POLYMER BLENDS INVOLVING COTTONSEED PROTEIN AND COTTONSEED MEAL

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Abstract

Polymer blending is a well-established method to generate new materials with modified properties adapted for particular applications. This method is especially valuable for agro-based materials, where improvements in end-use properties may be desired but chemical modifications may be undesirable. Blends usually do not contain covalent bonds between the components and can more easily satisfy regulatory and safety requirements during product development. In this paper, a review is given of polyblends produced with cottonseed protein or cottonseed meal for adhesive applications. In particular, cottonseed protein can be blended with soy protein to make products that retain some of the better features of both materials. For cottonseed protein/polysaccharides blends, non-ionic polysaccharides (like starch and cellulose) can serve as fillers that lower the cost of the protein, while some anionic polysaccharides (e.g., carboxymethyl cellulose, low-methoxy pectin, and alginate) provide enhanced adhesive strength and water resistance compared with cottonseed protein alone. The use of nanocellulose (NC), but not cellulose, has also shown improved adhesive performance relative to the protein by itself. Cottonseed meal has also been blended with polycaprolactone (together with a plasticizer, like cottonseed oil), and the blends show good melt adhesion properties. As shown in this review, many new and useful polyblends can be made from cottonseed protein and cottonseed meal for adhesive applications.

Introduction

Adhesives are needed for various wood applications. The global wood adhesives market was valued at $4.6 billion in 2018; most of these products are based on urea-formaldehyde, melamine-urea-formaldehyde, phenol-formaldehyde resins, or polyurethanes (Grandview Research, 2019). Because of environmental concerns with formaldehyde and the need to improve process sustainability, soy protein is increasingly being used as wood adhesives (Sun and Bian. 1999; Sun et al., 2002; Liu and Li, 2004; Liu and Li, 2007; United Soy Board, 2020), and commercial soy adhesives are available (Solenis, 2020; Cargill, 2020). Earlier, cottonseed protein was shown (Cheng et al., 2013) to provide equivalent or greater adhesive strength than soy protein when tested on maplewood veneer. In order to enhance the performance/cost ratio of cottonseed protein versus soy protein, the following approaches have been adopted.

1. Use of denaturing agents such as urea, sodium dodecyl sulfate, alkali, and guanidine hydrochloride. These reagents were shown to improve the adhesive and hot water resistance properties for cottonseed protein (Cheng et al., 2013; Cheng et al., 2017a); this approach also worked well with soy proteins, as shown earlier by others (Sun and Bian. 1999; Sun et al., 2002).
2. Use of promoters. Several promoters were found to enhance the adhesive strength of cottonseed protein; these included small molecules bearing a carboxylic functionality (Cheng et al., 2016a) and several phosphorus-containing compounds (Cheng et al., 2017). These promoters were specific to cottonseed protein and showed little or no effect on soy protein.
3. Use of washed cottonseed meal. Cottonseed meal was washed with water, NaCl solution, and phosphate buffer (He et al., 2014; He et al., 2016), and the washed materials showed roughly the same adhesive behavior as cottonseed protein isolate (CPI). Since the washing is more cost-effective than the preparation of protein isolate, this approach leads to lower material cost.
4. Use of blends and composites. The blends can be grouped into four categories: a) protein blends, b) protein/non-ionic polysaccharide blends, c) protein/anionic polysaccharide blends, and d) blends of protein with synthetic polymers. This is the approach that is being reviewed in this report.

Materials and Methods

The methods and materials used for these studies were reported earlier (Cheng et al., 2013; 2016b) and followed the previously published protocol (Sun and Bian, 1999; Sun et al., 2012). Briefly, CPI was prepared from the defatted

seed of glandless cotton plants by a base solubilization and acid (pH 5) precipitation process (Dowd and Hojilla-Evangelista, 2013). Soy protein isolate (SPI, Pro-Fam® 781) was supplied by ADM (Decatur, IL). Most of the other polymers used were obtained from Sigma-Aldrich (St. Louis, MO).

Maple wood veneers from Oakwood Veneer Company (Troy, MI) were cut into strips with the approximate dimensions of 13 mm x 89 mm (for dry tensile testing) or 25 mm x 89 mm (for hot water resistance testing). For CPI blends with SPI and non-ionic polysaccharides, 3 g of total testing materials (protein + second polymer, in different ratios) were added to 25 g water (giving 28 g total adhesive solution). For CPI with NC and anionic polymers, 3 g of CPI were used, and the NC or anionic polymer was added in addition to water, such that the total solution weight was 28 g. The adhesive solutions were stirred for 1-2 h at room temperature and applied with a brush to one end of two 12.7 mm x 88.9 mm wood veneer strips covering an area of 12.7 mm x 25.4 mm. After 10-15 min, a second layer was applied to the same strips. The tacky adhesive-coated areas of the wood veneer strips were then overlapped and bonded by hot-pressing at 2.76 MPa and 80°C for 20 min.

The hot water resistance was based on previous reports (Cheng et al., 2013) as adapted from earlier publications (Sun and Bian, 1999; Liu and Li, 2004; Liu and Li, 2007; Li et al., 2004) and one of the water exposure tests in ASTM D1151-00 (ASTM 2013). The same procedure as for the dry tensile strength testing was used to coat the adhesive formulations twice to a 25.4 mm x 25.4 mm area at the ends of a pair of 25.4 mm x 88.9 mm wood strips using a brush. The coated areas of each pair were overlapped and glued together by hot-pressing at 100°C and 1.38 MPa for 10 min. The glued wood strips were then immersed in water for 4 h at 63 ± 2°C, cooled for 24 h to room temperature, immersed in water again for 4 h at 63 ± 2°C, and finally cooled with tap water. The resulting wood strips were air-dried for at least 24 h.

A Zwick tensile tester (Model Z005, Ulm, Germany) was used to measure the tensile shear strength of the glued wood strip pairs in the lap-shear mode. The maximum tensile strengths at break (MPa) for the dry wood strips and the water-immersed wood strips were reported as the dry adhesive strength and hot water resistance, respectively. Ten pairs of glued wood strips were tested for each formulation, and the results reported as mean ± standard deviation. Analysis of variance was performed followed by Post Hoc Tukey tests.

Results

Protein Blends

The adhesive strength and hot water resistance of CPI, SPI, and their blends are shown in Fig. 1 (Cheng et al., 2016b). CPI and SPI samples showed dry adhesive strength of 2.58 MPa and 1.52 MPa, respectively. The dry adhesive strength for the blends was found to increase steadily with increasing levels of CPI in the blend. For hot water resistance, CPI (3.34 MPa) was superior to SPI (0.3 MPa). In the CPI/SPI blends, even with only 25% CPI added, the hot water resistance of SPI was improved to 2.95 MPa. Thus, for a wood adhesive based on SPI, the addition of CPI (25% or higher) can improve both the dry adhesive and water resistance properties.

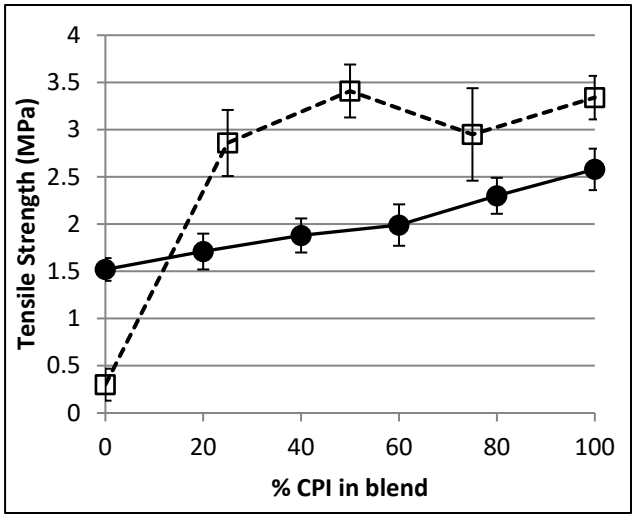

Fig. 1. Dry adhesive strength (black circles, solid line) and hot water resistance (open squares, dotted lines) for cottonseed protein isolate (CPI), soy protein isolate (SPI), and their blends. Adapted from Cheng et al., 2016b.

Protein/Non-ionic Polysaccharide Blends

Cottonseed and soy protein-based adhesives were also formulated with xylan, starch, or cellulose powder (20 µm size) to determine the influence of polysaccharide fillers on protein-based adhesive properties (Cheng et al., 2016b). In general, the addition of a non-ionic polysaccharide filler to CPI reduced the adhesive performance of CPI, but not proportionally. In some cases, the dry adhesive strength was retained even when the cottonseed or soy protein was blended with up to 75% polysaccharide. For CPI/polysaccharide formulations, hot water adhesive resistance was retained when the blend contains about 50% polysaccharides. In view of the ability of CPI/polysaccharide blends to retain the dry adhesive strength and hot water resistance of CPI alone, these blends may provide an opportunity to decrease the amount of CPI used in adhesive formulations, thereby decreasing cost.

As an example, the data for the blends of CPI and cellulose are shown in Table 1. When the % cellulose was increased up to 50%, both the dry adhesive strength and the hot water resistance of CPI were maintained. Even at 75% cellulose, the CPI/cellulose blend maintained about 85-92% of the adhesive performance of CPI (with respect to dry adhesive strength and hot water resistance).

Table 1. Adhesive properties of wood adhesives from CPI/cellulose blends. Adapted from Cheng et al., 2016b

CPI %	Cellulose, wt %	Dry adhesive strength* (MPa)	Hot water resistance* (MPa)
100	0	2.55 ± 0.26^{a}	3.34 ± 0.23^{a}
75	25	2.54 ± 0.19^{a}	2.67 ± 0.50^{b}
50	50	2.54 ± 0.26^{a}	3.43 ± 0.23^{a}
25	75	2.36 ± 0.33^{a}	2.83 ± 0.50^{b}
0	100	0.46 ± 0.08^{b}	0

*Data under each column were subjected to analysis of variance; the same superscript letters indicate that the values are not significantly different at $\alpha = 0.05$.

Whereas the use of CPI/cellulose blends (and CPI blends with xylan and starch) appeared encouraging, even better results were obtained with the use of NC in CPI-based wood adhesives (Table 2) (Cheng et al., 2019a). Both cellulose nanofibers (CNF), with aspect ratio of about 100, and cellulose nanocrystals (CNC), with aspect ratio of about 20, were evaluated. CNF filler was found to be most beneficial at about a 2% additive level, giving 22% improvement in dry adhesive strength over the CPI control. The CNC filler was optimal at about 10% additive level, giving 16% strength improvement relative to CPI alone. The hot water resistance of cottonseed protein isolate was improved with CNF addition, but not with CNC addition. Thus, CNF may be a useful additive to cottonseed protein formulations for wood adhesive applications.

Table 2. Adhesive properties of wood adhesives from blends of CPI and cellulose nanofibers (CNF) and cellulose nanocrystals (CNC). Adapted from Cheng et al., 2019a.

NC added	NC, wt %	Dry adhesive strength* (MPa)	% change	Hot water resistance* (MPa)	% change
None	0	2.5 ± 0.2 [c]	0	2.6 ± 0.3 [c]	0
CNF	0.5	2.8 ± 0.2 [a,b]	13	3.4 ± 0.4 [b]	29
CNF	2	3.0 ± 0.1 [a]	22	3.8 ± 0.4 [a]	46
CNF	5	2.8 ± 0.1 [a,b]	13	3.6 ± 0.3 [a,b]	38
CNF	10	2.7 ± 0.2 [b,c]	10	**	
CNC	2	2.5 ± 0.1 [c]	1	**	
CNC	5	2.8 ± 0.2 [a,b]	13	2.5 ± 0.5 [c]	-7
CNC	10	2.9 ± 0.3 [a,b]	16	2.8 ± 0.3 [c]	6
CNC	15	2.5 ± 0.2 [c]	4	2.4 ± 0.6 [c]	-9

*Data under each column were subjected to analysis of variance; the same superscript letters indicate that the values are not significantly different at α = 0.05. **Not tested.

Protein/Anionic Polysaccharide Blends

The polysaccharides described above are non-ionic. Blends of CPI with several *anionic* polysaccharides have been studied for their adhesive performance (Cheng et al., 2019b). Carboxymethyl cellulose (CMC), low-methoxy pectin, alginate, chondroitin sulfate, and three types of carrageenan have been tested. The best results were obtained for the CPI/CMC and CPI/pectin blends, followed by CPI/alginate blend (Table 3). Thus, the addition of 10% CMC to CPI gave 39% enhancement in dry adhesive strength and 34% in hot water resistance compared with CPI alone. These findings suggest that the CPI/anionic polysaccharide blends might be useful components in biobased wood adhesive formulations.

Table 3. Adhesive properties of wood adhesives obtained from blends of CPI and selected anionic polysaccharides. In each formulation, 3 g CPI was used. Adapted from Cheng et al., 2019b.

Polymer added	Polym wt %, actual wt	Dry adhesive strength*(MPa)	% change	Additive, wt %, actual wt	Hot water resistance* (MPa)	% change
None	0	2.46±0.37 [c]	0	0	2.87±0.33 [b]	0
CMC	10%, 0.340g	3.41±0.25 [a,b]	39	10%, 0.328g	3.86±0.26 [a]	34
	22%, 0.825g	3.83±0.44 [a]	56		**	
pectin	8%, 0.275g	3.06±0.28 [b,c]	24	9%, 0.284g	3.68±0.37 [a]	28
	15%, 0.549g	3.42±0.86 [a,b]	39		**	
alginate	9%, 0.294g	2.86±0.26 [b,c]	16	8%, 0.265g	3.12±0.47 [b]	9
	16%, 0.588g	3.13±0.39 [a,b,c]	27		**	

*Data under each column were subjected to analysis of variance; the same superscript letters indicate that the values are not significantly different at α = 0.05. **Not tested.

Blends of protein with synthetic polymers

Instead of biobased polymers, attempts were also made to blend CPI with synthetic polymers, e.g., anionic vinyl polymers, such as poly(acrylate), poly(acrylate-co-acrylamide), poly(vinyl sulfate), poly(vinyl sulfonate), and poly(vinyl phosphonate) (Cheng et al., 2019b). Whereas some improvements in the dry adhesive strengths were observed, no improvements in hot water resistance were found (e.g., Table 4).

Table 4. Adhesive properties of wood adhesives from blends of CPI and selected anionic vinyl polymers. In each formulation, 3 g CPI was used. Adapted from Cheng et al., 2019b.

Polymer added	Additive wt %, actual wt	Dry adhesive strength* (MPa)	% change	Additive, wt %, actual wt	Hot water resistance* (MPa)	% change
None	0	2.46±0.37 [c]	0	0	2.87±0.33 [a]	0

poly(vinyl sulfate)	7%, 0.235g	3.02±0.23 [a,b]	23	7%, 0.235g	2.49±0.39 [a]	-13
	14%, 0.469g	3.32±0.25 [a]	35		**	
poly(vinyl sulfonate)	16%, 0.564g	2.97±0.17 [b]	18	20%, 0.754g	2.66±0.44 [a]	-7
	27%, 1.128g	3.09±0.28 [a,b]	26		**	
poly(vinyl phosphonate)	11%, 0.365g	2.86±0.19 [b]	16	15%, 0.522g	2.69±0.43 [a]	-6
	20%, 0.729g	2.98±0.28 [a,b]	21		**	

*Data under each column were subjected to analysis of variance; the same superscript letters indicate that the values are not significantly different at $\alpha = 0.05$. **Not tested.

A different material is polycaprolactone (PCL), a biodegradable polymer made from petroleum sources. Blends of PCL and washed cottonseed protein meal (WCSM) plasticized with cottonseed oil were made and analyzed for their mechanical, adhesive, and thermal properties (Cheng et al., 2019c). The addition of WCSM and the plasticizer (up to a PCL:WCSM:cottonseed oil ratio of 60:40:20 by weight) did not change the adhesive performance of PCL on fiberboard. Thus, the combination of PCL/cottonseed protein/cottonseed oil seems to be a viable bioplastic, and one possible application for this material may be as a hot melt adhesive.

Urea formaldehyde (UF) resins are among the most widely used adhesives in wood-based composites. Blends of UF/soy protein were reported earlier (United Soybean Board, 2020). A separate study was reported of the blends of UF with WCSM and their adhesive performance (Liu et al., 2018). In this case, urea and formaldehyde were partially replaced by WCSM from 10% to 50% in weight. The hybrid adhesives showed thermal stabilities and rheological properties that were similar to (or better than) pure UF resins. The hybrid adhesives with 10% to 40% WCSM exhibited better adhesive strengths than UF resin or cottonseed meal alone (Liu et al., 2018). Thus, these UF/WCSM blends may also be regarded as possible ingredients in future wood adhesive applications.

Summary

Cottonseed protein is a promising material for use in adhesive applications. In this review, polymer blending has been shown to be a good method to enhance the performance/cost ratio of cottonseed protein-based wood adhesives. The choice of the blend components can have a large impact on the outcome. Some components, like non-ionic polysaccharides, when added to CPI, act like functional fillers; they help reduce the cost of the CPI adhesive. In contrast, the anionic polysaccharides and nanocellulose reviewed in this work behave like promoters that improve the adhesive performance of CPI. The synthetic polymers show variable effects on cottonseed protein adhesives. Thus, prudent selection and design of the cottonseed protein blends are needed in order to optimize the end results.

Acknowledgements

The authors thank Catrina Ford, Dorselyn Chapital, Wade Wyckoff, and Kaylin Kilgore for their technical assistance. This work was supported by the U.S. Department of Agriculture, Agricultural Research Service. Mention of trade names or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by USDA. USDA is an equal opportunity provider and employer.

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