



Cow blood adhesive: Characterization of physicochemical and adhesion properties

Hailin Lin^a, Sundaram Gunasekaran^{b,*}

^a Chemistry and Chemical Engineering Department, Zhongkai University of Agriculture and Technology, Guangzhou 510225, PR China

^b Biological Systems Engineering Department, University of Wisconsin–Madison, Madison, WI 53706, USA

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ABSTRACT

Adhesives were prepared from cow blood via alkali-modification. Their physicochemical and adhesion properties such as the degree of hydrolysis, viscosity, water solubility, curing time, and bonding strength were measured. The degree of hydrolysis increased with increasing basic pH value. The adhesive exhibited shear-thinning viscous behavior. Both viscosity and shear-thinning character showed a remarkable shift at pH 10.2 and at 50 °C. The curing time decreased with curing temperature within 60–80 °C range. The water solubility of the adhesive was the lowest when sodium silicate, the curing agent, was used during adhesive preparation at a concentration of at least 2.0% (v/v) regardless of the pH value. The adhesive bonding shear strength was independent of the pH and was comparable to that of phenol formaldehyde in the dry condition, but somewhat lower in the wet condition.

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1. Introduction

Many petroleum-based adhesives such as phenol formaldehyde, urea formaldehyde, resorcinol formaldehyde, and poly (vinyl acetate) are widely used in the production of plywood, composite wood panels, and furniture [1]. However, the rising cost of petrochemical-based products and growing awareness of environmental protection have prompted the development of “green” products from inexpensive and renewable resources [2]. For example, California Air Resources Board (CARB) has recently set strict limits on formaldehyde emission from composite wood products [3]. This has cost, compliance, testing, and certification requirement implications to the wood products industry. Therefore, protein-based adhesives have gained renewed attention and consideration [4–6]. During the past decade, research on protein-based adhesives has been largely directed toward soy protein. However, despite the low cost and plentiful availability soy proteins, adhesives prepared from soy proteins suffer from poor water resistance characteristic [7–9].

Several methods have been reported for preparing adhesives from animal blood since 1930s [10–16]. However, those methods require using dried blood powder. Since drying is an energy intensive process, blood adhesives produced using the past methods have not become economically viable alternatives to synthetic adhesives. Unlike polyol-based natural polymers, blood proteins are complex macromolecules and contain a number of chemically linked amino acid monomers, which form polypeptide chains and constitute the primary structure

[17,18]. These structural features can be changed by physical, chemical, or enzymatic treatments. Such treatments alter secondary, tertiary, or quaternary structures of the proteins without breaking the covalent bonds and lead to protein denaturation. It is well known that the native structure of proteins can be modified to increase the bonding strength of protein-based adhesives. Unfolded protein molecules have increased surface area and hence afford improved interaction with substrates [19–21]. Accordingly, the performance of blood protein adhesives is dependent on the dispersion and unfolding of the protein in solution.

The advantages of animal blood-based adhesives include: (1) animal blood is abundantly available and inexpensive because blood from slaughterhouses is mostly discarded, (2) blood glue is easy to handle because of its relatively low viscosity, and (3) blood glue can be applied using both hot and cold presses [22]. It has been shown that wood products bonded with blood protein adhesive are more water resistant than those bonded with plant protein adhesives [23].

The objectives of this research were to (1) prepare an adhesive from fresh cow blood without first drying it, (2) evaluate physicochemical properties of the adhesive prepared, and (3) determine bonding strength of the adhesive as a function of its alkaline pH.

2. Materials and methods

2.1. Materials

Fresh cow blood was obtained from the Muscle Science Department at the University of Wisconsin–Madison. Calcium

* Corresponding author. Tel.: +1 608 262 1019; fax: +1 608 262 1228.
E-mail address: guna@wisc.edu (S. Gunasekaran).

oxide (CaO), sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3) and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) (density = 0.9 g/cm^3) were purchased from Fisher Scientific (Fair Lawn, NJ). EDTA disodium salt ($\text{C}_{10}\text{H}_{14}\text{O}_8\text{Na}_2\text{N}_2 \cdot 2\text{H}_2\text{O}$), sodium azide (NaN_3), trichloro acetic acid (TCA) (CCl_3COOH) were purchased from Sigma Chemical Company (St. Louis, MO). Phenol formaldehyde (PF) resin (GP5778) was obtained from Georgia-Pacific Resins (Decatur, Ga.). Fiber aspen wood strips ($170 \times 170 \times 5 \text{ mm}$) were provided by the US Forest Products Laboratory (Madison, WI).

2.2. Sample preparation

Cow blood adhesive was prepared as described in Gunasekaran and Lin [24]. Briefly, 300 g (~25% solid content) of fresh blood was mixed with 5.5 mL EDTA (10%, w/w) and 0.5 mL sodium azide (1.0, w/w). About 10 g of CaO solution (1:3.5 w/w in water) and 10–15 g of NaOH (30% w/w) were added in stages while stirring. Then, about 12 g sodium silicate and ammonia were added in stages while stirring. The resulting product is a ready-to-use adhesive.

2.3. Degree of hydrolysis

Protein adhesive can hydrolyze under basic condition. The extent of hydrolysis varies depending on the protein type and pH. The prepared adhesives of pH 9.3; 10.2; and 11.2 were selected. At these pH conditions, because of the added NaOH, the adhesives undergo hydrolysis without further addition of any reagents. The degree of hydrolysis (DH, %) of the blood protein was determined by measuring the 10 % trichloroacetic acid (TCA)-insoluble nitrogen content as described by Edwards and Shipe [25]. During hydrolysis, 50 ml aliquots of glue were removed after 2, 4, 8, 16 and 48 h. At each time, triplicate samples were taken and 50 ml of 10% TCA was added. The solutions were centrifuged for 15 min and the supernatants were assayed for nitrogen by the Kjeldahl method [26]. samples taken directly from the hydrolysate were diluted and assayed for nitrogen content. The approximate DH value was calculated as follows [25]:

$$DH = \frac{N_b - N_a}{N_b} \times 100$$

where N_b and N_a = 10% TCA-insoluble nitrogen before and after hydrolysis, respectively.

2.4. Adhesive viscosity

The apparent viscosity of the adhesives was measured at $25 \pm 0.1^\circ\text{C}$ over a shear rate range of $10\text{--}250 \text{ s}^{-1}$ using a dynamic rheometer (Bohlin CVOR, Malvern Instruments Inc., Southborough, MA) equipped with cone-and-plate geometry (CP 4/40). Three replicate experiments were done within 24 h after preparation.

2.5. Effect of temperature on curing time

The relationship between temperature and curing time was investigated by performing isothermal dynamic rheological test by applying an oscillatory shear stress of 500 Pa at a frequency of 1 Hz. About 15–20 mL of adhesive (pH 10.2) was used at curing temperatures of 60, 70, and 80°C .

2.6. Water solubility of adhesive resin

Water solubility of the cured resin was tested according to the method of Paridah and Musgrave [27]. One gram of cured resin was

finely ground and soaked in 5 mL of water for five days. The water solubility was judged by visually evaluating the appearance of the soak solution. Any discoloration in the soak solution is an indication that the resin has not been fully cured and the adhesive is dissolving in water—the darker the color of the soak solution, the greater the solubility of the resin. The following criteria and scores were used based on the appearance of the soak solution: clear, 1; traces of color, 2; slight coloration, 3; and brownish color, 4.

2.7. Bonding shear strength

Blood adhesives of pH values 9.3, 10.2, and 11.2 were used to investigate the effect of pH on bonding shear strength. The dry bonding shear strength was measured according to ASTM standard (Method D906-98, Standard Test Method for Strength Properties of Adhesives in Plywood Type Construction in Shear by Tension Loading) [28]. The adhesives were applied to 3-ply Aspen wood pieces ($17.0 \times 17.0 \times 0.5 \text{ cm}$) and heat-pressed at 120°C for 5 min at 1.24 MPa (180 psi) in a hydraulic press (Model M, Type2745, Fred S. Carver Inc., USA). The wood pieces were cut into $8.0 \times 2.5\text{-cm}$ strips and conditioned for seven days at room temperature to a final moisture content of 6–10%. The test specimen is shown in Fig. 1. The bonding shear strength was also measured in wet condition, after soaking in water (Method D2559-04, standard specification for adhesives for structural laminated wood products for use under exterior (wet use) exposure conditions) [29], the bonding shear strength of soaked specimens was also measured according to ASTM standard (Method D906-98). Five replications were performed for each measurement both in the dry and wet conditions. Phenol formaldehyde glue applied specimens were used as controls.

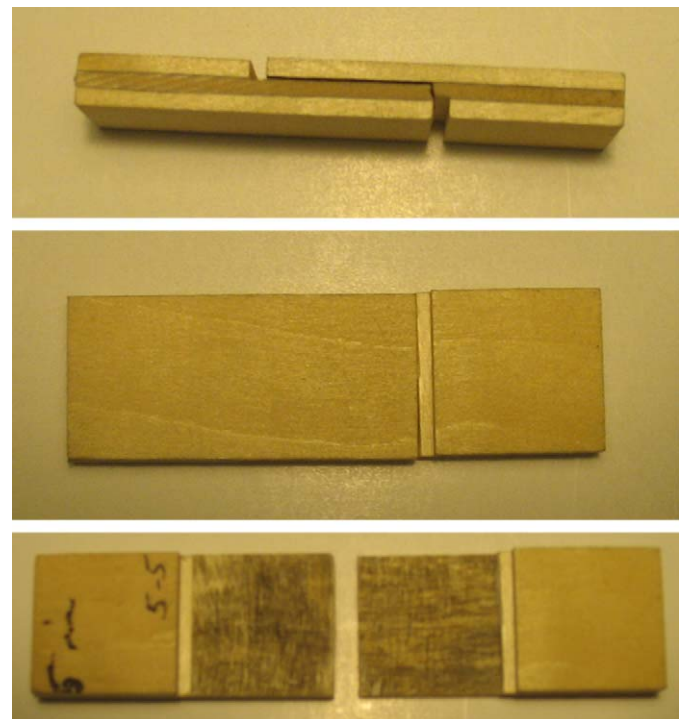
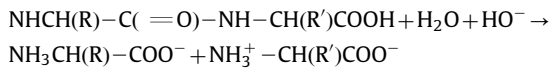


Fig. 1. Elevation (top) and plan (center) views of 3-ply tensile shear strength test specimen. Bottom image shows the glued area over which shear force was applied in tension by gripping the specimen at the grooves seen in the top image.

3. Results and discussion

3.1. Degree of hydrolysis

The degree of hydrolysis of alkaline-modified blood protein is depicted in Fig. 2 as a function of time. It is expected that soluble peptides are hydrolyzed to a greater extent at longer times yielding products of different component molecular weight distributions. Hydrolysis of blood proteins breaks their individual chains and opens up the side chain groups, which makes them available for bonding to the wood or crosslinking chemicals. Hydrolysis also alters the three-dimensional structure of the proteins. A more crosslinked structure should improve bond durability under wet conditions. The hydrolysis of a dipeptide can be expressed by the following reaction:



Results also show that the extent of hydrolysis increases with an increase in basic pH of the adhesive. Protein has a highly ordered structure, with most of the hydrophilic groups exposed on the outside and most of the hydrophobic groups buried inside. At higher pH, more carboxylic terminals could be esterified to ester groups, which are hydrophobic. More hydrophobic interaction might have been formed, which could be demonstrated to a higher molecular weight range. More peptide bonds could then be hydrolyzed and result in more unfolded proteins.

3.2. Effect of shear rate and temperature on adhesive

Viscosity is an important property governing the bonding property of adhesives. Different viscosity values have been suggested for different applications [30]: 0.5–5 Pa s for gluing materials which are highly absorbing such as paper, soft board and dried wood aggregates; 5–25 Pa s for most wood laminating; and > 50 Pa s for mastic consistency wood laminating. The viscosity values of the blood adhesives range from about 4.5 to 0.1 Pa s depending on number of factors (Figs. 3 and 4), and hence are ideal for highly absorbing materials mentioned above. Also, blood glue viscosity values are comparable to the lower end of viscosity values (from 0.5 to 75 Pa s) reported for soybean glues [30].

The viscosity curves (at 25 °C) of blood adhesives are presented in Fig. 3 as a function of pH. These curves represent a classic shear-thinning behavior—viscosity decreasing with increasing shear rate. At low shear rates, high molecular weight protein

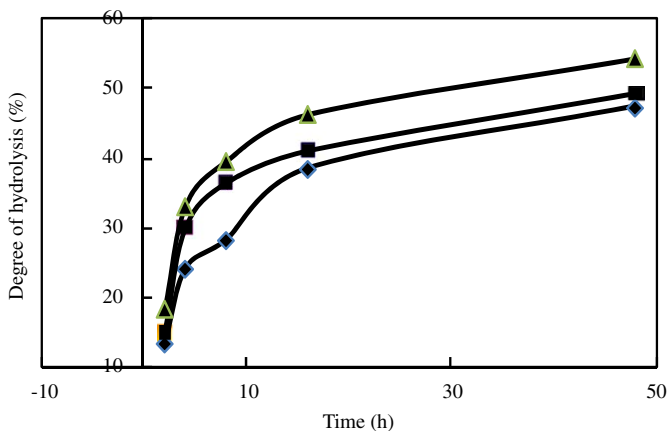


Fig. 2. Degree of hydrolysis of blood protein adhesives at different pH: 9.3 (◆), 10.2 (■), and 11.2 (▲).

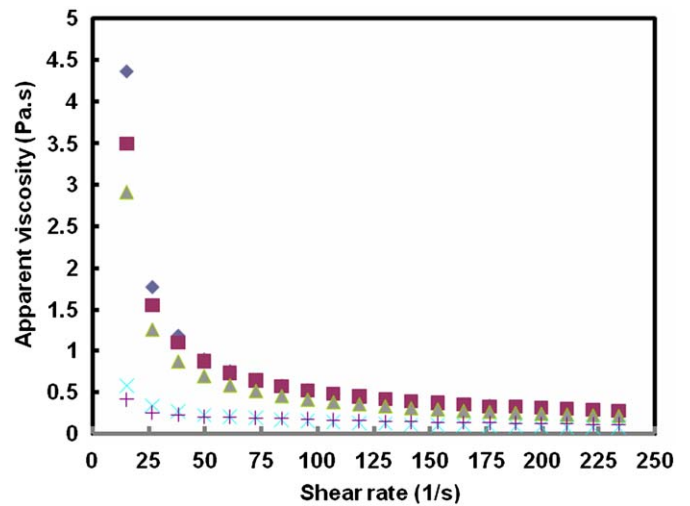


Fig. 3. Shear rate-dependence of apparent viscosity of blood adhesives at different pH values (at 25 °C): 9.0 (+), 9.3 (×), 10.2 (▲), 11.2 (■), and 12.1 (◆).

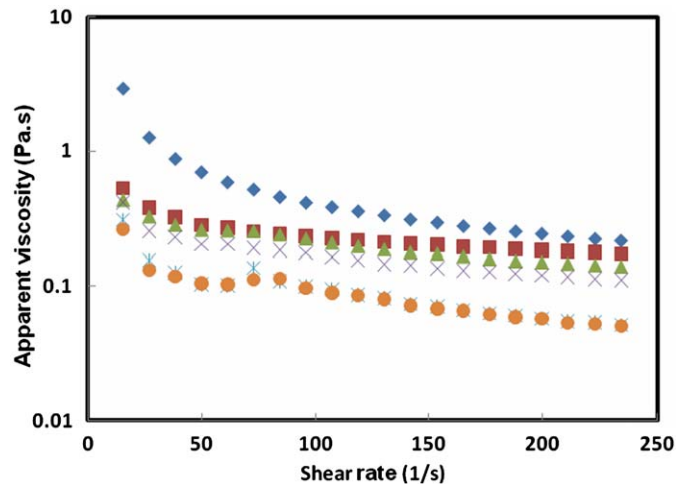


Fig. 4. Viscosity curve of blood adhesives (pH=10.2) at different temperatures: 25 °C (◆), 50 °C (■), 55 °C (▲), 60 °C (×), 70 °C (*), and 80 °C (●).

chains, which are probably in their natural random configuration, experience Brownian motion. As the shear rate sufficiently increases to overcome the Brownian motion, the protein chains become more ordered along the flow field and offer less resistance to flow and hence exhibit lower viscosity [31]. The relatively low viscosity at high shear rate makes adhesives easy to mix and pour; and high viscosity at low shear rate gives adhesives good suspension properties.

The effect of temperature on the apparent viscosity of the adhesive is shown in Fig. 4. A general decrease in the apparent viscosity of adhesives was observed with increase in temperature. This is attributed to the inability of protein molecules to form thermally stable “molecular clusters” in solutions as the temperature is increased. The viscosity curves were fit to power-law model:

$$\eta_a = K\dot{\gamma}^{n-1}$$

where η_a is apparent viscosity (Pa s), $\dot{\gamma}$ is shear rate (s^{-1}), K is consistency coefficient (Pa s^n), and n is flow behavior index.

Based on the K and n values listed in Tables 1 and 2, respectively, the adhesives are classified as pseudoplastic fluids

Table 1
Power-law parameter K and n of blood adhesive systems at different pH (at 25 °C).

pH	K (Pa s ^{<i>n</i>})	n	R^2
9.0	1.17 ^a	0.57 ^a	0.975
9.5	3.98 ^a	0.47 ^a	0.995
10.2	22.98 ^b	0.14 ^b	0.981
11.2	27.48 ^b	0.14 ^b	0.982
12.1	38.45 ^c	0.07 ^b	0.976

^{abc} Values in each column with different superscripts are statistically different at $\alpha=0.05$, while values with the same superscripts are not different.

Table 2
Power-law parameters K and n of blood adhesives at various temperatures (at pH 10.2).

T (°C)	K (Pa s ^{<i>n</i>})	n	R^2
25	22.9 ^a	0.14 ^a	0.982
50	1.32 ^b	0.59 ^b	0.976
55	1.29 ^b	0.63 ^b	0.982
60	1.17 ^b	0.57 ^b	0.975
70	1.15 ^b	0.44 ^b	0.918
80	0.90 ^b	0.49 ^b	0.920

^{ab} Values in each column with different superscripts are statistically different at $\alpha=0.05$, while values with the same superscripts are not different.

($K > 0$ and $0 < n < 1$). The K value increased with pH; however, the increase was rather insignificant when the pH changed from 9.0 to 9.5, but fairly substantial when pH value exceeded 10.0 (Table 1). On the other hand, n value decreased with pH and showed a significant change around pH 10.0, as observed with the K value, and the adhesive became extremely shear thinning at pH 12.1. As with the pH effect, there were two trends in K and n values when comparing the values at 25 and at ≥ 50 °C (Table 2). While temperature is a significant factor affecting material viscosity, it is surprising that K and n values of cow blood adhesive did not change significantly past 50 °C.

These results indicate that rheological properties of cow blood glue can be readily adjusted via pH and/or temperature control. It is likely that some kind of chemical structuring taking place around pH 10 and at ~ 50 °C, which was not further explored during this investigation.

3.3. Effect of temperature on cure time

Dynamic moduli of cow blood adhesives are presented in Fig. 5, which shows the trends of elastic modulus (G') and loss modulus (G'') with curing time. Initially, both G' and G'' are low and fairly constant; G'' being greater than G' indicates strong viscous character of the adhesive. With time both G' and G'' increase, but G' values change more rapidly than those of G'' and eventually the G' curve crosses over the G'' curve. The time taken for G' and G'' curves to cross over is identified as the curing time for the adhesive, which were 341 ± 6 , 317 ± 6 and 272 ± 5 s, respectively, at 60, 70 and 80 °C. Thus, the adhesives cure more rapidly at higher curing temperature, as has been reported previously [32].

Thermal treatment is one of the commonly used processes causing protein association and aggregation. At high temperatures, protein adhesives lose water quite rapidly into adjacent dry wood. It is thought that bonding strength increases due to the relaxation of internal stress, which occurs during curing. Normally, higher temperature will ensure more fully cured adhesive, leading to better bond quality. A strong adhesive joint requires both high adhesion to the cellulose substrates and high cohesive

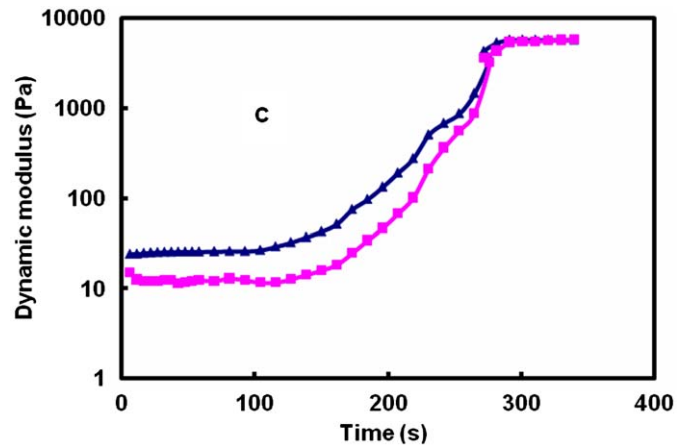


Fig. 5. Dynamic moduli, G' (■) and G'' (▲), during isothermal curing at 80 °C.

Table 3
Solubility scores: (clear, 1; traces of color, 2; slight coloration, 3; and brownish color, 4) of cow blood adhesive (pH 10.2) prepared with different amounts of curing agent sodium silicate over five days.

Time (d)	Sodium silicate (%)				
	0.5	1.0	1.5	2.0	2.5
1	2	1	1	1	1
2	3	1	1	1	1
3	3	2	1	1	1
4	4	2	1	1	1
5	4	3	2	1	1

strength within the protein layer. Blood protein is heart-shaped with disulfide bonds between helical segments. Heating causes the blood protein to partially unfold and facilitates protein–protein interactions. Heat-induced formation of disulfide bonds is the main mechanism by which to strengthen the protein films [33].

3.4. Water solubility of cured adhesive resin

The water solubility scores of the cured resin samples (Table 3) improved with sodium silicate content. The samples scored the best over the entire five day test duration when sodium silicate concentration was at least 2.0% (v/v). The lowering of water solubility with sodium silicate suggests that its addition helps forming some insoluble protein network. It is known that a certain amount of curing agent is needed to form block copolymers in mixed systems and maintain entanglement and crosslink structure and to improve water resistance. We also determined when the pH of adhesive increases from 9.0 to 12.1, there was no significant difference in solubility of cured resins (data not reported). It indicates that the use of gradually increasing concentration of sodium hydroxide does not appreciably change the solubility of resins. It suggests that the hydrophobic groups may have already been exposed and may remain so. Since proteins can form aggregates via hydrophobic interactions, strong hydrophobic interactions offset electrostatic repulsions, facilitating a moderate solubility over basic condition.

3.5. Bonding shear strength

Bonding shear strengths of cow blood adhesives of different pH values tested at dry and wet conditions are shown in Fig. 6 along with those of phenol formaldehyde (PF), the control. The average

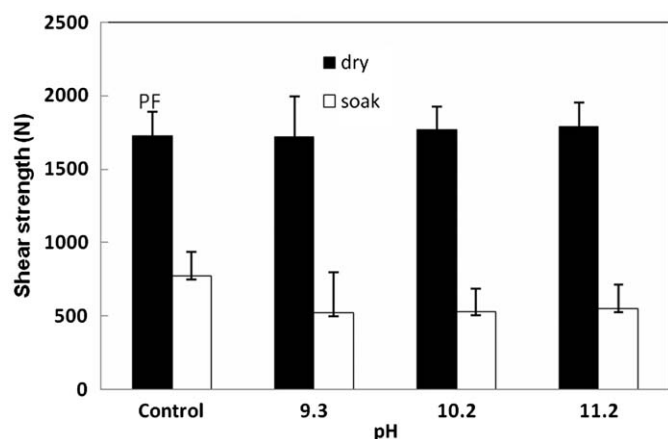


Fig. 6. Dry and wet (soak) bonding shear strength of cow blood adhesives at different pH and that of control PF (phenol formaldehyde).

bonding strengths at dry conditions were 1.72, 1.77, and 1.79 kN at pH 9.3, 10.2, and 11.2, respectively. Statistical analysis indicated that the bonding strength was independent ($p > 0.05$) of pH. Thus, there was no significant change in the hydrophobicity of blood in the alkaline media. Bonding shear strength of the protein glue depends on its ability to disperse in water and on the interaction between apolar and polar groups of the protein with those of the substrate. In the native protein, most of the polar and apolar groups are unavailable due to internal bonds resulting from van der Waals forces, hydrogen bonds, and hydrophobic interactions. Normally, dispersion and unfolding of protein are enhanced by hydrolysis or by increasing the pH to a desirable value. It is supposed that when pH value was changed from 9.3 to 11.2, as the protein unfolds, polar and apolar groups are exposed and are able to interact with other materials. These interactions can lead to increased adhesive strength of modified blood protein with wood. The dry bonding strength of blood adhesive was not significantly different than that of phenol formaldehyde (1.71 kN).

Bonding shear strengths of the wet samples were significantly lower, being about 30% of the values of those of their dry counterparts. And, just as with dry bonding strength, the wet bonding strength was also independent ($p > 0.05$) of pH. The control PF performed relatively better in the wet condition than blood adhesives. Thus cow blood glue can be considered comparable to PF in terms of bonding strength for dry (indoor) applications but somewhat inferior for wet (outdoor) uses.

Since both in dry and wet bonding strengths of blood adhesives were independent of pH, it offers an opportunity to select a pH depending on the end-use requirements. For example, as noted before, pH around 10 is desirable if higher viscosity adhesive is needed.

4. Conclusions

Fresh cow blood is readily converted into an adhesive via alkali modification. The adhesive viscosity and shear-thinning character are strongly pH and temperature dependent. Addition of sodium silicate $> 2\%$ (v/v) improved water resistance of the adhesive regardless of its pH. The cow blood adhesive cured in about 5 min; the curing time decreased with temperature but was independent of the adhesive pH. The bonding shear strength was substantially greater in dry condition than in wet condition. In terms of bonding strength, blood adhesive was comparable with phenol formaldehyde in dry condition but

was slightly inferior in wet condition. Since bonding strength, water solubility, and curing time were unaffected by pH of the adhesive, viscosity of the adhesive can be easily adjusted by changing pH depending on the end-use requirements. Overall, cow blood adhesive is a suitable alternative for phenol formaldehyde in dry condition without overly compromising its bonding strength in wet condition.

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