PHYSICOCHEMICAL AND FUNCTIONAL PROPERTIES, MICROSTRUCTURE, AND STORAGE STABILITY OF WHEY PROTEIN/POLYVINYLPYRROLIDONE BASED GLUE STICKS

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A glue stick is comprised of solidified adhesive mounted in a lipstick-like push-up tube. Whey is a byproduct of cheese making. Direct disposal of whey can cause environmental pollution. The objective of this study was to use whey protein isolate (WPI) as a natural polymer along with polyvinylpyrrolidone (PVP) to develop safe glue sticks. Pre-dissolved WPI solution, PVP, sucrose, 1,2-propanediol (PG), sodium stearate, defoamer, and preservative were mixed and dissolved in water at 90 °C and then molded in push-up tubes. Chemical composition, functional properties (bonding strength, glue setting time, gel hardness, extension/retraction, and spreading properties), microstructure, and storage stability of the prototypes were evaluated in comparison with a commercial control. Results showed that all WPI/PVP prototypes had desirable bonding strength and exhibited faster setting than PVP prototypes and control. WPI could reduce gel hardness and form less compact and rougher structures than that of PVP, but there was no difference in bonding strength. PVP and sucrose could increase the hygroscopicity of glue sticks, thus increasing storage stability. Finally, the optimized prototype GS3 (major components: WPI 8.0%, PVP 12.0%, 1,2-propanediol 10.0%, sucrose 10.0%, and stearic sodium 7.0%) had a comparable functionality to the commercial control. Results indicated that whey protein could be used as an adhesive polymer for glue stick formulations, which could be used to bond fiber or cellulose derived substrates such as paper.

INTRODUCTION

Whey protein includes a group of globular proteins (mainly β-lactoglobulin (β-Lg), α-lacalbumin (α-La), bovine serum albumin (BSA), and immunoglobulins (Ig)) (Onwulata and Huth 2008). Whey protein isolate (WPI), comprised of more than 90% of protein, is obtained through ultrafiltration and ion-exchange of whey, a by-product of cheese manufacturing (Onwulata and Huth 2008). Utilization of whey has been a concern for a long time in the cheese industry since direct discard of whey causes severe environmental pollution. The applications of whey protein in the food industry have been extensively studied in the past decades. In order to increase whey utilization, applications in nonfood preparations are being explored. The adhesives industry is a potential area where whey protein could be used. Globular structures of whey protein could be unfolded

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by heat treatment (Gezimati *et al.* 1996; Hoffmann and Mil 1997; Gao *et al.* 2011) or solvent polarity change (van der Leeden *et al.* 2000) and come to resemble the structures of synthetic polymers. In addition, whey protein molecules contains both hydrophilic and hydrophobic parts (Fox and McSweeney 2003) and can attract the surfaces of many kinds of materials, especially those of fibrous substrates like paper, which is made from fibers derived from cellulose pulp. Thermal denaturation or polymerization makes the whey protein molecules more flexible and easier to interweave into networks to exhibit adhesive power. As early as the 1950s, a whey-based adhesive made from condensed liquid whey with addition of dextrin and caustic soda was patented (Tschabold and Mueller 1953). However, no literature on whey protein-based adhesive in the following decades have appeared until recent publications describing the use of whey protein in wood adhesives (Gao *et al.* 2011; Wang *et al.* 2011).

A glue stick is a type of solidified or gelled glue mounted in a twist push-up applicator (Cognard 2006). The world's first glue stick was invented and commercialized by Henkel AG & Co (Düsseldorf, Germany) in 1969. A glue stick has some advantages over liquid glue, including ease and cleanness of use without wrinkles or shrinkage of paper. It soon became one of the most popular types of office glue. Glue sticks are produced by hot mixing all the ingredients (aqueous vehicle, adhesive ingredients, solidifier, and auxiliaries), and then injecting or pouring the molten mixture into push-up tubes, which are finally solidified into glue sticks.

Many polymers have been used as adhesive ingredients for glue sticks, including polyvinylpyrrolidone (PVP) (Mestetsky and Pa 1974; Sitaramiah and Jorgensen 1995; Columbus and Anderson 1997), polyurethane (Gierenz *et al.* 1994), and polyvinylacetate (Dickmann *et al.* 1982). The most prevalent adhesive ingredient used for glue sticks is soluble PVP (Mestetsky and Pa 1974; Gierenz *et al.* 1994; Columbus and Anderson 1997), which is also known as Povidone. PVP is the polymerization product of N-vinylpyrrolidone; it possesses a number of favorable properties that make it widely used in pharmaceutical and adhesive products (Buhler 2005).

There are some obstacles to the application of whey protein as a binder in glue sticks. In order to obtain a glue stick with desirable solid shape and bonding strength, the total solids content should be no less than 30% of the total weight, and the adhesive ingredient content usually ranges from 15% to 25% of the total weight (Columbus and Anderson 1997). However, whey protein solutions with concentration higher than 15% form an irreversible gel under thermal treatment above 70 $^{\circ}$C (Fox and McSweeney 2003), and this causes the mixture to congeal during the process of hot mixing. As a result, not only does packaging of the mixture become impossible, but the adhesive power is reduced. Therefore, a stabilizer to prevent high content whey protein solution from hot congealing is necessary for the application of whey protein in glue sticks. Previous studies indicated that PVP, already being used as a protein stabilizer (Jiang *et al.* 2006; Hamada *et al.* 2009), could bind to the exposed hydrophobic patches of whey protein molecules during thermal treatment and prevent aggregation. Therefore, the aim of this study was to develop safe glue sticks based on WPI with PVP as a co-binder and stabilizer. Comparative studies of functional properties of the prototypes and commercial control was carried out to evaluate the quality of WPI/PVP-based glue sticks.

EXPERIMENTAL

Materials

Whey protein isolate (WPI) with a protein content of 92.4% was purchased from Fonterra Ltd. (Auckland, New Zealand). Polyvinylpyrrolidone (PVP) K-90 with an average molecular weight of 360,000 Da was purchased from Aldrich Chemistry (St. Louis, MO, USA). Sodium stearate (stearic acid, sodium salt, 96%, mixture of stearic and palmitic fatty chain) and 1,2-propanediol (PG) with 99% purity were purchased from Acros-Organics (New Jersey, USA). Fine granulated sucrose was purchased from a local Hannaford supermarket (South Burlington, VT, USA). Silicor 1311 FG emulsion (defoamer) and Proxel® BD-20 (preservative) were generously provided by Defoamer.com Inc. (Bartlett, IL, USA) and Arch Chemical Inc. (Norwalk, CT, USA), respectively. Fine cotton paper (WT 134 lbs) used as a glue substrate was purchased from Crane & Co. (Dalton, MA, USA). Avery® glue sticks (1.27 oz, Product ID: A198-071) used as commercial reference (COM) and empty Avery glue stick tubes (1.27 oz) were obtained from Avery Dennison Corporation (Brea, CA, USA).

Methods

Procedure of making glue sticks

WPI powder was first dissolved into distilled water at room temperature. Then PVP powder, sucrose, PG, sodium stearate, silicor 1311, and proxel BD-20 were added to the WPI solution. The mixture was heated from room temperature to 90 °C at a rate of 5 to 8 °C /min with constant stirring at 300 rpm, and held at 90 °C for 20 min until the vicious mixture became homogenous.

The melted mixture was immediately poured into the glue stick tubes and molded into sticks by cooling down naturally. Four WPI/PVP-based glue stick prototypes (GS1a, GS1b, GS2, and GS3), and three PVP-based glue stick prototypes (CTR1, CTR2, and CTR3) were formulated in comparison with the Avery® commercial control (COM) (Table 1).

Table 1. Formulations of Prototypes

Ingredients	GS1a	GS1b	GS2	GS3	CTR1	CTR2	CTR3
WPI powder (g)	8.0	6.0	8.0	8.0	0.0	0.0	0.0
PVP powder (g)	8.0	10.0	14.0	12.0	16.0	22.0	20.0
Sucrose (g)	20.0	20.0	0.0	10.0	20.0	0.0	10.0
Others ingredients (g)	PG: 10.0, sodium stearate: 7.0, Silicor 1311: 1.0, Proxel BD20: 0.4, and water was added up to 100.0						

Chemical composition

Total nitrogen content was tested following the method of ASTM E258-07, and the contents of ash and total solids were analyzed according to ASTM D4906-95. The pH values were determined by IQ240 pH meter (IQ Scientific Instruments, Inc. San Diego, CA, USA) with a slanted tipped stainless steel probe.

Bonding strength

Bonding strength of glue sticks was tested according to the modified method of ASTM D1002. The crane fine cotton paper was cut into strips with dimensions of 101.6 mm × 25.4 mm, and then about 0.02 g glue was applied evenly to the end region of

one paper strip, and then was lapped by another strip. The lap length was 6.3 mm, and the bond width was 25.4 mm. After the glue was totally dry and cured, the bonding strength was tested using an Instron 5566 universal testing machine (Instron Corp., Canton, MA, USA).

The specimen was clamped at two ends by grips ($\pm$500 N max. load). The crosshead was moving upward at a rate of 12.7 mm/min until the bonded specimen was torn apart. The lap shear bonding strength was obtained by averaging the strength at rupture of 10 valid tests.

Percentage of paper failure (%PF)

Paper failure, a concept inspired by wood failure according to ASTM D 5266, indicates the rupturing of paper fibers in bond strength tests on bonded specimens. The %PF is the percentage of broken area in the total bonded area. The ruptured adhesive joints after bonding strength tests were digitally imaged with use of a Sony® DSC-H20 digital camera (Sony Corp., Tokyo, Japan). The broken and total bonded areas were calculated by ImageJ 1.46 software (http://rsbweb.nih.gov/ij/download.html, available for download). The %PF was calculated based on Eq. 1,

$$\% PF = \frac{S_b}{S_t} \times 100\% \tag{1}$$

where S_b is the broken bonded area and S_t is the total bonded area.

Glue setting time

The initial paper tear time was measured as an indicator of glue setting time (Columbus and Anderson 1997). The bonded paper specimens were subjected to bonding strength tests at 1 to 10 min after application. The types of adhesive failure were examined. The time when initial substrate failure observed was recorded as glue setting time.

Gel hardness

The hardness of the glue stick was measured using a uniaxial Instron 5542 testing machine (Instron Corp., Canton, MA, USA) by compressing the sample between a load cell (Diameter: 40 mm, Max load: 50 N) and a heavy-duty platform (Diameter: 90 mm) (Xiong *et al.* 2002). Glue sample was cut into a cylindrical shape with a diameter of 15.0 mm and a height of 16.0 mm. The test specimen was placed on the center of the platform.

The crosshead was moving toward the specimen at 25 mm/min. When the load cell approached the glue specimen, it compressed the specimen from an original height of 16.0 mm to 12.8 mm at a rate of 200 mm/min, and then the crosshead returned upwards to the original site immediately at a rate of 200 mm/min. The maximum load (N) was recorded as the hardness of the glue gel.

Extension/retraction and spreading properties

The terms "easy", "slight resistance to extension", and "some resistance to extension" were used to describe extension properties, and the terms "easy" and "failed" were used to describe retraction property. Likewise, the terms "easier spreading with excess glue applied", "easy spreading", and "spreading required additional pressure" were used to describe the spreading characteristics (Columbus and Anderson 1997). Since there was no standard lexicon to describe the extension/retraction and spreading

property of glue sticks, and the definitions of those terms were very subjective, an Avery glue stick product was used as the reference sample. The extension/retraction and spreading property of the Avery control were pre-defined as "easy" and "easy spreading", respectively. The experimental samples were evaluated by comparison with the commercial reference.

Microstructural analysis

The microstructure of cured glue stick was analyzed by using an FEI Quanta 200 FEG ESEM Mark II scanning electron microscope (SEM) (FEI Company, Eindhoven, The Netherlands) (Hendricks and Hadley 1983). The glue composition was cured at room temperature for seven days and then frozen in liquid nitrogen. The frozen sample was placed on a pre-cooled steel block and fractured using a cooled knife. The fractured pieces were collected and thawed under vacuum.

The pieces were mounted on aluminum stubs with silver conductive paste followed by carbon coating and then sputter coating with Au/Pd (approximately 4 nm) before being examined through the SEM at 5 and 10Kv. All images were recorded digitally using Scandium software (Olympus Soft Imaging Solutions GmbH, Munster, Germany).

Storage stability

The samples were divided into two groups and stored at 23 ^{o}C and 40 ^{o}C for 12 months, respectively. The growth of molds and yeasts were visually observed throughout the storage. Bonding strength was tested at an interval of 2 months. Moisture contents of the samples were tested at the beginning and end of 12 months of storage. Absolute moisture loss (g) (the grams of moisture evaporated from a glue stick sample of an initial weight of 100 g) and relative moisture loss (%) (the ratio of grams of moisture evaporated versus its initial total grams of moisture) were calculated according to the following formulae,

$$AL_x(g) = 100 - \frac{100 \times TS_i}{TS_x}$$
(2)

$$RL_x(\%) = \frac{AL_x}{100 - 100 \times TS_i} \times 100\%$$
(3)

where AL_x is the absolute moisture loss (g) at X months; RL_x is the relative moisture loss (%) at X months; TS_i is the initial total solid (%) of the glue stick sample; and TS_x is the total solid (%) of the glue stick sample tested at X months. TS_i and TS_x were determined by the method of ASTM D4906-95.

Statistical analysis

One-way ANOVA analysis was conducted with SPSS 16.0 software (SPSS Inc, Chicago, IL, USA).

RESULTS AND DISCUSSION

Chemical Composition

The general chemical composition and pH of the prototypes and control are listed in Table 2. The nitrogen contents of all the prototypes and control were contributed by WPI and PVP. The commercial control (COM) had the highest ash content (3.07± 0.63%) among all the samples (Others ranged from 1.23±0.01% to 1.94±0.10%). The order of total solids contents was: GS1a, GS1b and CTR1 > GS3 and CTR3 > COM > GS2 and CTR2. All the samples exhibited weak alkalinity, but the prototypes (pH ranged from 8.8 to 9.8) were less basic than the COM (pH 11.3). The higher levels of ash content and pH value of COM might be contributed by the higher addition of fatty acid salt.

Table 2. Chemical Composition, Adhesive Properties, and Hardness of Prototypes and Control

	Total nitrogen (%)	Ash (%)	Total Solids (%)	pH	Bonding strength (MPa)*	Setting time (min)	Hardness (N)
GS1a	2.17±0.06	1.53±0.00	51.75±0.35	9.0±0.2	1.36±0.09^a	30	20.11±0.64
GS1b	2.05±0.23	1.54±0.02	52.06±0.16	8.9±0.3	1.34±0.13^a	40	27.63±3.32
GS2	2.80±0.10	1.94±0.10	34.24±1.07	8.8±0.3	1.20±0.15^b	10	10.57±0.30
GS3	2.51±0.30	1.75±0.01	46.12±0.37	9.0±0.2	1.24±0.13^b	20	23.48±3.42
CTR1	1.75±0.20	1.23±0.01	51.38±0.27	9.4±0.1	1.20±0.15^b	>60	55.45±5.47
CTR2	2.29±0.15	1.87±0.03	33.89±0.64	9.6±0.3	1.22±0.16^b	15	36.39±2.32
CTR3	2.09±0.21	1.56±0.04	45.32±0.87	9.8±0.2	1.31±0.11^{ab}	30	48.20±4.98
COM	2.06±0.19	3.07±0.63	38.64±0.10	11.3±0.2	1.30±0.19^{ab}	20	21.14±1.82
* The superscript letters indicate the significance level (P=0.05).							

Bonding Strength and Glue Setting Time

The results for bonding strength of the prototypes and control are shown in Table 2. The bonding strengths of GS1a (1.36±0.09 MPa) and GS1b (1.34±0.13 MPa) were significantly higher (P<0.05) than that of GS2 (1.20±0.15 MPa) and GS3 (1.24±0.13 MPa), but no significant difference (P>0.05) between GS2 and GS3 was observed. The bonding strength of CTR1 (1.20±0.15 MPa), CTR2 (1.22±0.12 MPa), and CTR3 (1.31±0.11 MPa) were not significantly different (P>0.05) from one another. The preliminary study showed that WPI, PVP, and sucrose had positive effects on the bonding strength. However, when the total polymer content (sum of WPI and PVP) was 15% or higher, further increase of the content of WPI, PVP, or sucrose no longer raised the bonding strength but still increased the hardness of glue stick (data not shown). In this study, there were three levels of total polymer contents among the prototypes: 16.0% (GS1a, GS1b and CTR1), 20.0% (GS3 and CTR3), and 22.0% (GS2 and CTR2), all of which were higher than 15%. This explains why the bonding strength of those samples did not vary too much from each other, and the maximum and minimum values of bonding strength were 1.36±0.09 MPa (GS1a) and 1.20±0.15 MPa (GS2), respectively. All prototypes had comparable bonding strength to COM (P>0.05) (Table 2). All including COM obtained 100% of paper failure, which indicated that these WPI/PVP prototypes (GS1a, GS1b, GS2, and GS3) had a comparable quality to COM and the PVP prototypes (CTR1, CTR2, and CTR3) in terms of bonding strength.
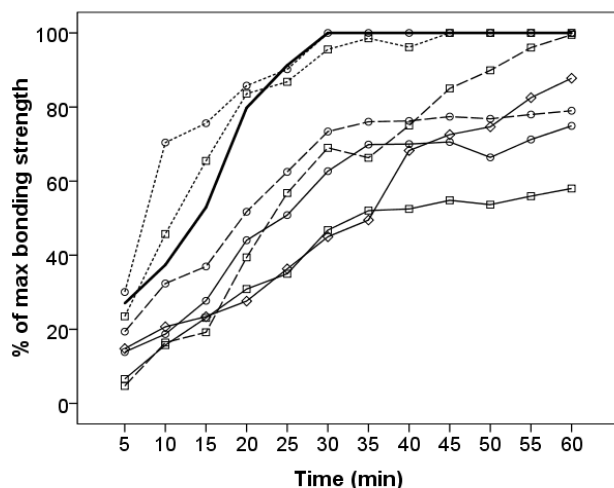
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Fig. 1. Effect of drying time on the bonding strength of prototypes and control
(─⊖─ : GS1a; ─◇─ : GS1b; -⊙- : GS2; ─⊙─ : GS3; ─▣─ : CTR1; -▣- : CTR2; ─▫─ : CTR3; and
── : COM)

WPI and PVP had no effects on bonding strength when the sum of WPI and PVP contents was higher than 15%, but they affected the glue setting time significantly. The results of glue setting time are listed in Table 2. Addition of WPI decreased the glue setting time, *i.e.* GS1a (30 min) and GS1b (40 min) versus CTR1 (> 60 min), GS2 (10 min) versus CTR2 (15 min), and GS3 (20 min) versus CTR3 (30 min); likewise, GS1a, and GS1b had the same formulation except a different ratio of WPI and PVP, and GS1a (8.0% of WPI and 8.0% of PVP) set 10 min faster than GS1b (6.0% of WPI and 10.0% of PVP). Sucrose was another factor that prolonged the glue setting time. CTR1, CTR2, and CTR3 contained 20.0%, 0.0% and 10.0% of sucrose, and their glue setting time were: >60 min (CTR1), 15 min (CTR2), and 30 min (CTR3), respectively. The glue setting time of GS1a and GS1b (30 min and 40 min) was longer than GS3 (20 min) that was longer than GS2 (10 min), which was as well in accordance with the order of their sucrose contents, *i.e.* GS1a and GS1b (20.0%) > GS3 (10.0%) > GS2 (0.0%). GS2, CTR2, CTR3, and COM achieved their maximum bonding strength in 30 min, 45 min, 60 min, and 30 min, respectively, while GS1a, GS1b, CTR1, and GS3 only obtained 75%, 88%, 58%, and 80% of their maximum bonding strength in 60 min (Fig. 1). Initial paper failure was usually observed when the bonding strength reached 0.80 to 0.90 MPa, which was around 70% of the maximum bonding strength (Table 2 and Fig. 1). The effects of PVP and sucrose on prolonging the glue setting time may be contributed by their high hygroscopicity. Once glue was applied, the moisture evaporated quickly, and when it decreased to a certain level, the polymer molecules started to form solid networks, thus bonding the substrates (Pizzi and Mittal 2003). When highly hygroscopic substances were presented in the glue compositions, the rate of moisture evaporation was slowed down, causing the glue to require a longer time for setting.

Gel Hardness, Extension/Retraction and Spreading Characteristics

Glue sticks with PVP as the only adhesive polymer had harder glue gel structures compared with those composed of WPI and PVP. Results of hardness tests are shown in Table 2. The hardness of CTR1 (55.45±5.47 N) was significantly (P<0.05) higher than

GS1a (20.11±0.64 N) or GS1b (27.63±3.32 N). The hardness of CTR2 (36.39±2.32 N) and CTR3 (48.20±4.98 N) was significantly ($P<0.05$) higher than GS2 (10.57±0.30 N) and GS3 (23.48±3.42 N), respectively. When the total polymer content was fixed, the higher the levels of PVP or lower levels of WPI in the formulation, the harder were the structures of glue gel. For example, GS1a (WPI: PVP = 8:8) and GS1b (WPI: PVP =6:10) with the same total polymer content but different ratios of WPI and PVP had no significant effects ($P>0.05$) on the bonding strength, but the gel hardness of GS1b (27.63±3.32 N) was significantly higher than GS1a (20.11±0.64 N) ($P<0.05$). The total solids content also had positive effects on the glue gel hardness. The descending orders of the hardness of WPI/PVP and PVP prototypes were: GS1b > GS3 > GS2 and CTR1> CTR3 > CTR2, respectively, which were in accordance to their total solids contents. However, there was an exception in the cases of GS1a and GS3. The total solids of GS3 (46.12±0.37%) was lower than GS1a (51.75±0.35%), but the hardness of GS3 (23.48±3.42 N) was slightly higher than GS1a (20.11±0.64 N). This might be explained by the higher content of PVP in GS3 (12.0%) than in GS1a (8.0%). The hardness values of CTR1, CTR2, and CTR3 were higher than any other WPI/PVP prototypes no matter of their total solids content. GS1a and GS3 had the closest hardness to COM among all the samples.

The hardness of glue gel was closely related to the extension/extraction and spreading properties. All prototypes and control had "easy" extension properties, and all except GS2 had "easy" retraction properties. The glue gel of GS2 failed to be retracted due to the softness of gel (10.57±0.30 N), and it had an easy spreading property but with crumbling and excess glue applied. GS1a, GS1b, and GS3 could be spread as easily as COM, while CTR1, CTR2, and CTR3 needed additional pressure to spread the glue on to paper surface due to the hard structure of their glue gels. In general, GS1a, GS1b, and GS3 had comparable extension, extraction, and spreading properties as COM.

Microstructure

PVP is a typical polymer molecule that is mainly comprised of random coils (Buhler 2005), while whey protein molecules contain β-sheets, α-helices, and random coils. For example, β-Lg is composed by 8% of α-helices, 45% of β-sheets, and 47% of random coils (Frushour and Koenig 1975; Dong *et al*. 1996). The complex structure of whey protein molecular is responsible for forming a network not as compact as synthetic PVP.

The SEM images of GS3, CTR3, and COM are shown in Fig. 2. Firstly, no insoluble particles or separated phases were observed in either GS3 or CTR3, which indicated that all ingredients were well dissolved and WPI had good miscibility with PVP. PVP can bind to the exposed hydrophobic patches of whey protein molecules due to its hydrophobic nature to obtain well miscibility and protect WPI from forming irreversible network during thermal treatment (Jiang *et al.* 2006; Hamada *et al*. 2009). The surface of GS3 (WPI and PVP based) was rougher and less compact than CTR3 (PVP based), which could be an explanation of why the gel hardness of WPI/PVP based prototypes were softer than the PVP prototypes (as discussed before), but no negative effects of the defects of microstructure on the bonding strength or other adhesive performance were observed.
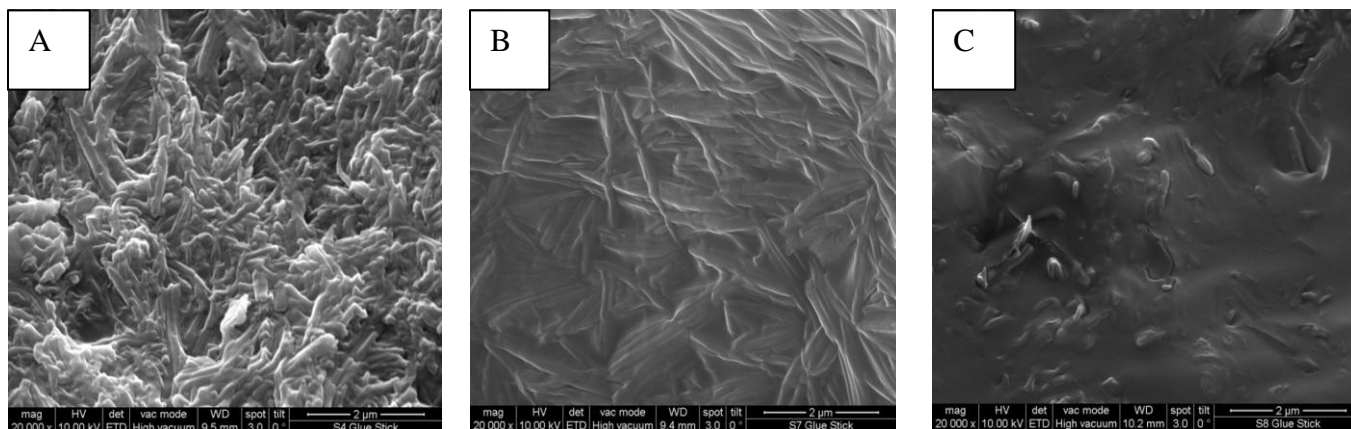
Fig. 2. Scanning electron microscopic images of cured samples. A: GS3 (WPI/PVP based), B: CTR3 (PVP based) and C: COM (commercial control)

Storage Stability

All prototypes and the control obtained 100% of PF at the beginning of storage; however, after having been stored at 23 °C for 12 months, the %PF of GS1a, GS1b, and CTR1 were reduced to 93%, 61%, and 55%, and the %PF of GS1a, GS1b, GS2, and CTR1 were reduced to 5%, 27%, 0%, and 46 % after being stored at 40 °C for 12 months, respectively (Table 3). The decrease of %PF might be contributed by the loss of moisture of glue gel during storage. In order to bond substrate, the glue composition needed to be able to first wet the surface of substrate, then the adhesive molecules must penetrate into the porous substrate to form a linkage between adhesive and substrate molecules after the glue was cured (van der Leeden *et al*. 2000; Wang *et al*. 2011). When water molecules between the adhesive molecules escaped during storage, adhesive sites such as hydroxyl groups and other polar groups of polymer molecules approached each other closely to bond together. In this case, there were less adhesive groups available to bind substrate molecules; furthermore, glue wettability decreased due to the loss of moisture; hence, the adhesive force (force between adhesive and substrate) decreased and cohesive force (force within the adhesive bulk) increased (van der Leeden *et al*. 2000), which led to the decrease of %PF. Glue stick usually has a higher total solid contents as compared with other liquid paper glue. Furthermore, glue stick containers are hardly airtight, and they are uncapped for use very often during their lives, which allows the escape of moisture during storage. The excess loss of moisture could cure or harden glue sticks to cause the decrease in bonding strength.

Ingredients with high hygroscopicity such as PVP, sucrose, and PG are supposed to be able to extend the shelf life of the glue stick products by reducing moisture loss during storage. The values of both absolute moisture loss (g) and relative moisture loss (%) of glue compositions after being stored at 40 °C for 12 months were higher in GS1a and GS1b, GS2, and GS3 than the PVP prototypes (Table 3). Furthermore, the content of PVP in GS1b (10%) was higher than in GS1a (8%), and the relative moisture loss (%) at 40 ℃ for 12 months of GS1b (24.58%) was lower than the GS1a (38.52%). These results indicated that PVP had a better ability than WPI to decrease moisture loss during storage. The sucrose molecule has eight hydroxyl groups on the carbon skeleton. The hydroxyl groups could form hydrogen bonds with water to avoid evaporation; thus the hygroscopicity of glue compositions is increased. The relative moisture loss of GS2 (contain no

sucrose) was 76.98%, which was higher than any other prototypes or control after being stored at 40 ^{o}C for 12 months, at which point the bonding strength had been decreased to 0 (Fig. 3B).

Table 3. Changes in Moisture Contents of Prototypes and Control During Storage at 23 ^{o}C or 40 ^{o}C for 12 Months

|	Before storage		23 ^{o}C, 12 months				40 ^{o}C, 12 months			
	Moisture (%)	%PF (%)	Moisture (%)	AL(g)	RL (%)	%PF (%)	Moisture (%)	AL(g)	RL (%)	%PF (%)
GS1a	51.74±1.07	100	39.72±0.19	19.93±0.10	38.52±0.18	93	47.50±0.77	8.16±0.13	15.76±0.26	5
GS1b	53.41±0.19	100	46.37±0.31	13.12±0.09	24.58±0.16	61	51.01±0.31	4.90±0.03	9.17±0.06	27
GS2	69.40±0.02	100	34.30±0.08	53.42±0.12	76.98±0.18	100	67.86±0.41	4.76±0.03	6.86±0.04	0
GS3	59.25±0.52	100	47.33±0.90	22.62±0.43	38.19±0.73	100	51.24±0.53	16.42±0.17	27.7±0.29	100
CTR1	52.81±0.02	100	48.71±0.07	7.98±0.01	15.12±0.02	55	51.13±0.27	3.41±0.02	6.47±0.03	46
CTR2	68.95±0.35	100	61.70±0.31	18.92±0.10	27.45±0.14	100	67.80±0.13	3.42±0.01	4.97±0.01	100
CTR3	59.84±0.86	100	44.02±0.08	28.26±0.05	47.23±0.09	100	54.39±0.19	11.96±0.04	19.98±0.07	100
COM	62.79±0.77	100	48.26±0.72	28.08±0.42	44.72±0.67	100	58.58±0.30	10.14±0.05	16.16±0.08	90
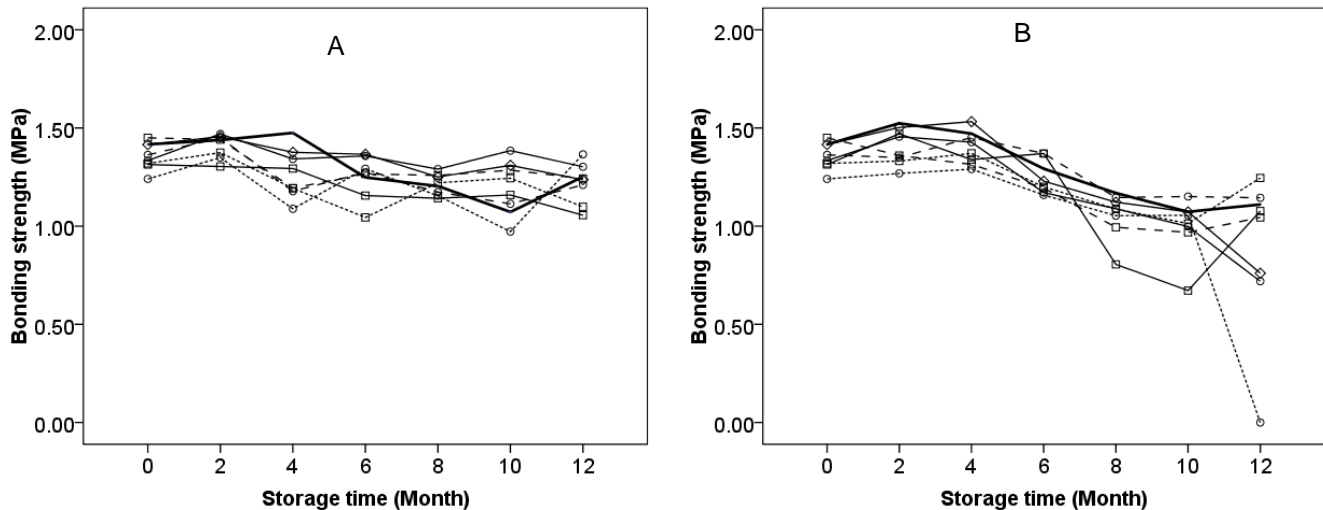
Fig. 3. Changes in bonding strength of prototypes, control during storage, A (23 ^{o}C), B (40 ^{o}C). —⊖— : GS1a; —◇— : GS1b; -⊙-· : GS2; —⊙— : GS3; —⊟— : CTR1; -⊡-· : CTR2; —⊡— : CTR3; and —— : COM

As shown in Fig. 3A, the bonding strength of prototypes and control were stable, and no obvious reduction was observed after storage at 23 ^{o}C for 12 months. The bonding strength of the WPI/PVP prototypes and commercial control after 12 months' storage at 40 ^{o}C were around 54% (GS1a), 54% (GS1b), 0% (GS2), 84% (GS3), and 78% (COM) of their initial bonding strength measured at the beginning of storage (Fig. 3B). The %PF values at the end of storage at 40 ^{o}C were 5% (GS1a), 20% (GS1b), 0% (GS2), and 100% (GS3), compared with the 90% of commercial control (Table 3). Prototype GS3 showed the best storage stability among all prototypes and was comparable to the commercial control. According to the moisture loss analysis, the rates of moisture loss of different samples at 40 ^{o}C were 2 to 3 times faster than at 23 ^{o}C on average (Table 3). Sample GS3 could be stored at 40 ^{o}C for at least 1 year and still be kept at a desirable quality; thus it

could be conjectured that GS3 should have a stable shelf life of more than 2 to 3 years at room temperature, which would make it feasible to be commercialized.

CONCLUSIONS

1. All of the WPI/PVP prototypes (GS1a, GS1b, GS2, and GS3) exhibited 100% of paper failure and had comparable or higher bonding strength than PVP prototypes (CTR1, CTR2, and CTR3) and commercial control. With the addition of WPI, the WPI/PVP prototypes exhibited a faster setting speed than the PVP prototypes and control.

2. The hardness of glue sticks made from WPI and PVP were softer than those made from PVP as the only polymer. SEM images showed that the WPI/PVP based glue sticks had less compact and rougher surfaces than the PVP-based prototypes and the control. All prototypes had comparable bonding strength, extension/retraction, and spreading properties to the commercial control.

3. All prototypes were stable at 23 ^{o}C, and all except GS2 still could obtain partial paper failure after being stored at 40 ^{o}C for 12 months.

4. Finally, prototype GS3 (major components: WPI 8.0%, PVP 12.0%, PG 10.0%, Sucrose 10.0%, and sodium stearate 7.0%) had a comparable values of bonding strength (1.24 ±0.13 MPa), hardness (23.48±3.42 N), and glue setting time (20 min) with those of the commercial control (1.30±0.19 MPa, 21.14±1.82 N, and 20min, respectively), and exhibited comparable extension/retraction and spreading properties and storage stability to the commercial control as well.

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