength (MPa)	Formaldehyde Emission (mg/L)
5%	1.80 (0.36)	1.76 (0.28)	0.332 (0.011)
12%	1.68 (0.11)	1.46 (0.22)	0.134 (0.007)
19%	1.98 (0.37)	1.73 (0.26)	0.067 (0.005)
26%	1.70 (0.22)	1.64 (0.17)	0.112 (0.007)
33%	1.76 (0.22)	1.81 (0.25)	0.089 (0.006)
PF control	2.34(0.24)	1.75(0.14)	0.119(0.006)
Note: the value in the parentheses refers to the standard deviation			

Phenol is more toxic than formaldehyde because it can be harmful to humans via skin absorption, vapor inhalation, or ingestion, resulting in serious health problems including muscle weakness, convulsions, and coma (Bruce *et al*. 1987). Phenol may also be harmful to the biota, such as reduced fertility, decreased survival of the young, and inhibition of growth (Babich and Davis 1981). HPLC analysis in Fig. 2 showed that there was only one HPLC peak of 0.5% phenol solution, which was attributable to un-reacted phenol at a retention time of 19.46 min, while the extracted solutions of PFO-modified adhesives had no HPLC peak at the retention time of the phenol peak. The results confirmed that the PFO-modified whey protein adhesives (either cured or before curing)

do not have any un-reacted phenol. They also implied that the free phenol of PFO was absorbed by the whey protein adhesives themselves. The phenol absorption of PFO-modified adhesives should be mainly attributable to the reactions of phenol with the proteins. It is well known that phenol denatures proteins (WHO 1994) and is able to disrupt disulphide bridges in proteins (Brooks and Riviere 1996). *In vitro* tests have shown covalent binding of phenol to tissue and plasma protein, some phenol metabolites also bind to proteins (WHO 1994).

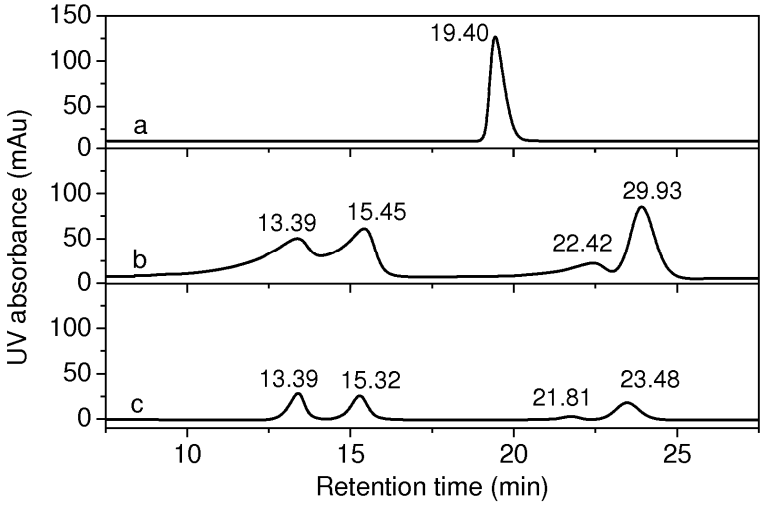


Fig. 2. HPLC chromatograms of phenol solution (a), extract solutions from uncured adhesive (b), and cured adhesive (c)

CONCLUSIONS

1. PFO synthesized under the mild conditions exhibited good water solubility and low viscosity, characteristics that are preferable for the modifying of whey proteins.
2. After the pH is neutralized by formic acid and free formaldehyde scavenged by ammonia/sodium sulfite combinations, the post-treated PFO can be used to formulate environmentally safe whey protein adhesives for structural plywood manufacture.
3. Ammonia/sodium ratio and the amount of ammonia/sodium had major impacts on the formaldehyde emission of plywood panels bonded PFO-modified whey protein based adhesives, but slightly affected the bond properties of plywood.
4. Plywood panels bonded by the PFO-modified whey protein adhesive had very little formaldehyde emission (0.067mg/L) and an undetectable level of free phenol according to HPLC tests.
5. The PFO modified whey protein adhesive may be considered as a safe alternative to petroleum-based wood adhesives on the market.

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