Novel Whey Protein-Based Aqueous Polymer-Isocyanate Adhesive for Glulam

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ABSTRACT: Whey, a by-product of cheese making, contains whey proteins, lactose, vitamins, and minerals. Whey and whey proteins are still not fully used. In this study, whey protein-based aqueous polymer-isocyanate (API) adhesives were developed and characterized by bond test, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscope (SEM) for bond strength, chemical structures, and morphology. The optimized whey protein-based API adhesive for Glulam had a 28-h boiling-dry-boiling wet strength of 6.81 MPa and a dry strength of 14.34 MPa. Results indicated that the addition of polyvinyl acetate emulsion can prolong the work life of the API adhesive. Addition of crosslinker polymeric methylene bisphenyl diisocyanate (P-MDI) not only increased the cohesive strength of the cured adhesive by crosslinking whey proteins but also resulted in strong chemical bonds via urethane linkage in wood bondlines. Addition of polyvinyl alcohol (PVA) further increased the crosslinking density of the cured adhesive due to its capability of crosslinking whey proteins through the reaction with P-MDI. Nanoscale $CaCO_3$ powder (3.5 wt %) as filler significantly improved bond strength due to its mechanical interlock with the polymers in the adhesive. SEM examinations confirmed that both PVA and nanoscale $CaCO_3$ improved the compatibilities of the components in the optimized whey protein-based API adhesive. FTIR results revealed that P-MDI reacts mainly with the residual amino groups rather than the hydroxyl groups of whey proteins. J Appl Polym Sci 120: 220–225, 2011

Key words: adhesives; adhesion; FTIR; SEM; whey proteins

INTRODUCTION

Glulam (glued-laminated timber) is a structural wood composite manufactured by gluing individual smaller pieces of wood together using adhesives. Because of the advantages of large sizes, long lengths, excellent dimensional stability, and good strength, Glulam is used in a wide variety of applications in Europe, North America, and Japan, ranging from headers or supporting beams in residential framing to major structural elements in nonresidential buildings including recreational buildings, industrial structures requiring large column free spaces, and high quality architectural/structural uses in churches, shopping centers, etc.[1] The common adhesives for the Glulam are resorcinol-formaldehyde (RF) resin, phenol-RF (PRF) resin, and aqueous polymer-isocyanate (API) adhesive [the mixture of crosslinker polymeric methylene bisphenyl diisocyanate (P-MDI) with water-based polymers generally prepared using polyvinyl alcohol (PVA) solution and the mixtures of PVA with polyvinyl acetate (PVAc) emulsion, styrene-*co*-butadiene rubber (SBR) emulsion, ethylene-*co*-vinyl acetate (EVA) emulsion, or their mixtures], and melamine-urea-formaldehyde-based honeymoon adhesive.[2–4] With the increased interest in the use of renewable materials to substitute fossil-based ingredients, some biomass based adhesives have been developed for Glulam, such as tannin-RF (TRF) adhesive[5] and TRF honeymoon adhesive.[6]

During cheese making $\sim$ 9 L of whey is generated for every kilogram of cheese manufactured, and $\sim$ 90.5 billion pounds of whey was estimated to be generated in the United States in 2008, according to the Annual Summary of Dairy Products, USDA National Agricultural Statistics Service. However, >30% of whey is disposed to the environment in the United States, thus, there is an increasing economical and environmental needs for developing new applications for whey products such as whey proteins. Whey proteins are often so-called "waste protein" because they are generally composed of compact globular proteins with lower molecular weight and multiple components (commonly 50–53% β-lactoglobulin, 19–20% α-lactalbumin, 6–7% bovine serum

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TABLE I
Bond Strength of Whey-Protein Based API Adhesives Prepared with Various Formulations

Adhesive ID	Composition of the water based polymer (wt %, liquid basis)	Strength (MPa)	
		Dry state	Wet state
Control*	WPI (100%)	2.06 (0.26)	≈0 (N/A)
A	WPI (100%)	5.78 (0.48)	2.64 (0.61)
B	WPI (70%) + PVAc (30%)	6.02 (0.52)	3.70 (0.38)
C	WPI (58.3%) + PVA (11.7%) + PVAc (30%)	10.56 (0.98)	5.65 (0.86)
D	WPI (55.4%) + PVA (11.1%) + $CaCO_3$ (3.5%) + PVAc (30%)	13.38 (1.07)	6.81 (0.62)
E	PVAc (54%) + PVA (24%) + SBR (11%) + $CaCO_3$ (11%)	12.98 (1.26)	6.37 (0.54)

Note: The Control was 40 wt% of denatured WPI solution without crosslinker P-MDI.

The value in parentheses refers to the standard derivation of the bond strength.

albumin, and 12–13% immunoglobulin in bovine milk);[7,8] these characteristics are generally undesired for the applications of whey proteins in adhesives.

However, whey proteins are readily soluble in water and able to form a homogenous "solution" with concentration up to 40% by weight;[9] in addition, whey proteins are rich in free hydroxyl groups (totally up to 0.1 mol per 100 g whey proteins) and residual amino groups (totally up to 0.13 mol per 100 g whey proteins).[10] As a result of these characteristics, the whey protein solution could be used to prepare API adhesive for structural wood after certain modifications. There is no publication or patent reported on wood adhesive prepared from whey proteins for structural use. In this study, we are aiming to develop a novel API adhesive using whey proteins for Glulam. Bonding evaluation was used to investigate the effects of formulation and processing technology on bond strength of the whey protein-based API adhesives, and Fourier transform infrared (FTIR) and scanning electron microscope SEM were used to analyze the microstructures and bonding chemistry of optimized API adhesives.

EXPERIMENTAL MATERIALS

Whey protein isolate (WPI) with 92.4% protein content was purchased from Fonterra (New Zealand). WPI solution (40 wt %) was prepared before use. PVA with degree of hydrolysis 98.0–98.8% and molecular weight ~ 65,000 was purchased from Celanese (TX). PVA solution (15 wt %) in water was prepared before use. P-MDI with NCO weight content 31.4% and functionality 2.8 was purchased from Huntsman Polyurethane (TX). PVAc with solid content 55% was purchased from Hexion Specialty Chemicals (OH). Nanoscale calcium carbonate, HG-01, with particle size <40 nm, was purchased from Shanghai Huijing Subnanoseale New Materials (Shanghai, China). SBR emulsion with solid content 53.6% was purchased from BASF Chemical Company (Ludwigshafen, Germany). Unless stated otherwise, the materials were used as received without further treatments.

Preparation of whey protein-based API adhesives

A total of six API adhesives were prepared and investigated in this study. The weight ratio of crosslinker P-MDI to water-based polymer (as shown in Table I) was 3/20 on liquid basis. For API adhesives A and B, the 40 wt % WPI solution was thermally denatured at 60–63°C for 35 min. For API adhesives C and D, the WPI solution was thermally denatured at 60–63°C for 25 min then PVA solution was added and held at 60–63°C for another 10 min. For API adhesive D, the fine $CaCO_3$ powder was charged into the denatured WPI/PVA mixture at ~ 25°C. The adhesive E (control) is a commercial API product.

Wood bonding performance

Wood bonding performances of the adhesives were evaluated by the 28-h boiling-dry-boiling wet compressive shear strength (wet strength) and dry compressive shear strength (dry strength) at breakage according to Japanese Industrial Standards.[11] The birch (*Betula platyphylla* Suk.) blocks with dimensional size 30 mm × 25 mm × 10 mm, length (fiber direction) × width × thickness, were used to evaluate the bond strength and durability of adhesives. After the adhesive was spread onto the block surface manually, the two block surfaces with adhesive were coupled by lap jointing and then pressed at 1.5 kN for 2 h [20°C, 60% RH (relative humidity)] in an Instron-5566 mechanical machine (Instron, MA) to form a lap joint (bondline).

Shear strength refers to the maximum shear stress which a material can withstand without rupture, or the ability of a material to withstand shear stress. The shear strength determined under compression model is called compressive shear strength. In this study, the compressive shear strength refers to the maximum stress that put onto the two adhered wood blocks in compressive shear state to slide one wood block past the other (to break the adhesion). The wet strength reflected not only the bond strength but also the bond durability, because the bondlines for wet strength underwent two 4-h boiling treatments and a 20-h dry treatment at 60°C and were tested under wet state. The dry strength reflected only the bond strength, because the bondlines for dry strength were tested under dry state without further treatment.

FTIR analysis

The samples for FTIR analysis were freeze dried at −58°C and 15 kPa for a week. Before freeze drying, each mixture of WPI/P-MDI, PVA/P-MDI, and WPI/PVA/P-MDI was cured at ambient temperature for 7 days after the water-based polymer mixed with P-MDI. The dried sample was mixed with KBr crystal at a weight ratio of 1/150 then ground into fine powder, and then pressed in a special mold to form a FTIR sample folium. The folium was scanned using a Magna IR560 FTIR instrument (Nicolet Instrument Corp., Madison, WI).

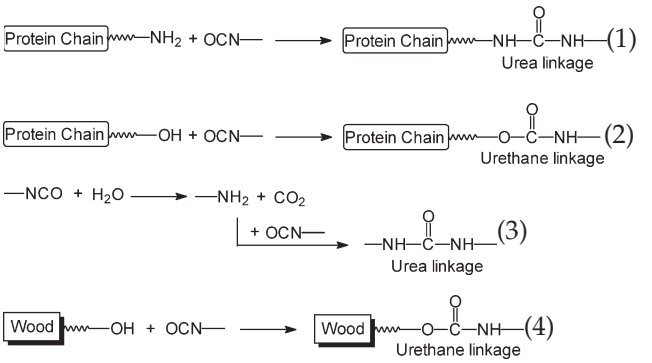
SEM observation

The SEM was used to observe the bulk morphologies of the cured adhesives. The SEM samples were prepared as follows: put enough fresh liquid adhesive into the 2-mm gap between two wood blocks and jointed them together, then kept at ambient temperature (20–25°C) for 7 days. The bondline was broken and a piece from fractured surface of the cured adhesive was taken for SEM examination. The SEM samples were coated with ~ 10–20 nm of gold before examination using a QUANTA-200 SEM (FEI, Hillsboro, OR).

RESULTS AND DISCUSSION

API adhesive is a two-component system composed of water-based polymer and the crosslinker, polyisocyanate. Typically, the water-based polymer of commercial API adhesive is PVA solution and the mixture of PVA with PVAc emulsion, SBR emulsion, EVA emulsion, or a combination of these.[3] The crosslinker polyisocyanate is commonly a crude form of P-MDI or MDI. Because of its relative lower cost compared with other structural adhesives and environmental safety, API adhesive is widely used to bond wood for both structural and nonstructural applications.

Because of their lower molecular weight compared with other proteins such as soy protein and casein and good water solubility (able to form homogeneous water solution with concentration up to 40 wt %), whey proteins have very poor cohesive strength and water resistance.[7–9] When untreated whey protein solution was used alone as wood adhesive to bond wood, it only yielded a dry strength of 2.06 MPa that was much lower than the required value (9.81 MPa) for structural use according to the JIS K6806-2003 Standard. The wood bondlines could not bear 28 h boiling-dry cycle and yielded almost no wet strength, indicating very poor bond durability, as shown in Table I. The dry bond strength of whey protein solution only mainly resulted from the bond mechanism involving both the adsorption of polar groups (amino, hydroxyl, amide, carboxyl, etc.) of whey proteins on wood surface and the mechanical interlocking between protein and porous wood.



When 15 wt % of P-MDI (liquid basis) was added into whey protein solution as crosslinker in adhesive A, the prototype of the novel whey protein-based API adhesive, the crosslinker would quickly react with the active groups, mainly residual amino groups and free hydroxyl groups, of whey proteins. This was due to the highly reactivity of isocyano group (NCO) of P-MDI, as shown in eqs. (1) and (2). When P-MDI reacted with either amino or hydroxyl groups of whey proteins, the molecular weights and crosslinking densities of whey proteins were increased after crosslinking reaction, which improved the cohesive strength of final API adhesive. The results shown in Table I indicated that the wood bondlines with adhesive A had not only much higher dry strength (5.78 MPa) than that of the control (2.06 MPa), but had better bond durability. The bondlines with adhesive A were able to bear 28 h boiling-dry cycle and yielded a wet strength of 2.64 MPa. This fact also implied that P-MDI did react with whey proteins, as shown as eq. (1) or (2) or both eqs. (1) and (2), because the wood blocks spread with only P-MDI could not be bonded together under the same bonding conditions (pressing at 1.5 kN for 2 h, 20°C, 60% RH).

Patel and Desai[12] assigned the IR absorptions at ~ 1700 cm^{-1} and at ~ 1640 cm^{-1} to urethane linkage and urea linkage, respectively. The FTIR (spectrum c in Fig. 1) of cured adhesive A did not detect the C=O stretching mode of urethane at ~ 1700 cm^{-1}, but detected a strong absorption at ~ 1649 cm^{-1} that is assigned to the C=O stretching mode of both urea and protein. In the cured mixture of PVA solution with P-MDI, FTIR (spectrum f) detected not only a strong peak at ~ 1649 cm^{-1} but also a middle-strong peak at ~ 1705 cm^{-1}, indicating that P-MDI reacted with OH groups in the presence of water. These observations implied that the crosslinking reaction of whey proteins by P-MDI was mainly with NCO-amino reaction as illustrated in eq. (1), not via NCO-OH reaction as illustrated in eq. (2). It was

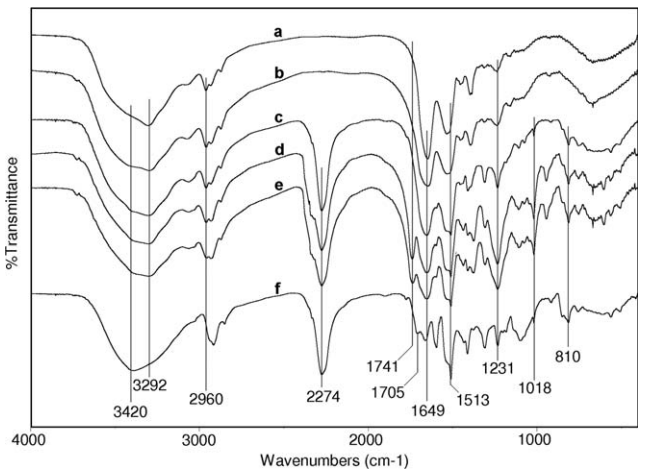


Figure 1 FTIR spectra of whey protein-based API adhesives and cured samples. (a) WPI only; (b) WPI/PVA; (c) WPI/P-MDI; (d) WPI/PVAc/P-MDI; (e) WPI/PVA/PVAc/P-MDI; and (f) PVA/P-MDI.

attributed to the much higher reactivity of NCO-amino reaction than that of NCO-hydroxyl one.

When a water-based polymer is mixed with P-MDI, the water in adhesive also reacted with NCO as shown in eq. (3), and it was reported that NCO-water reaction is very fast.[13] However, results of FTIR analysis showed in Figure 1 revealed that there are still considerable levels of free NCO groups in all mixtures of various water-based polymers with P-MDI, cured at ambient temperature for 7 days. This indicated that the powerful chemical (or covalent) bonding between adhesive and wood can be formed by the reaction of free NCO with hydroxyl groups on wood surface, as illustrated in eq. (4). This is the important reason why API adhesives can bear 28-h boiling-dry-boiling treatment.

The work life of API adhesive refers to the time from water-based polymer mixed with P-MDI to the moment that the mixture cannot be spread onto wood surface. The work life of adhesive A was very short, $\sim$ 30 min, because whey proteins have abundant and active amino groups that in this case quickly reacted with P-MDI, as illustrated in eq. (1). Soon after blending of whey protein solution and P-MDI, the adhesive became very viscous and formed many particle-like accumulates due to the formation of insoluble polyurea chains, as shown in the SEM micrograph Figure 2(a). To improve the work life, 30 wt % of PVAc emulsion (liquid basis) was added into WPI solution. This addition diluted the concentration of amino groups and therefore reduced the NCO-amino reaction rate because PVAc does not react with P-MDI. The results indicated that adhesive B had much longer work life (2.3 h) and 40% higher wet strength than those of adhesive A. However, their dry bond strengths were comparable (6.02 MPa versus 5.78 MPa). This further confirmed that P-MDI mainly reacted with the amino groups of whey proteins. The lower NCO-amino reaction rate due to the dilution by adding PVAc resulted in more free NCO groups remaining for chemical bonding reaction, as illustrated in eq. (4), and consequently improved the wet strength.

PVA is composed of the repeating $-CH_2-CH(OH)-$ units that are rich in hydroxyl groups that can react with P-MDI. This is the main reason that the PVA solution is chosen as one of most common water-based polymer in commercial API adhesives. In addition, it was reported that the PVA is crosslinkable to whey proteins.[14,15] Therefore, several more water based polymers were obtained (from C1 to C5 in Table II), by introduction 0–20 wt % of PVA into whey protein solution, with expectation of improving the bond strength and durability via increasing the crosslinking density of API adhesives. The bond tests in Tables I and II showed that both dry strength and wet strength of the resulting API adhesives increased gradually up to 11.7% PVA (adhesive C in Table I or adhesive C3 in Table II), and then decreased with further increase of PVA content. The dry strength (10.56 MPa) and wet strength (5.65 MPa) of adhesive C (or C3) were the best among these adhesives, with 75.4 and 52.7%, respectively, higher than those of adhesive B (or C1) without PVA addition. This confirmed that proper amount of PVA could effectively increase the crosslinking density of final cured adhesives via the crosslinking of PVA with both WPI and P-MDI, resulting in significant improvement of the bond strength. The dry strength of adhesive C3 was higher than the required value of commercial standard for structural use (9.81 MPa); whereas the wet strength was still a little lower than the required value (5.88 MPa).

Though the FTIR spectrum of the WPI/PVA mixture was quite similar with that of WPI alone, some differences were observed in the SEM micrographs of adhesives A to C. Because PVAc chains are hydrophobic and WPI are hydrophilic, PVAc did not have good compatibility with WPI. As a result, some PVAc phases were separated from WPI phases in the cured adhesive B as indicated as the arrows in Figure 2(b). PVA contained both hydrophilic hydroxyl and hydrophobic methylene chains ($-CH_2-CH-$), which can act as an emulsifier to increase the compatibility of PVAc and WPI. Therefore, the PVAc phases were all tightly bond to the WPI phase without separation and the size of PVAc phase became smaller as shown in Figure 2(c), which obviously increased both dry strength and wet strength of adhesive C.

It has been reported that many mechanical properties of adhesives could be significantly improved with the addition of nanoscale fillers[16,17] because of the large surface area of the nanoscale fillers and

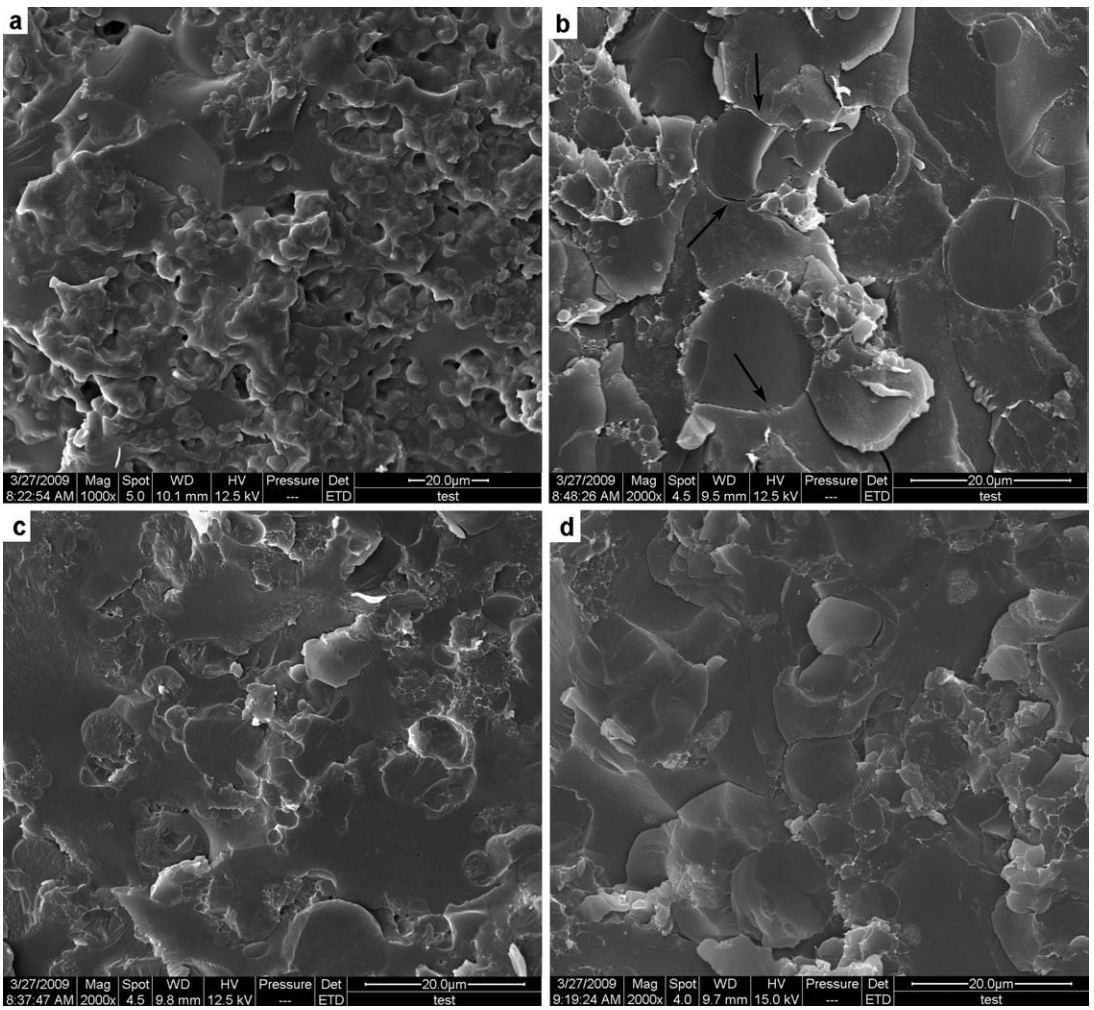


Figure 2 SEM micrographs of cured whey protein-based API adhesives. (a) WPI/P-MDI; (b) WPI/PVAc/P-MDI; (c) WPI/PVA/PVAc/P-MDI; (d) WPI/PVA/PVAc/nano-$CaCO_3$/P-MDI.

their ability to mechanically interlock with polymers.[18] Therefore, 0–9.2 wt % of nanoscale $CaCO_3$ powder was introduced, with rapid mechanical mixing (1200–1500 rpm), into the water-based polymer of adhesive C to obtain new water-based polymers (from D1 to D4 in Table III). The results in Table III showed that both dry strength and wet strength increased at first and then decreased with the nanofiller content increased from 0 to 9.2%. Higher levels of nanofiller made the API adhesives too viscous to be blended and hard to spread onto wood. The best level of nanoscale $CaCO_3$ powder was 3.5%, resulting in an API adhesive (D2) with wet strength (6.81 MPa) that was higher than the required value (5.88 MPa) of JIS K6806-2003 standard and 20.5% higher than that without nano-$CaCO_3$ filler (C or D1, 5.65 MPa). The dry strength (13.38 MPa) was also much higher than the required value (9.81 MPa) of JIS

TABLE II
Bond Strength of Whey-Protein Based API Adhesives with Various Levels of PVA

Adhesive ID	Composition of the water based polymer (wt %, liquid basis)	Strength (MPa)	
		Dry state	Wet state
C1(B)	Denatured WPI (70.0%) + PVAc (30%) + PVA (0%)	6.02 (0.52)	3.70 (0.38)
C2	Denatured WPI (63.6%) + PVAc (30%) + PVA (6.4%)	10.66 (0.70)	3.92 (0.64)
C3	Denatured WPI (58.3%) + PVAc (30%) + PVA (11.7%)	10.56 (1.07)	5.65 (0.32)
C4	Denatured WPI (53.8%) + PVAc (30%) + PVA (16.2%)	9.26 (0.55)	4.65 (0.73)
C5	Denatured WPI (50.0%) + PVAc (30%) + PVA (20%)	7.42 (0.69)	4.65 (0.51)

The value in parentheses refers to the standard derivation of the bond strength.

TABLE III
Bond Strength of Whey-Protein Based API Adhesives with Various Levels of Nano-$CaCO_3$

Adhesive ID	Composition of the water based polymer (wt %, liquid basis)	Strength (MPa)	
		Dry state	Wet state
D1(C)	WPI (58.3%) + PVAc (30%) + PVA (11.7%) + $CaCO_3$ (0%)	10.56 (0.98)	5.65 (0.86)
D2	WPI (55.4%) + PVAc (30%) + PVA (11.1%) + $CaCO_3$ (3.5%)	13.38 (1.42)	6.81 (0.79)
D3	WPI (53.0%) + PVAc (30%) + PVA (10.6%) + $CaCO_3$ (6.4%)	14.34 (1.16)	6.12 (0.84)
D4	WPI (50.7%) + PVAc (30%) + PVA (10.1%) + $CaCO_3$ (9.2%)	8.99 (0.74)	4.01 (0.52)

The value in parentheses refers to the standard derivation of the bond strength.

K6806-2003 standard and 26.7% higher than that without nano-$CaCO_3$ filler (C or D1, 10.56 MPa).

As expected, the addition of sufficient nano-$CaCO_3$ powder resulted in the further increase of bond strength and bond durability. This was attributed to the strong mechanical interlocking of nano-$CaCO_3$ with the polymers, which improved the compatibilities of each component in the adhesive and increased the cohesive forces of the cured API adhesive. It was confirmed by the SEM micrograph in Figure 2(d) that the PVAc phases and WPI phases became indiscernible.

Adhesive E was a commercial API adhesive for structural use. Its water-based polymer is composed of 54 wt % of PVAc emulsion, 11 wt % of SBR emulsion, 24 wt % of PVA solution, and 11 wt % of nano-$CaCO_3$ (liquid basis). The test results showed that the commercial API adhesive had dry bond strength of 12.98 MPa and wet bond strength 6.37 MPa. Results indicated that the whey protein-based API adhesive D had comparable bond strength and durability with the commercial API adhesive. The novel whey protein-based API adhesive optimized may have a potential for commercial applications for the structural wood bonds.

CONCLUSIONS

Based on the bond strength evaluations of various formulations of whey protein-based API adhesives for Glulam, a novel API adhesive was developed using whey proteins as a main ingredient, which was composed of water-based polymer (consisted of 55.4% WPI, 11.1% PVA, 3.5% $CaCO_3$, and 30% PVAc, by weight on liquid basis) and crosslinker P-MDI. This optimized whey protein-based API adhesive had a 28-h boiling-dry-boiling wet strength of 6.81 MPa and a dry strength of 14.34 MPa. The bond strength of the newly developed API adhesive was comparable to the commercial API adhesive for structural use and could be used for manufacturing Glulam.

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