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Adhesive Properties of Corn Zein Formulations on Glass Surfaces

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Adhesive properties on glass of commercial zein and an inexpensive zein−lipid mixture isolated from dry-milled corn were investigated. A method was developed for uniformly preparing bonded glass panels and measuring the amount of pull required to separate the panels. The adhesive strength of commercial zein to glass was greater at 29% than at 52% relative humidity (RH). Bonded samples prepared from zein isolates were less sensitive to changes in RH. Bonds using commercial zein formulations containing plasticizer reached a maximum strength at 10% poly(ethylene glycol) regardless of RH. Formulations that required the least amount of ethanol (35−42%) were obtained by adjusting its pH to 3 or 10 with a volatile acid or base. These formulations completely bonded to the glass panels at low sample concentrations as estimated by 100% cohesive failure and exhibited lower Young's Modulus values than most of the other bonding materials tested. Samples bonded with a polyvinyl acetate emulsion adhesive were not as strong as the zein-bonded samples and were sensitive to changes in RH.

KEYWORDS: **Corn; zein; adhesive; bonding; glass; polyvinyl acetate; emulsion**

INTRODUCTION

To support expansion of the corn ethanol process, profitable markets must be identified for new nonstarch coproducts derived from corn. Protein is seen as the major byproduct of ethanol production because of its higher value relative to other components of corn. If it is removed before hydrolysis and fermentation, it is less likely to be denatured and should be of higher quality.

Zeins, the storage proteins of maize endosperm, are commercially extracted from corn gluten meal, a byproduct of the wet milling industry (*1*). Zein−lipid mixtures, which are reported to be significantly cheaper than commercial zein, are isolated by aqueous alcohol extraction from dry-milled corn (*2*). Today, zein is principally used in formulations for coating tablets or as a coating for nuts and confections. A review of the processing and use of zein cites early patents describing zein as a possible adhesive or binder (*3*). Zein was considered a good adhesive for wood veneers (*4*) or as a binder for cork (*5*) but saw limited use because of its prohibitive cost that is currently between $10/lb and $22/lb. More recently, linear low-density polyethylene bilayer films coated with zein reduced oxygen permeability (*6*). Hettiarachchy et al. investigated the use of soy protein as a wood glue (*7*). They showed that the adhesive strengths of alkali- and trypsin-modified soy protein were 730 and 743 N, respectively, as compared with 340 N for unmodified soy protein.

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In an effort to develop soluble zein formulations of higher water content, we observed excellent adhesion of the zein formulations to polymeric materials and glass. In this study, we measured the adhesive strength of commercial zein and zein−lipid-based formulations on glass panels in order to develop an adhesive with improved water resistance properties.

MATERIALS AND METHODS

Materials. Commercial corn zein F-4000, 90% protein, 1% lipid, and 0% starch (dry basis), was obtained from Freeman Inc. (Tuckahoe, NY). Zein−lipid extracts were prepared by batch extraction of dry-milled corn for 2 h using aqueous ethanol at 60 °C according to the method of Dickey et al. (*8*). Composition (dry basis) of the concentrate used for this study was approximately 82% protein, 13% lipid, and 0% starch. Microslides, clinical grade, 3 in. × 1 in., were obtained from Thomas Scientific (Philadelphia, PA) and a general purpose adhesive, polyvinyl acetate emulsion from Steven Industries Inc. (Bayonne NJ).

Formula Preparation for Adhesion Testing. Formulations were prepared by dissolving corn zein or zein concentrate in 90% ethanol to yield a 1.0, 5.0, 10.0, or 20.0% (w/w) mixture. The mixture was heated with stirring at 60 °C for 10 min. More aqueous (pH modified) formulations were prepared by first dissolving various amounts of corn zein in a solution containing 12.5 g of ethanol, 5 g of poly(ethylene glycol), average MW ∼400 (PEG), and 2 mL of 5 N ammonia or 2 mL of 1.7 M acetic acid. The solution was heated to 60 °C followed by addition of 10 g of water to yield a 1.0, 5.0, 10.0, or 20.0% (w/w) mixture.

Sample Preparation for Adhesion−Lap Shear Testing. The method used was a modification of ASTM D1002-01 (*9*). Adhesion of the samples was determined by measuring the tensile force required to

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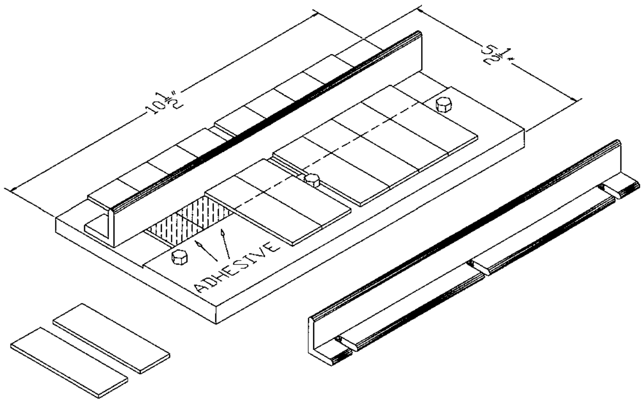

Figure 1. Bonding jig.

separate a lap shear-bonded specimen. The bonding jig used permitted two microslides containing the adhesive material to be held in place with a 1.0 in.^{2} overlapped area (**Figure 1**). Bonded slides were cleaned with absolute ethanol and allowed to air-dry. A small amount (0.15 mL) of the formulation was applied to the slide on the jig. A second slide was positioned so that it overlapped with the first slide, and then, both were secured in place. The slide samples in the jig were cured for 16 h in a vacuum oven set at 50 °C and 10 in. Hg. Curing conditions were the same for polyvinyl acetate-bonded samples except that room temperature was used instead of 50 °C. The slides were removed from the jig and stored at 23 ± 1 °C in a desiccator held at 29 or 52% relative humidity (RH) by means of a saturated solution of calcium chloride hexahydrate or sodium hydrogen sulfate in a dish in the bottom of the desiccator for a minimum of 48 h.

Tensile Property Measurements. Tensile properties of conditioned bonded slides were determined using an upgraded Instron model 1122 tensile tester and Testworks 3.1 data acquisition software (MTS Systems Corp., Minneapolis, MN) with a 500 kg load cell. Four replicates were run for each material. The jaw clamps were operated using 60 psi air pressure, a gage length of 7.5 cm, and a strain rate of 10 mm/min.

Estimation of Cohesive Failure. After tensile testing, the bonded surfaces of the separate panels were examined and cohesive failure was estimated. Complete adhesion to both panels was considered to be 100% cohesive failure. If either panel of a bond is completely clean, this was considered to be an adhesive failure. Fractional cohesive failures listed in the last columns of the tables are the subjective determination of fractional area of overlap of the separated slides covered with adhesive.

RESULTS AND DISCUSSION

Zein-bonded glass samples were cured at heated subatmospheric conditions in order to accelerate drying and improve adhesive strength by promoting interchain cross-linking of the zein proteins (10). Adhesion testing of commercial zein formulations, prepared in 90% ethanol, indicated that bonding was stronger with increasing zein concentration, and separation of glass panels occurred primarily because of cohesive failure (**Table 1**). An important requirement of an adhesive is its ability to retain bonding quality under different environmental conditions. For this study, adhesion was measured at 29 and 52% RH. Adhesive strength of commercial zein to glass was greater at lower humidity. This can probably be attributed to a reduction in the spacing between macromolecules in the adhesive due to the lower concentration of water molecules. At a sample concentration of 20% (w/w) and 29% RH, adhesive strength approached 800 N. Bond strengths of samples prepared from zein concentrates were apparently less sensitive to changes in RH as compared with those prepared from commercial zein (**Table 1)**. This could be due to lipid present in the isolate, which is composed primarily of free fatty acids (FFA) (*11*). FFA have been used as a plasticizer for zein coatings and are responsible

Table 1. Effect of Zein Concentration and RH on Adhesive Strength[a]

sample concentration[b] (%, w/w)	RH (%)	adhesive strength[c] (N)	cohesive failure (%)
commercial zein[d]			
1.0	29	126.1[g,h]	25
5.0	29	377.3[d,e]	75
10.0	29	439.8[c,d]	75
20.0	29	783.6[a]	75
1.0	52	28.4[h]	25
5.0	52	144.8[f−h]	75
10.0	52	303.8[d−f]	75
20.0	52	388.6[d,e]	75
zein concentrate[e]			
1.0	29	0[h]	25
5.0	29	247.0[e−g]	75
10.0	29	688.3[a,b]	75
20.0	29	700.8[a,b]	75
1.0	52	0h	50
5.0	52	105.1[g,h]	75
10.0	52	578.9[b,c]	75
20.0	52	778.0[a]	75

[a] Within the adhesive strength column, means with no letters in common are significantly different at $p < 0.05$ using the Bonferroni LSD multiple comparison method. [b] Prepared in 90% ethanol. [c] Values are means of four measurements. [d] Freeman F-4000. [e] Zein concentrate 171-8.

for more uniform coatings (*12*). Similarly, shear strength of fiberboard bonded by sodium dodecyl sulfate (SDS)-modified soy protein increased with SDS concentrations (*13*). The surfactant properties of the FFA in protein formulations are probably responsible for greater adhesive strengths because it permits the formulations to spread more uniformly on the substrate surface. At a sample concentration of 20% (w/w), adhesive strengths were greater than 700 N at 29 and 52% RH. As observed for commercial zein samples, panel separation for the zein concentrate laminate occurred primarily because of cohesive failure.

Commercial zein films and coatings are generally brittle and require the addition of plasticizer. Park et al. (*14*) found that glycerol-plasticized films were very brittle and that glycerol tends to migrate to the surface of new zein films within a few hours after preparation resulting in a loss of film flexibility. Elongation, however, improved significantly when PEG, a more hydrophobic plasticizer, was used. Bonds using commercial zein formulations containing plasticizer reached maximum adhesive strength at 10% PEG regardless of RH (**Table 2**). The adhesive strength of the zein concentrate, containing 13% lipids, was surprisingly similar to commercial zein containing 10% PEG regardless of RH further demonstrating the plasticizer effect of lipid in the concentrate.

Because the use of organic solvents poses safety issues for most chemical operators and restricts the utility of zein, we investigated methods for reducing the amount of alcohol required to form stable zein formulations. Limited proteolysis of commercial zein or the concentrate did not significantly improve their water solubility (data not shown). Replacing some of the water with plasticizer did however improve zein water solubility (data not shown). Formulations that required the least amount of ethanol (35−42%) to form uniform, stable solutions were obtained by adjusting its pH to 3 or 10 with a volatile acid or base (**Table 3**). These bonding materials exhibited complete adhesion to the glass panels at low sample concentrations. Adhesive strengths were greater when samples were conditioned at 29% RH. The pH-modified bonded samples tended to be tacky as compared to commercial zein samples

Table 2. Effect of Plasticizer Concentration on Adhesive Strength[a]

sample[b]	RH (%)	plasticizer	adhesive strength[c] (N)	cohesive failure (%)
commercial zein[d]	29	0% PEG	439.8[b−d]	75
	29	10%	636.1[a]	75
	29	20%	570.2[a−c]	75
	29	30%	430.2[b−d]	50
zein concentrate[e]	29	13% lipid	688.3[a]	75
commercial zein[d]	52	0% PEG	303.8[d]	25
	52	10% PEG	569.4[a−c]	25
	52	20% PEG	392.1[c,d]	25
	52	30% PEG	296.7[d]	25
zein concentrate[e]	52	13% lipid	578.9[a,b]	25

[a] Within the adhesive strength column, means with no superscript in common are significantly different at $p < 0.05$ using the Bonferroni LSD multiple comparison method. [b] Prepared 10% (w/w) commercial zein or zein concentrate in 90% ethanol. [c] Values are means of four measurements. [d] Freeman F-4000. [e] Zein concentrate 171-8.

Table 3. Adhesive Strength of pH Modified Commercial Zein[a] Formulations[b]

sample concentration (%, w/w)	ethanol[c] (%)	RH (%)	adhesive strength[d] (N)	cohesive failure (%)
acid				
1.0	42	29	2.5[f]	100
5.0	40	29	56.7[e,f]	75
10.0	38	29	352.3[c]	75
20.0	35	29	622.5[a,b]	75
1.0	42	52	7.2[f]	100
5.0	40	52	7.3[f]	100
10.0	38	52	204.5[d]	75
20.0	35	52	420.4[c]	75
alkaline				
1.0	42	29	4.1[f]	100
5.0	40	29	43.2[e,f]	75
10.0	38	29	541.5[b]	25
20.0	35	29	700.0[a]	50
1.0	42	52	3.7[f]	100
5.0	40	52	4.0[f]	100
10.0	38	52	150.0[d,e]	75
20.0	35	52	343.7[c]	75

[a] Freeman F-4000. [b] Within the adhesive strength column, means with no superscript in common are significantly different at $p < 0.05$ using the Bonferroni LSD multiple comparison method. [c] Percent ethanol in formulations. [d] Values are means of four measurements.

prepared in 90% ethanol. Their adhesion to the glass surface was also better. The pH modified and commercial zein bonding materials containing 30% PEG were more elastic and exhibited Young's Modulus between 4 and 7 MPa. The modulus for all other materials was between 9 and 12 MPa.

In general, samples bonded with the polyvinyl acetate emulsion were not as strong as the corn zein-bonded samples. For eight replicates bonded with the same amount of synthetic adhesive as was used for the corn zein formulations, the mean adhesion value was 343.1 and 185.8 N at 29 and 52% RH, respectively.

The results show that commercial corn zein and the zein concentrate can be used to bond glass surfaces. These adhesives are prepared from a renewable agricultural resource. In addition to glass, other materials need to be tested and a convincing argument also needs to be made that these adhesives have an economic advantage over synthetic adhesives and sealants.

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