IOP Conf. Series: Materials Science and Engineering **137** (2016) 012045 doi:10.1088/1757-899X/137/1/012045

The effect of acrylic latex-based polymer on cow blood adhesive resins for wood composites

J Yan[1], H L Lin[1], G Z Feng[1] and S Gunasekaran[2, 3]

[1]Chemistry & Chemical Engineering Department, Zhongkai University of Agriculture and Technology, Guangzhou 510225, P.R. China
[2]Biological Systems Engineering Department, University of Wisconsin-Madison, WI, 53706, U.S.A

E-mail: guna@wisc.edu

Abstract. In this paper, alkali-modified cow blood adhesive (BA) and blood adhesive/acrylic latex-based adhesive (BA/ALB) were prepared. The physicochemical and adhesion properties of cow blood adhesive such as UV- visible spectra, particle size, viscosity were evaluated; share strength, water resistance were tested. UV- visible spectra indicates that the strong bonding strength of BA/ALB appeared after incorporating; the particle size of adhesive decreased with the increase of ALB concentration, by mixing ALB and BA, hydrophilic polymer tends locate or extand the protein chains and provide stability of the particles; viscosity decreased as shear rate increased in concordance with a pseudoplastic behavior; both at dry and soak conditions, BA and ALB/BA show significant difference changes when mass fraction of ALB in blend adhesive was over 30% ($p < 0.05$). ALB/ BA (ALB30%) is not significant different than that of phenol formaldehyde which was used as control. A combination of cow blood and acrylic latex-based adhesive significantly increased the strength and water resistance of the resulting wood.

1. Introduction

Wood adhesives in use today are normally synthetic polymers from petroleum chemicals.Toxic emissions from wood adhesives are of major concern [1-3]. One of the goals of the wood-products industry is to use natural materials as adhesives and reduce dependency on petrochemical [4-9]. Proteins from both plant and animal sources have been used to prepare adhesives with varying degrees of success. Weakley and Mehltretter [10] developed moisture-resistant plywood adhesives by cross-linking casein with dialdehyde. Ash and Lumbuth [11] prepared plywood glues containing high blood solids blended with phenol-formaldehyde (PF) resins that required a special mixing procedure to avoid high viscosity. Golick and Dike [12] formulated exterior phenolic plywood glues containing up to 70% dried blood. Thames, Cook and Mendon [13] formulated an adhesive by mixing of soy protein isolate; a polyolplasticizer and a vegetable oil derivative was used to impart water resistance. Trocino [14] prepared adhesives by copolymerizing hydrolyzed vegetable protein that has been functionalized with methylol groups, the adhesives were able to maintain long-term strength and water resistance. Wang, Wang and Sun [15] studied the effects of hexadecyltrimethyl ammonium bromide, ethylhexadecyldimethyl ammonium bromide and benzydimethylhexadecyl ammonium chloride, results indicate that electronic and hydrophobic interactions between soy protein isolate and detergent help improve adhesive performance. Jiang, Qin, Hse et al. [16] replaced phenol in the synthesis of

phenol-formaldehyde resin with feather protein, performed as well as the PF resin. Qi, Li and Wang [17] found $NaHSO_3$-modified soy protein adhesives had many advantages over traditional soy protein isolate adhesive. Li, Qi, Sun et al. [18] proved that canola protein could be used as bio-degradable wood adhesives. $NaHSO_3$ could cleave disulfide bonds in the protein, induce extra charges ($RS\text{-}SO_3^-$) on the protein surface, reduce adhesives' apparent viscosity and improve the flow ability properties of canola protein adhesives. It had insignificant effects on the adhesion performance of the wood adhesives. Although different methods had been used to reduce viscosity, the viscosity of these protein-based glues were still very high.

Blood adhesives suffer from relatively lower adhesive strength and higher viscosity than chemical synthetic adhesives. The high viscosity of the modified blood protein adhesives is a result of increased intermolecular interactions of the unfolded protein molecules. Adhesive with high viscosity has poor flow ability and is not easy to spread in application. Possible approaches to solving the high viscosity problem are to minimize intermolecular interactions and enhance physicochemical factors that weaken or disrupt these forces without adversely affecting adhesive strength. Improved adhesive strength and water resistance have been observed for adhesives prepared from alkali-modified blood protein in our previous study [19]. Ionic environments have been known to weaken the electrostatic interactions between protein molecules. Thus the viscosity of protein can be varied by treating protein with salts or by using reducing agents without affecting the adhesive strength or water resistance. However, relatively little is known about acrylic latex-based adhesive blending with blood adhesive.In most latex applications, acrylic acid is often used for coating and adhesive formulations [20-21]. The carboxylic acid groups of acrylic provide colloidal stability through electrosteric stabilization [22]. It is an adhesive with superior bonding and water resistance properties, it is non-flammable, non-toxic and low viscosity. Cow-blood has higher protein ratio compared to other types of animal blood that could reach better adhesive properties through modifing. The objective of this study was to investigate the adhesive and water resistance properties and viscosity of blending acrylic latex-based adhesive and cow-blood adhesive.

2. Materials and methods

2.1. Materials

Fresh cow blood was purchased from Muscle Science Department, UW-Madison. Sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3), calcium oxide (CaO) and ammonia ($NH_3.H_2O$) (density =0.9 g/cc) were purchased from Fisher Scientific (Fair Lawn, NJ). Sodium azide (NaN_3), EDTA disodium salt ($C_{10}H_{14}N_2Na_2O_8.\ 2H_2O$), were purchased from Sigma Chemical Company (St, Louis, MO). Acrylic latex-based synthetic adhesive (ALB) was obtained from Soil Net Inc., (Madison, WI, USA).

2.2. Preparation of blood adhesive

Adhesive of alkaline modified cow blood adhesive (BA) was made as follows [19]: 300 g of cow blood was mixed with 0.5 mL sodium azide (1.0%, w/w)and 5.5 mL EDTA (10%, w/w) by stirring. Calcium hydroxide (1: 3.5 w/w) about 20 g, caustic soda (30% w/w) 10 to10.5 g was added in stages under stirring at room temperature (25 to 28 °C). Then about 3 g ammonia solution (10%) and 12 g sodium silicate were added in stages while stirring. The resulting product is adhesive and the pHs of the adhesives are around 10.0.

2.3. Preparation of blend adhesive

The BA adhesive was blended with ALB adhesive. The mass fraction of ALB in the blend adhesives was 0.00, 0.21, 0.33, 0.52, 0.75, 0.85 and 1.00, respectively. The mixture was stirred for about 20 minutes at room temperature under 300 rpm.

2.4. UV testing

The UV-Vis spectra of the samples were recorded for the wavelength range of 200 to 800 nm at room temperature using a UV-Vis spectrophotometer (UV-1601PC, Japan).

2.5. Rheological analysis

Rheological analysis was performed at 25℃ within 12 h after preparation. A standard rotational rheometer equipped with plate-plate geometry (CP 4/40) / (Bohlin CVOR, Malvern Instruments Inc., Southborough, MA) was used in steady state by varying the shear rate from 10 to 250 s^{-1}. The distance between plate and plate was set to 150 μm for all measurements. Three replicate measurements were performed for each type of adhesive.

2.6. Particle size testing

Surface-area-average diameter of the adhesives was determined by particle size analyzer (90Plus, Brookhaven Instruments Corporation, New York, USA). In all experiments, adhesives were diluted with distilled water prior to particle size measurements, to keep the concentration typically between 10^{-5} and 10^{-2} volume fraction to prevent multiple scattering effects. The particle size was calculated by the autocorrelation function of the ALV Sizer software. Each measurement was done in triplicate.

2.7. Dry and wet bonding shear strength

Bonding shear strength was measured using an Instron testing systems (Model 1000, Canton, MA). Two hard maple wood strips (10.0 × 1.2 × 0.08 cm) were bonded over a bonding area of 2.0× 1.0 cm by applying the adhesive (Figure 1). The wood strips were heated to 120℃ and held compressed at 220 N for two minutes. Bonding shear strength of dry specimens (moisture content 6 to 10%) was performed at a crosshead speed of 10 mm/min. Five replications were performed for each measurement. The bonding shear strength was also measured after soaking the specimens in water for 24 h at room temperature and then drying at room temperature in a fume hood for 24 h. Both in dry and soak tests, phenol formaldehyde (PF) was used as control.

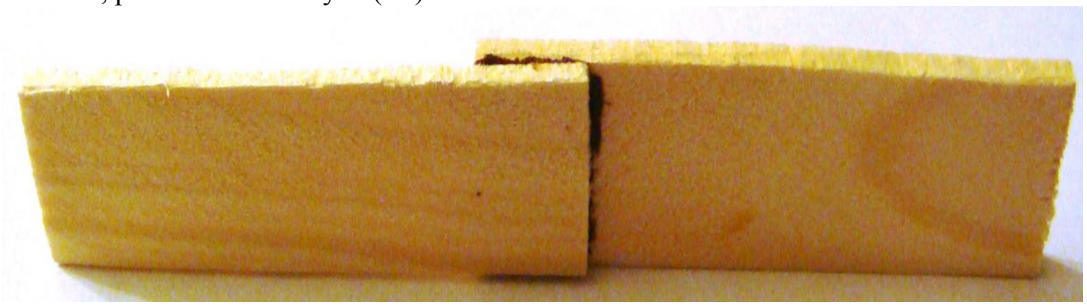

Figure 1. Maple wood strips bonded by adhesive.

3. Results

3.1. UV-Vis spectrophotometer

UV-Vis spectroscopy can provide information on possible denaturation of blood protein, particularly that of conformational change. UV-Vis spectra of BA, ALB and ALB/BA (w/w) are shown in Figure 2. The UV-Vis spectrum of BA exhibits a strong Soret absorption at 421 nm.

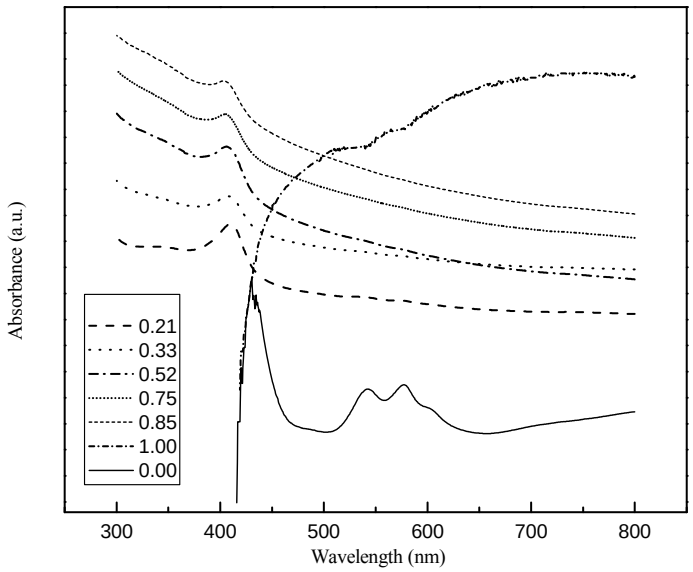

Figure 2. UV spectra of ALB in BA solution with different concentration.

ALB doesn't exhibit absorption peak. When ALB is combined with BA, Soret band absorption at 421 nm exhibits a shifts in the wavenumber. These results indicate that interactions between BA and ALB occurred. On the other hand, the shift phenomenon is more significant with higher ALB content. This indicates that stronger bonding strength of ALB/BA appeared after incorporating more amount of ALB because of more lateral hydrogen bonds formed.

3.2. Effects of ALB amount on viscosity

Adhesive of moderate viscosity is needed for wood products applications. To evaluate the behavior of the binary formulations of adhesive, rheological flow properties of the binary systems were evaluated. The flow curve of viscosity vs. shear rate of the adhesive system was reported in Figure 3. It shows all the BA has higher viscosities at lower shear rates, but has lower viscosity at higher shear rates, exhibiting a shear thinning behavior. At low shear rates, high molecular weight BA chains are subjected to Brownian randomization. The molecular chains become more ordered along the flow field hence exhibit lower viscosity as shear rate sufficiently increases to overcome the Brownian motion, The high viscosity at low shear rate gives BA good suspension property. It is also evident in Figure 3 that viscosity trended downward with an increase in ALB content in the adhesive. The situation can be attributed to osmotic pressure change in the system due to the change in charge density and structure from BA and ALB. The viscosity curves were fit to power-law model (equation 1).

$$\eta_\alpha = K\,(\gamma)^{n-1} \tag{1}$$

Where, η_α is apparent viscosity (Pa.s), γ is shear rate (s^{-1}), K is consistency coefficient (Pa s^n), and n is flow behavior index. K and n values are listed in Table 1. Based on these, the blood adhesives examined are classified as pseudoplastic fluids (K> 0, 0 <n< 1). At the same time, we can see from Table 1 that K appeared to decrease with increasing mass fraction of ALB. K showed significant decline when mass fraction of ALB increased from 0.00 to 0.21, it means that viscosity of blood adhesive decreased apparently when ALB was added, more ALB was added, lower viscosity was obtained. Shear thinning character decreased gradually as judged from the increase in n value from 0.70 to 0.94 when mass fraction of ALB varied from 0.00 to 0.85.

Table 1. Power-law parameter K and n of BA with addition of ALB (25℃)

Mass fraction of ALB	K(Pa s^n)	n	R^2
0.00	9.81	0.70	0.97
0.21	4.38	0.82	0.96
0.33	3.30	0.83	0.96
0.52	1.88	0.92	0.95
0.75	1.49	0.93	0.94
0.85	0.84	0.94	0.81
1.0	0.82	0.95	0.80

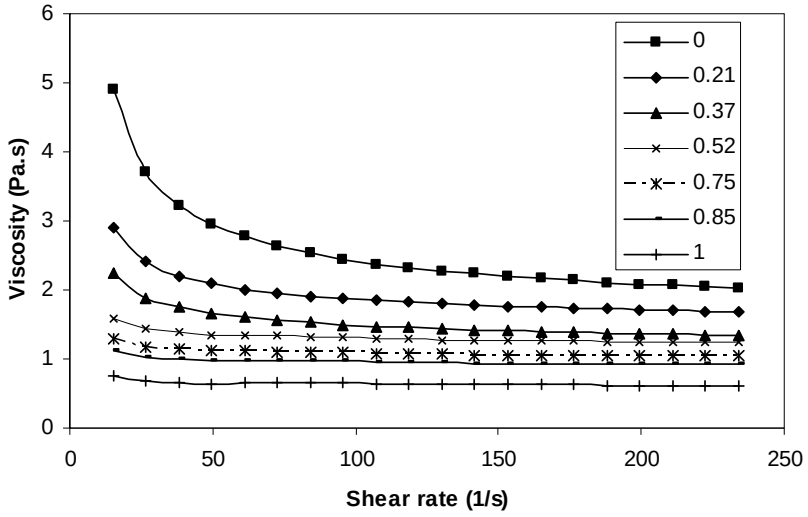

Figure 3. Viscosity curves of adhesives (pH = 10.2) at different mass fraction of ALB.

3.3. Effects of ALB amount on particle size changing and stability

Figure 4 shows the mean particle size decreased with the increasing of ALB content. This phenomenon is probably due to the decreased of viscosity of the internal phase, which increases the net shear stress and weakens the formation of large droplets. In addition, the decreasing viscosity could promote rapid dispersion of ALB into the blood adhesive aqueous phase, resulting in hindering aggregation of blood adhesive and decreasing smaller droplets. The carboxylate groups at basic condition resulted in dipoles and metal ions can joint in these dipolar interactions, which lead to a type of cross-linking [22]. It means that ALB was sufficient to cover the protein emulsion droplets which avoid the coalescence of protein droplets and then cause the formation of adhesive with smaller size. More ALB can be incorporated onto the protein surface, a large number of carboxylate groups extending into the continuous phase then could be cross-linked, forming a layer at the surface to avoid aggregation of protein molecules.

At the same time, more ALB can be oriented to reduce efficiently the interfacial tension which result in significant increase in the net shear stress at a constant energy density [23, 24] during emulsification and promoted the formation of smaller emulsion droplets. The mean particle size of adhesive decreased with the increase of ALB concentration, by mixing ALB and BA, hydrophilic polymer tends locate or extend the protein chains and therefore, provide stability of the particles.

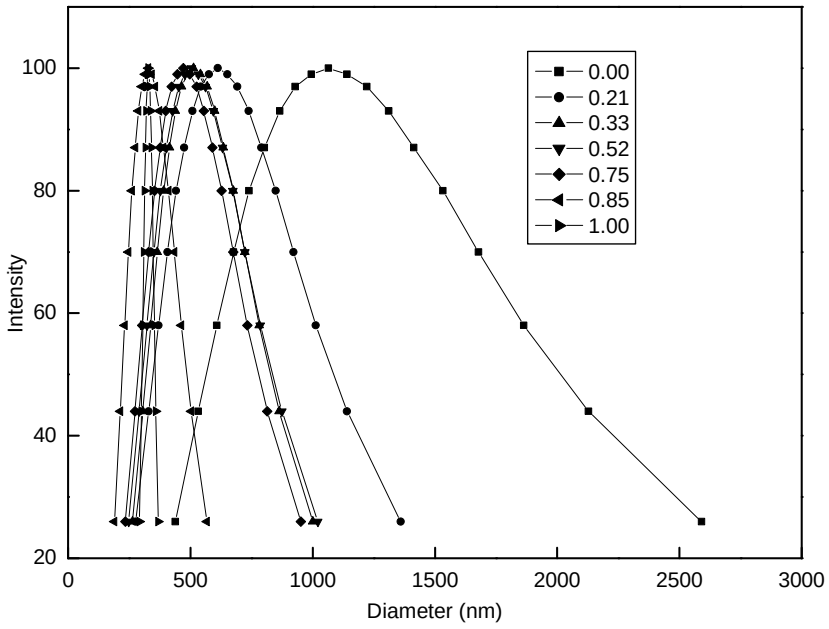

Figure 4. Particle size recorded at various mass fraction of ALB for blood protein-based adhesive.

3.4. Dry and soak bonding shear strength

Bonding shear strengths of blend adhesive at different mass fraction of ALB for both dry and soak tests are shown in Figure 5. It is clear that content of ALB greatly increased the bonding shear strength and water-resistances of plywood samples. In dry condition, the average shear strengths were 1110, 1241, 1368, 1598, 1601 and 1621 N when mass fraction of ALB were 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50, respectively. BA adhesive and ALB/BA adhesive do not show significant difference changes ($p > 0.05$) when mass fraction of ALB was less than 20% at dry condition, but BA adhesive and ALB/BA show significant difference changes when mass fraction of ALB is over 30% ($p < 0.05$). ALB/BA (30%) is not significantly different than that of control phenol formaldehyde (PF, 1611 N).

Bonding shear strength of the samples soaked in water shows the trends like in dry condition. The average shear strength of blood adhesive was 229, 398, 643, 695, 703 and 721 N at soak condition when mass fraction of ALB are 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50, respectively. BA and ALB/BA adhesive show significant difference changes when mass fraction of ALB are over 30% ($p < 0.05$). ALB/BA (30%) is not significantly different from that of control phenol formaldehyde (PF, 760 N). This suggests that the mixed adhesive are competitive with phenol formaldehyde for bonding shear strength in dry and soak conditions.

The bonding between blood protein molecules links mainly by hydrogen bonds, all kinds of salt-type keys and disulfide bonds are chemical cross-linking part. However, this is weak. The formation of protein-polymer (BA/ALB) complexes can be employed to improve functional properties of adhesive. Because ALB is easy to form hydrogen bonds, it also has high chemical activity and easy through grafting or cross - alliance to get a variety of branched-chain or mesh modifier system which has water resistance capability. ALB with certain chain length can form limited tangles points with BA, because there are many amino acids polar groups in BA. When BA adhesive blends with ALB, they will form a number of physical-chemical cross-linking points which guarantees reinforcement, bond strength and water resistance.

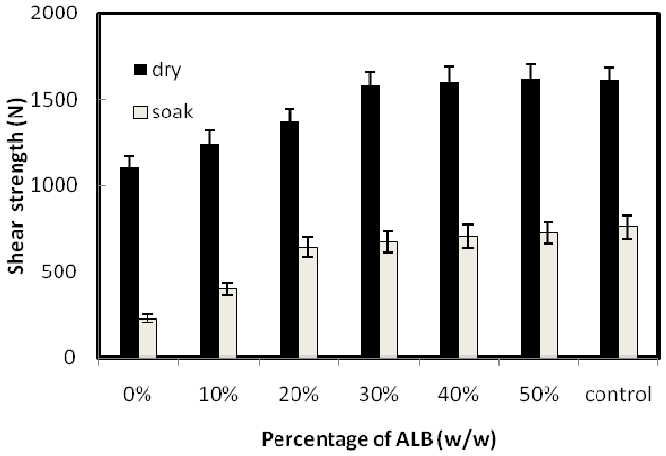

Figure 5. Dry and soak bonding shear strength at various mass fraction of ALB for blood protein-based adhesive and that of control phenol formaldehyde (PF).

4. Conclusions

ALB adhesive was successfully combined with blood adhesive. ALB adhesive increased the net shear stress and decreased viscosity of internal phase of blood adhesive, at the same time, provide stability of the blood protein particles. When BA adhesive blend with ALB adhesive, they will form a number of physical-chemical cross-linking points which guarantees the reinforcement, bond strength and water resistance.

Acknowledgments

Supported by the project of Guangdong Science and Technology (20140503, 2015B020215012), Chinese National Natural Science Foundation (31371880).

References

[1] Henderson J T 1979 *Tappi J* **62** 9396
[2] Heck H D Casanova M and Starr T B 1990 *Crit. Rev. Toxicol* **20** 397-426
[3] Edoga M O and Kovo A S 2006 *J Pract Technol* **8** 41-48
[4] Liu Z B Zhang Y L and Wang X M 2015 *Mater. Sci. App.* **6** 567-575
[5] Bekhta P Ortynska G and Sedliacik J 2014 *Drvna Industrija* **65** 293-301
[6] Hemmilä V Trischler J and Sandberg D 2013 *Pro Ligno* **9** 118-125
[7] Vazquez G Santos J Freire M S Antorrena G and Álvarez J G 2012 *J Therm Anal Calorim* **108** 605-611
[8] Vazquez G Pizzi A Freire M S Santos J and Antorrena G 2013 *Wood Sci Technol* **47** 523-535
[9] Garcia-Becerra F Y Acosta E J and Allen D G 2012 *J. Am. Oil Chem. Soc.* **89** 1315-1323
[10] Weakley F R and Mehltretter C I 1964 U.S. Patent 3153597
[11] Ash J R and Lumbuth A L 1954 U. S. Patent 2817639
[12] Golick A J and Dike T W 1941 U.S. Patent 2368466
[13] Thames S F Cook R C and Mendon S K 2004 U.S. Patent 6790271
[14] Trocino F S 2008 U.S. Patent 20080255333.
[15] Wang Y Wang D and Sun X S 2005 *J. Am. Oil Chem. Soc.* **82** 357-363
[16] Jiang Z H Qin D C Hse C L Lao Z H Wang G and Yu Y 2008 *J. Wood Chem. Technol.* **28** 240-246
[17] Qi G Y Li N B and Wang D H 2013 *J. Am. Oil Chem. Soc.* **90** 1917-1926
[18] Li N B Qi G Y Sun X S and Wang D H 2012 *J Polym. Environ.* **20** 905-915
[19] Lin H L and Gunasekaran S 2010 *Int. J. Adhes. Adhes.* **30** 139-144

[20] Ghim D and Kim J H 2016 *Korean J. Chem. Eng.* **33** 707-710
[21] Xiang A S Yan W L and Koel B E 2013 *J Nanopart Res* **15** 1705-1714
[22] Wang T Canetta E and Weerakkody T G 2009 *ACS Appl. Mat. Interfaces* **1** 631-639
[23] Mainardes R M and Evangelista R C 2005 *Int. J. Phytorem* **290** 137-144
[24] Nandi A Khakhar D V and Mehra A 2001 *Langmuir* **17** 2647-2655