ACS Sustainable Chemistry & Engineering

Research Article

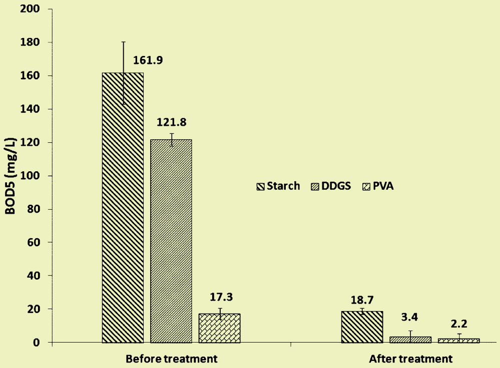
pubs.acs.org/journal/ascecg

Corn Distillers Dried Grains as Sustainable and Environmentally Friendly Warp Sizing Agents

Narendra Reddy,[†] Yue Zhang,[†] and Yiqi Yang*,[†,‡,§]

[†]Department of Textiles, Merchandising & Fashion Design, [‡]Department of Biological Systems Engineering, and [§]Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, 234, HECO Building, East Campus, Lincoln, Nebraska 68583-0802, United States

ABSTRACT: Corn distillers dried grains with solubles (DDGS) were used as sustainable and environmentally friendly warp sizing agents for cotton, polyester, and polyester/cotton (P/C) in an effort to find potential substitutes for starch and poly(vinyl alcohol) (PVA). Sizing is an essential textile process to reduce warp breakages and protect the yarns from the stress, strain, and abrasion experienced during weaving. Starch-based sizes are inexpensive and provide good sizing performance on cotton, but starch sizes are brittle and cause shedding during weaving, are unstable and difficult to desize, and are also not suitable for sizing synthetic fibers and their blends. PVA provides excellent sizing performance on synthetic fibers and their blends but is expensive and does not degrade in textile effluent treatment plants. DDGS is a widely available and inexpensive ($100−$125/ton) coproduct that contains proteins and carbohydrates. In this research, DDGS was pretreated with alkali, and the extractants obtained were used to size cotton, polyester and P/C rovings, and fabrics. The influence of extraction conditions, composition of the extractants, and sizing conditions on the cohesiveness, abrasion resistance, and biodegradation were studied in comparison to starch and poly(vinyl alcohol). The DDG size provided a similar increase in Roving strength, better abrasion resistance, and substantially higher biodegradation than PVA.



KEYWORDS: *Warp sizing, Textile industry, Effluents, Pollution sustainability*

■ INTRODUCTION

The textile industry worldwide is facing considerable challenges due to concerns on price and availability of raw materials, increasing environmental restrictions, and lack of technological breakthroughs that can reduce cost and/or develop new products. Heavy dependence on nonrenewable petroleum resources, energy and labor-intensive processes, environmental regulations, and competition from developing countries have made commodity textile production almost extinct in the United States and other developed countries.[1] Reducing the use of nonrenewable resources, relying on indigenously available raw materials, and developing environmentally friendly processes are some of the approaches that could make textile production competitive in the United States.[2]

The United States is the largest agricultural producer in the world. Agricultural production in the United States generates considerable amounts of byproducts and coproducts that are low cost, available in large quantities, and renewable and sustainable resources. Instead of the traditional fiber crops that require land, water, energy, and other scarce natural resources, agricultural byproducts such as corn stover, wheat, and soybean straw that are inevitably generated and do not have major industrial applications can be used to produce inexpensive and environmentally friendly natural cellulose fibers.[3] Similarly, synthetic fibers such as poly(lactic acid) that are biodegradable have been developed using renewable resources such as corn, and regenerated protein fibers have been developed from soy proteins, wheat gluten, and chicken feathers.[3,4]

In addition to identifying sustainable sources for raw materials and developing green textile products, textile processing should also be made more environmentally friendly for the industry to survive in the long run. Textile processes such as sizing and desizing, bleaching, and dyeing consume considerable amounts of water and energy and are also the primary sources of pollution from the textile industry. Processing a kilogram of textiles requires about 95−400 L of water, which is mostly released as effluent. Among the various textile processes, sizing and desizing account for a major portion of water consumption and effluent release depending on the type of sizing agent, fabrics, and sizing and desizing conditions used. Sizing agents such as starch and starch derivatives are environmentally friendly and are widely used for sizing cotton. However, starch and starch derivatives are not suitable for sizing polyester or other synthetic fibers and their blends, which are extensively used. Poly(vinyl alcohol) (PVA) is the most commonly used sizing agent for synthetic fibers and their blends. Although PVA provides excellent sizing performance, PVA is expensive and does not biodegrade in textile

Received: June 28, 2013
Revised: August 30, 2013
Published: September 13, 2013

dx.doi.org/10.1021/sc4002017 | *ACS Sustainable Chem. Eng.* 2013, 1, 1564−1571

effluent treatment plants. The presence of PVA has been reported to be one of the major causes for the pollution from the textile industry. For instance, PVA has shown to be persistent and accounts for 45% of the total biochemical oxygen demand (BOD) load from textile effluent treatment plants.[5,6] Attempts have been made to replace PVA with biodegradable sizing agents. For instance, starch has been modified by grafting synthetic polymers and has been used to size polyester and their blends in an effort to replace PVA.[7,8] Recently, we have demonstrated that plant proteins such as wheat gluten and soy proteins have excellent sizing performance and could replace PVA.[9−11]

Distillers dried grains (DDG) are inevitably generated as coproducts (up to 30%) during ethanol production from corn. Major constituents in DDG include about 8−11% oil, 25−30% protein, and 35−50% carbohydrates. At about $100−$125 per ton, DDG is one of the cheapest coproducts of grain processing. Currently, DDG is mainly used as animal feed, but attempts have been made to use DDG for industrial applications. In our previous research, we had shown that the components in DDG can be extracted for various high value applications.[12,13] Recently, we have shown that DDG can be acetylated under acid and alkaline conditions and used to develop thermoplastic films.[14,15] Because DDG contains proteins and carbohydrates that have been used for warp sizing, we hypothesized that DDG could be a good sizing agent.

In this research, DDG was treated with alkali, and the extracted components were used to size rovings and fabrics made from cotton, polyester, and their blends. An increase in the peak load of the rovings, abrasion resistance of the fabrics, biodegradability of the sizing solution in activated sludge, and ability of DDG to be removed from the fabrics were studied in comparison to starch and PVA.

■ MATERIALS AND METHODS

Materials. Corn distillers dried grains were supplied by Abengoa Bioenergy Corporation, York, NE. Polyvinyl alcohol (PVA)-based commercially available size (obtained from a major chemical manufacturer in the United States) and untreated corn starch (purchased from the National Starch Company) were used to compare the sizing performance of DDGS. Cotton and polyester/cotton (65−35) rovings were supplied by Mount Vernon Mills, Inc. (Mauldin, SC, USA). Polyester (100%) rovings were supplied by Shuford Yarns, LLC, Hickory, NC. Fabrics used (cotton type 400 and polyester type 54, P/C type 7435) were purchased from Test Fabrics Inc., West Pittston, PA). Before sizing, fabrics were washed with detergent in a washing machine to remove any finishing chemicals on the surface. Hydrochloric acid, sodium hydroxide, potassium sodium tartrate, salicylic acid, sodium nitroferricyanide, ammonium chloride, sodium hypochlorite, and other chemicals used were reagent grade and purchased from VWR International. Activated sludge was collected from the City of Lincoln Wastewater and Solid Waste Operations Plant.

Methods. *Pretreating DDGS.* To prepare the sizing solution, DDGS was added into water (1:20 w/w ratio) containing 0.25, 0.5, 1, or 2% (w/w) alkali and heated at 90 °C for 1, 2, or 3 h. After heating, the DDGS mixture was cooled, and the pH of the solution was adjusted to 7 by adding 37% hydrochloric acid. Later, the mixture was centrifuged at 8000 rcf, and the supernatant was collected and used for sizing after appropriate dilutions were made to obtain the desired percent add-on. Supernatant obtained was evaporated in an oven, and the solids remaining after evaporation were weighed to determine the percent yield of DDGS after the different extraction conditions. The yield of DDGS after treating with 0.25% alkali was considerably low and therefore not used for sizing. The solid portion of the DDGS obtained after centrifuging was discarded but could potentially be used as animal feed or for other applications.

Sizing. The cotton, polyester, and polyester/cotton rovings and fabrics were sized with DDGS extracted at various extraction conditions. To size the rovings, the rovings were wound onto a frame and immersed in the sizing solution. For fabric sizing, the samples were immersed in the sizing solution at 90 °C for 5 min and later squeezed in a laboratory padder to help the size spread evenly on the fabrics. The percent wet-pick up was determined to ensure that the fabrics had the desired percent add-on. For comparison, cotton rovings and fabrics were sized with starch and also with a PVA-based commercially available sizing agent under the manufacturer's recommended conditions. After sizing, the rovings and fabrics were conditioned at 21 °C and 65% relative humidity before testing.

Desizing. Ability of the DDGS size to be removed (desized) from the fabric was evaluated by treating the sized fabrics in water at various conditions. Temperature, number of rinses, and ratio of fabric to water were varied to study the desizeability at different conditions. Fabrics treated with PVA and starch were also desized under similar conditions for comparison. Fabrics were precisely weighed before and after sizing, and the percent weight loss was used to calculate the desizeability.

Viscosity of Size Solutions. A rheometer (Brookfield, Model R/S plus) was used to determine the apparent viscosity of the sizing solutions. DDGS, starch, and PVA size (6% w/w) were heated at 90 °C for 30 min, and the viscosity was measured using a CC-25 spindle and cup. A water bath was used to maintain the rheometer at 90 °C, and viscosity in terms of mPas was recorded for 1 h.

Evaluating Sizing Performance. Cohesiveness of Rovings. The ability of the size to bind the fibers and provide strength to the rovings was used as an indication of the cohesiveness. To measure the cohesiveness, the sized and conditioned rovings were tested for their tensile properties on a MTS (Model Qtest 10) tensile testing machine. A gauge length of 10 cm, crosshead speed of 50 mm/min, and a 500 N load cell were used for the measurement. At least 20 samples each from three different rovings that were sized separately were tested for each condition.

Abrasion Resistance. Fabric abrasion resistance was measured on a QM Universal Wear Tester (Model CS-ZZC) using 0 emery paper according to ASTM D3886. Unidirectional abrasion was performed on the samples after the diaphragm was inflated to a pressure of 28 kPa. A 0.5 lb load was used for cotton and P/C fabrics, and a 1 lb load was used for the polyester fabrics. At least nine samples from three different sizings were tested for each condition. Number of rubbing cycles required to form a hole in the fabric was recorded. The higher the cycles required, the higher is the resistance to abrasion and vice versa.

Effect of Relative Humidity. Influence of relative humidity on the tensile properties of the rovings was determined to assess the performance of DDGS during weaving at different environments. Rovings were placed in a conditioning chamber (Caron Environmental Chamber) at 21 °C and 55%, 65%, and 75% humidity for 24 h. Later, the rovings were tested for their tensile properties as reported above.

Film Preparation and Properties. Films were prepared from DDGS that was extracted at various sodium hydroxide concentrations and pretreatment time. The solution was cast on Teflon-coated glass plates and allowed to dry at 50 °C in the oven. After the films were dried, they were washed with distilled water three times to remove the salt formed during neutralization with acid. Films were later placed in 21 °C and 65% relative humidity for 24 h and collected. Tensile properties of the films were tested according to ASTM D822 on an MTS (Qtest 10) tensile tester using a gauge length of 2 in. and traverse speed of 10 mm/min, using samples with dimensions of 1.5 mm × 8 mm. Ten samples obtained from every film casted were tested, and each experimental condition had samples from three separately casted films.

Biodegradation. Biodegradation of the sizing solutions were determined in terms of chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and changes in total nitrogen and ammonia nitrogen. To determine the biodegradation of the sizing solutions,

Table 1. Yield and Composition of DDG Size after Extraction at Various Conditions

			composition		
conc. of alkali (%)	yield (%)	extraction time (h)	ADF[a] (%)	hemicellulose (%)	protein (%)
0.5	58.2 ± 0.04	1	6.2 ± 0.07	41.9 ± 0.06	40.9 ± 2.7
	64.4 ± 0.02	2	3.9 ± 0.04	43.0 ± 0.03	42.4 ± 2.8
	68.6 ± 0.02	3	4.7 ± 0.03	45.7 ± 0.02	42.1 ± 3.0
1	68.2 ± 0.01	1	4.6 ± 0.04	43.8 ± 0.01	42.3 ± 0.9
	68.3 ± 0.02	2	8.2 ± 0.11	42.3 ± 0.05	41.3 ± 0.3
	68.6 ± 0.01	3	6.4 ± 0.28	40.9 ± 0.10	40.6 ± 4.5
2	68.1 ± 0.01	1	7.7 ± 0.11	41.7 ± 0.05	39.7 ± 2.3
	69.7 ± 0.01	2	4.9 ± 0.06	44.3 ± 0.04	42.0 ± 2.7
	69.4 ± 0.01	3	5.2 ± 0.04	46.8 ± 0.01	41.5 ± 1.6

[a] Acid detergent fiber.

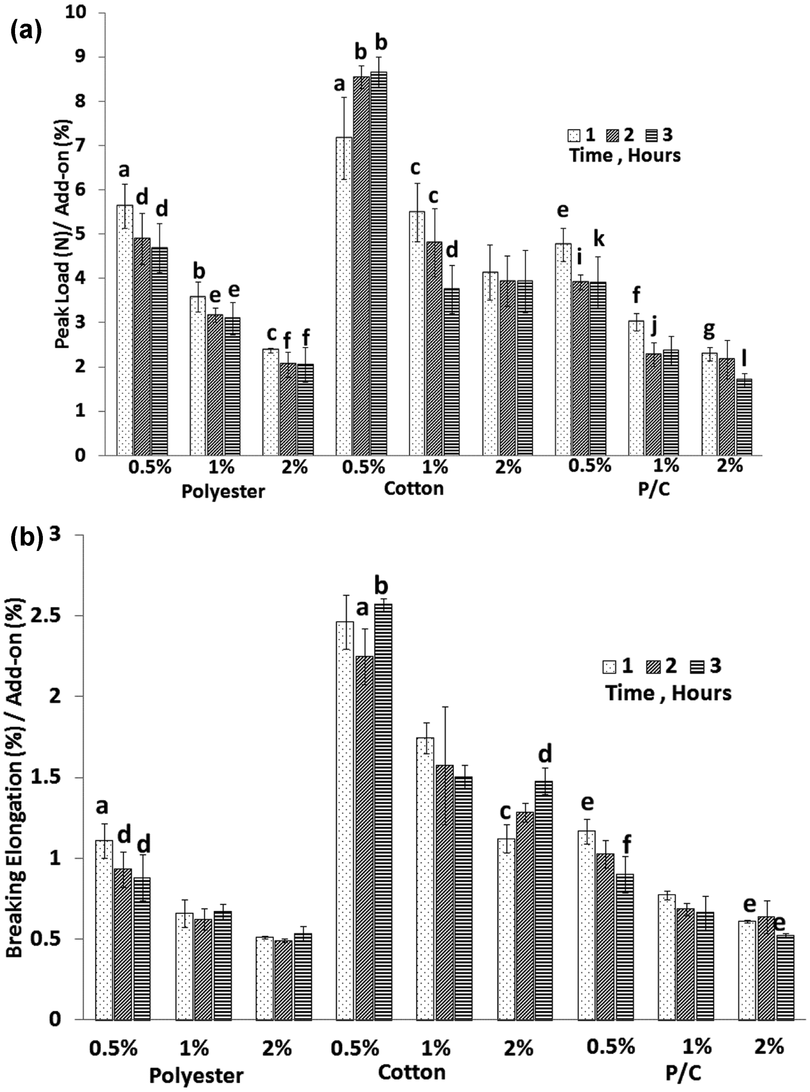


Figure 1. Effect of DDG extraction conditions on the strength and elongation of the polyester, cotton, and P/C rovings at three different concentrations (0.5%, 1%, and 2%) of alkali used at three different extraction times (1, 2, and 3 h). Sizing was done at 90 °C for 5 min. For each extraction condition, different letters, if any, represent statistically significant differences.

wastewater sludge from the local wastewater treatment plant was used. The sludge was first diluted and then aerated in the laboratory for 2 days to acclimatize the microorganisms. The sizing solutions were added into the sludge at a concentration of 300 ppm, which is higher than the typical (100−150 ppm) concentration of size in textile effluent treatment plants. The DDGS size was added into the activated sludge and aerated for up to 10 days. Solution at the top of the aerated sludge was collected and used to analyze the changes in COD, BOD_5, and total and ammonia nitrogen.

Chemical Oxygen Demand (COD). COD was measured according to Test Method 8000 of the United States Environmental Protection Agency. According to the test, 2 mL of sample collected from the activated sludge at 24 h intervals was added into a COD test kit (Hach Company, TNT 822) vial. The vial was later heated at 150 °C for 2 h

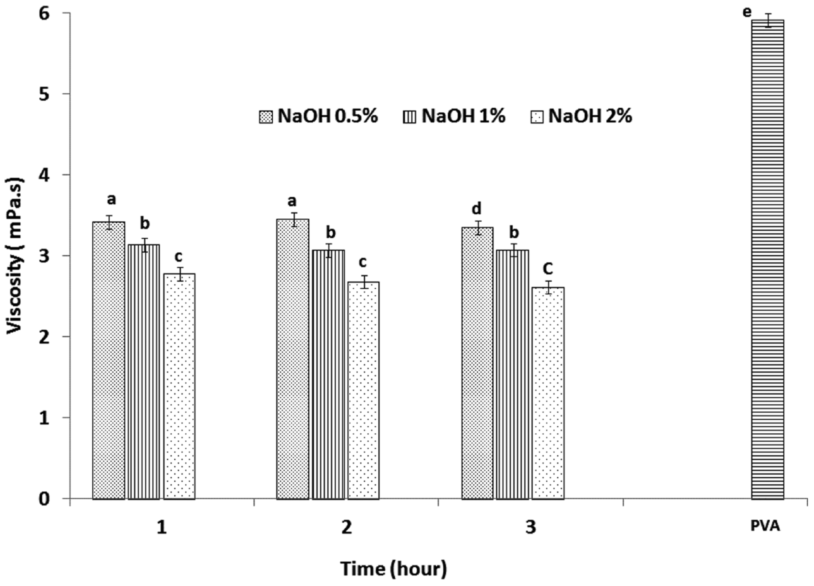


Figure 2. Viscosity of the DDG sizing solution obtained using different extraction conditions compared to PVA. For each extraction condition, different letters, if any, represent statistically significant differences.

on a heating block (Hach DRB 200). The sample was later cooled, and the absorbance of the solution was measured on a spectrophotometer (Hach DR 3900) at a wavelength of 620 nm. The spectrophotometer directly measured the concentration of COD in terms of mg/L. At least three samples were tested for each condition, and the average and ± one standard deviation are reported.

5-Day Biochemical Oxygen Demand (BOD$_5$). The BOD$_5$ test to determine the biodegradability of the DDGS size was performed according to the standard method for the examination of water and waste water published by the American Public Health Association. Size samples at a concentration of 300 ppm were added into the BOD test bottles containing water and nutrient buffer. Water used for the test confirmed to the standard and had an oxygen depletion of less than 0.2 mg/L in 5 days. The initial level of dissolved oxygen in the bottles was measured using a dissolved oxygen probe (Hach Company, Model HQ440D multi), and the bottles were later stored in the dark at 20 °C for five days. After five days, the concentration of oxygen in the bottles was measured. Differences in the concentration of dissolved oxygen at 0 and 5 days were considered to calculate the BOD$_5$ values.

Total Nitrogen. Total nitrogen released from the DDGS during degradation in activated sludge was determined to understand if the proteins in DDGS could inhibit biodegradation. Activated sludge containing the size was combined with alkaline potassium persulfate solution in a high pressure canister and heated at 120 °C for 40 min. After the high temperature digestion, the samples were cooled, and distilled water (blank) was added. Absorbance of the solution was measured on a spectrophotometer (Beckman Coulter, Model Delsa nano 720) at wavelengths of 220 and 275 nm. Calibration curves with $R^2 > 0.999$ prepared earlier with known concentration of nitrogen were used to calculate the amount of total nitrogen released from DDGS. Ar, absorbance difference between sample and blank, was calculated using eqs 1−3.

$$\mathrm{Ab} = \mathrm{Ab}_{220} - 2\mathrm{Ab}_{275} \quad (1)$$

$$\mathrm{As} = \mathrm{As}_{220} - 2\mathrm{As}_{275} \quad (2)$$

$$\mathrm{Ar} = \mathrm{As} - \mathrm{Ab} \quad (3)$$

where Ab220 is the absorbance of blank at 220 nm; Ab275 is the absorbance of blank at 275 nm; As220 is the absorbance of sample at 220 nm; and As275 is the absorbance of sample at 275 nm. The total nitrogen ρ (mg/L) was calculated using eq 4

$$\rho = (\mathrm{Ar} - a)/bV \times f \quad (4)$$

where ρ is the concentration of total nitrogen (mg/L); Ar is the absorbance difference between sample and blank; a is the intercept of the calibration curve; b is the slope of the calibration curve; V is the volume of sample; and f is the dilution factor of sample.

Ammonia Nitrogen. The concentration of ammonia nitrogen in the DDGS-containing sludge samples was determined by mixing the sludge with salicylate and hypochlorite in an alkaline phosphate buffer. After standing for 1 h at room temperature, the solution turns to an emerald green color, which is proportional to the concentration of ammonia in the solution. The concentration of ammonia in the solution was determined by measuring the absorbance on a spectrophotometer at a wavelength of 697 nm. A calibration curve ($R^2 > 0.999$) prepared using known concentrations of ammonium chloride was used to determine the ammonia in the sludge samples.

Statistical Analyses. All the data obtained were analyzed by the one-way analysis of variance with Tukey's pairwise multiple comparison using the SAS program. A p value smaller than 0.05 was considered to be a statistically significant difference. In each figure, data points with the different letters are statistically significantly different from each other.

RESULTS AND DISCUSSION

Yield and Composition of the Sizing Solution. Table 1 provides a comparison of the yield and composition of DDG at various extraction conditions. The yield of DDG was about 68% when treated with 0.5% NaOH for 3 h but slightly lower when extracted with 0.5% alkali for 1 and 2 h. The DDG sizing solution mainly consisted of proteins and hemicellulose as shown in Table 1. Varying the concentration of alkali and extraction time did not significantly affect the amount of hemicellulose or proteins, but the ADF (cellulose + lignin) content had variation ranging from 3.9% to 8.2%. Lignin, ash, and starch accounted for the remaining composition of the sizing solution. On the basis of the results in Table 1, an alkali concentration of 0.5% and extraction time of 3 h or higher alkali concentration but shorter extraction time could be used to obtain the sizing solution.

Influence of Extraction Time and Concentration of Alkali Used. The concentration of alkali used for extraction of DDGS had a substantial influence on the peak load for the cotton, polyester, and P/C rovings as shown in Figure 1a, whereas extraction time did not show a major effect on the strength of the rovings. Increasing extraction time from 1 to 2 h with 0.5% alkali increased the peak load for cotton but decreased the peak load for polyester and P/C rovings. However, increasing extraction time with higher concentrations of alkali decreased the peak load for all the rovings when 1% alkali was used. For 2% alkali-extracted DDG, there was no major difference in peak load for any of the rovings at the three extraction times studied. Concentration of alkali and time of extraction are related, and both influenced the peak loads. At lower concentrations and extraction times, there is lower yield of the components and more importantly less damage to the proteins in DDG. Therefore, the rovings treated with DDG extracted at low concentration of alkali and shorter time had higher strength. When the concentration of alkali was 2%, treatment even for 1 h damaged the polymers leading to lower tensile strength. Elongation of the rovings did not show a major difference when sized with DDG extracted for different times, but changes in the concentration of alkali led to a decrease in elongation as shown in Figure 1b. Cotton rovings had a 50% decrease in elongation when treated with 2% alkali for 1 h compared to treating with 0.5% alkali for 1 h. Similar changes were also observed for the polyester and P/C rovings. Increasing alkali concentration results in hydrolyzed proteins and carbohydrates with lower molecular weights that do not provide good elongation. Therefore, the elongation of the rovings decreased with increasing alkali concentration.

Viscosity of Sizing Solution. Viscosity of the DDG sizing solution was considerably lower than that of PVA as shown in Figure 2. There was no significant difference in viscosity with increasing extraction time, but the viscosity decreased as the concentration of the alkali increased. Higher concentrations of alkali damaged the polymers in the sizing solution, decreased their molecular weights, and therefore reduced their viscosity. However, the DDG solution with lower viscosity should be able to penetrate more easily into the fabrics than PVA. Viscosity reported here for DDG is similar to the viscosity of other biopolymers such as starch-based derivatives that have been used for sizing.[16]

Abrasion Resistance. Improving the abrasion resistance of yarns is one of the primary requirements for a size.[17] Figure 3 shows that an increasing concentration of alkali considerably affects the abrasion resistance of the fabrics especially for polyester. Abrasion resistance of the polyester fabrics treated with the 2% alkali-extracted DDG was nearly 40% lower than the fabrics treated with 0.5% alkali-extracted DDG. A similar trend was also observed for the cotton and P/C fabrics. Increasing the concentration of alkali damages the polymers in the sizing solution and decreased the properties of the films on the surface of the fabrics. Therefore, the abrasion resistance decreased with increasing alkali concentration. Polyester fabrics had a higher abrasion than the cotton and P/C fabrics due to the fabric structure and inherent higher resistance of polyester compared to cotton. The highest abrasion resistance obtained using the DDG size for cotton fabrics was 116 cyles, 127 cycles for P/C, and 1420 cycles for polyester. At a similar percent add-on, cotton treated with starch, P/C, and polyester fabrics treated with PVA had abrasion resistances of 87, 79, and 300 cycles, respectively, demonstrating that DDG provided better abrasion resistance to the fabrics compared to starch or PVA. The DDG size provided better abrasion resistance despite poor film properties compared to PVA, most likely due to the better compatibility and adhesion between the fibers and DDG.

Tensile Properties of DDG films. Films formed from the extracted DDG solution had considerably low strength and elongation compared to PVA films (2.0 MPa, 442%) as shown in Figure 4a and b, respectively. Increasing the concentration of alkali decreased the strength of the films, but increasing time

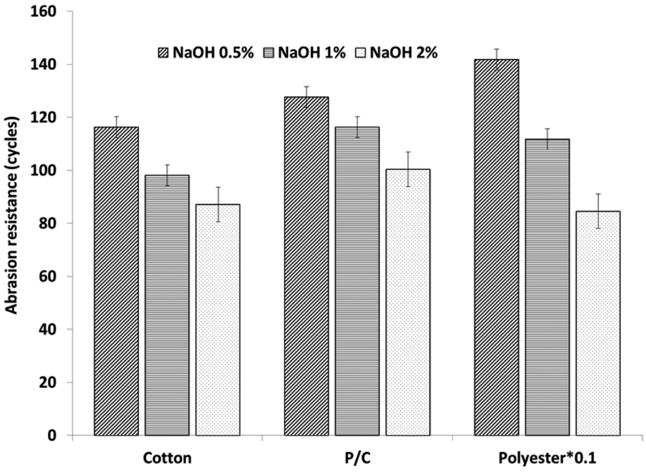


Figure 3. Abrasion resistance of the cotton, P/C, and polyester fabrics treated with DDG size extracted at three different alkali concentrations. For each extraction condition, different letters, if any, represent statistically significant differences.

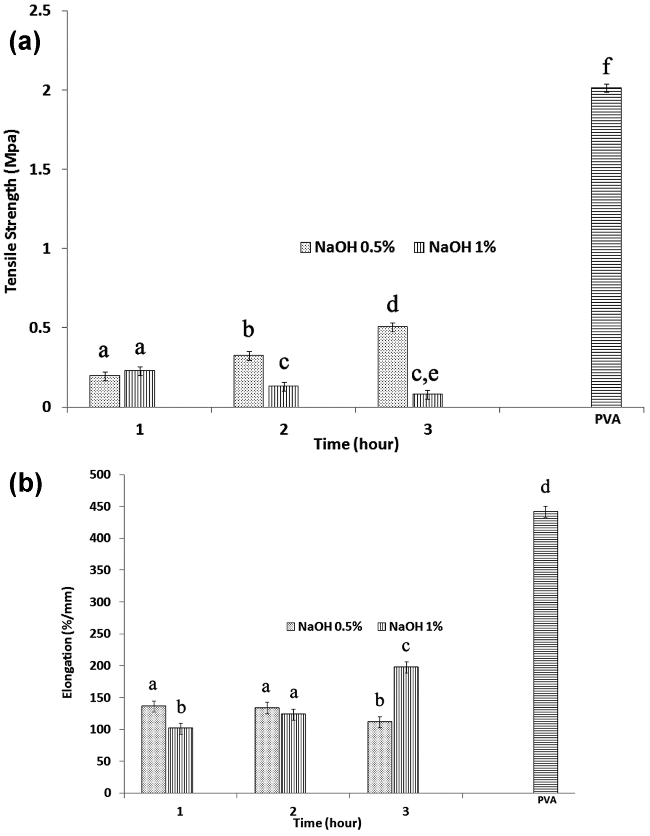


Figure 4. (a) Tensile strength of the films formed after extracting DDG using two different concentrations of alkali at three different times compared to PVA. (b) Elongation of the films formed after extracting DDG using two different concentrations of alkali at three different times compared to PVA. For each extraction condition, different letters, if any, represent statistically significant differences.

had a different effect at the two concentrations studied. When 0.5% alkali was used for extraction, increasing the extraction time considerably increased the strength, but the elongation did not change appreciably. Contrarily, increasing the extraction time decreased the strength of the films but increased elongation when the DDG was extracted with 1% alkali. Properties of the films depend on the composition of the DDG solution and the extent of damage to the polymers. As shown in Table 1, extraction using 0.5% alkali for 1 h had considerably lower yield and also lower amounts of protein and hemicellulose. In addition, lower alkali concentration will have lesser damage to the polymers even when extracted for 3 h. Therefore, the strength of the films increased with increasing extraction time when treated with 0.5% alkali. At a twice higher alkali concentration (1%), the films had similar strength to the 0.5% alkali-extracted films, but the strength decreased drastically when films were formed with DDG extracted with 1% alkali for 2 and 3 h. Considerable damage to the proteins should be the major reason for the substantially low strength of the DDG films extracted using 1% alkali for 3 h. DDG extracted with 2% alkali even for 1 h resulted in very weak films that could not be tested, further substantiating that the proteins and carbohydrates were damaged. The ability of the DDG size to provide good sizing performance despite having poor tensile properties compared to PVA should be due to the better affinity between proteins and carbohydrates and the cotton and polyester fibers.

Comparison of Sizing Performance between DDG, PVA, and Starch. Figure 5 provides a comparison of the peak load of the cotton, P/C, and polyester rovings treated with DDG, PVA, and starch. As shown in Figure 5, the polyester and P/C rovings sized with DDG have similar performance to that of PVA-sized rovings. The cotton rovings sized with DDG had similar peak loads compared to starch but at a considerably higher percent add-on. Differences in peak load between the three types of rovings are due to the varying size of rovings and also properties of the polyester and cotton fibers. The ability to obtain similar sizing performance to PVA and starch means that DDG has the potential to replace PVA. Although higher percent add-ons may be required to obtain similar sizing performance, the low cost of DDG ($120−$125 per ton) and the simple alkaline pre-treatment needed to prepare the sizing solution make the DDG-sizing process cost effective and easily adaptable to existing sizing machinery.

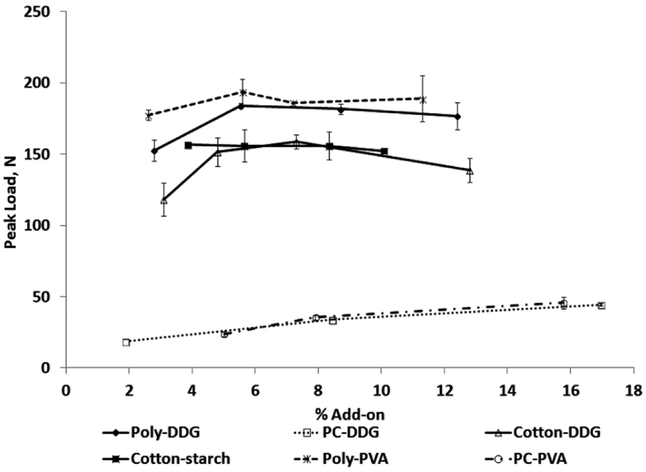


Figure 5. Comparison of the improvement in roving strength at different percent add-ons after treating with DDG and commercially available PVA-based size for P/C and polyester and starch for cotton.

Desizing. Table 2 shows that the DDG size can be easily removed from the fabrics even at room temperature, whereas both PVA and starch had poor desizing under the same conditions. More than 90% of the DDG size is removed from the fabrics even when the fabric to water ratio during washing is 1:5. Compared to DDG, the maximum PVA that was removed was only about 49%, even when considerably high ratios of water (1:20) was used for washing and rinsing. During typical textile processing, desizing is done at 90 °C for PVA, and starch-based sizes also require the use of enzymes in addition to high temperatures.[18] Desizing at room temperature has also been considered to reduce energy costs. The ability of the DDG size to be removed from the fabrics when desized at room temperature and using low amounts of water will help to save energy and also reduce the amount of water released into the effluent treatment plants.

Table 2. Comparison of the Desizing Ability of the DDG, PVA, and Starch Sizes on Polyester, P/C, and Cotton Fabrics at Room Temperature

	desizing conditions				
	fabric to water ratio		% size removed		
type of fabrics	washing	rinsing	DDG	PVA	starch
polyester	1:5	1:5	91.1 ± 2.1	26 ± 2.9	
		1:10	90.4 ± 2.8	27.7 ± 2.4	
		1:20	91.7 ± 4.9	31.4 ± 3.8	
	1:10	1:5	90.4 ± 2.3	32.4 ± 6.5	
		1:10	93.4 ± 0.5	39.1 ± 8.5	
		1:20	96.5 ± 3.8	44.9 ± 4.7	
	1:20	1:5	95.0 ± 4.3	42.6 ± 8.0	
		1:10	95.3 ± 2.4	46.9 ± 5.3	
		1:20	98.6 ± 2.4	49.2 ± 4.7	
poly/cotton	1:5	1:5	91.5 ± 1.7	34.1 ± 4.7	
		1:10	93.6 ± 2.9	35.5 ± 4.8	
		1:20	93.3 ± 1.6	36.7 ± 2.4	
	1:10	1:5	98.4 ± 0.9	38.1 ± 4.3	
		1:10	99.2 ± 2.9	40.3 ± 2.3	
		1:20	98.8 ± 2.0	43.9 ± 8.3	
	1:20	1:5	98.4 ± 0.8	42.1 ± 7.1	
		1:10	99.2 ± 1.5	44.9 ± 7.9	
		1:20	99.0 ± 1.7	46.5 ± 4.2	
cotton	1:5	1:5	68.7 ± 3.4		7.3 ± 3.7
		1:10	71.0 ± 7.5		6.7 ± 2.3
		1:20	79 ± 7.5		6.7 ± 1.8
	1:10	1:5	77.8 ± 2.3		10.1 ± 0.9
		1:10	81.4 ± 5.0		13.4 ± 1.2
		1:20	85.4 ± 5.8		15.8 ± 2.7
	1:20	1:5	86.3 ± 2.3		18.6 ± 2.2
		1:10	90.4 ± 3.8		22.2 ± 5.5
		1:20	91.7 ± 2.2		22.0 ± 2.3

Biodegradation. *Chemical Oxygen Demand (COD).* Figure 6 a−c depicts the biodegradability of the DDG size in comparison to PVA and starch. DDG, PVA, and starch have similar COD values before treating in activated sludge. Treating in the activated sludge degraded starch much faster than DDG

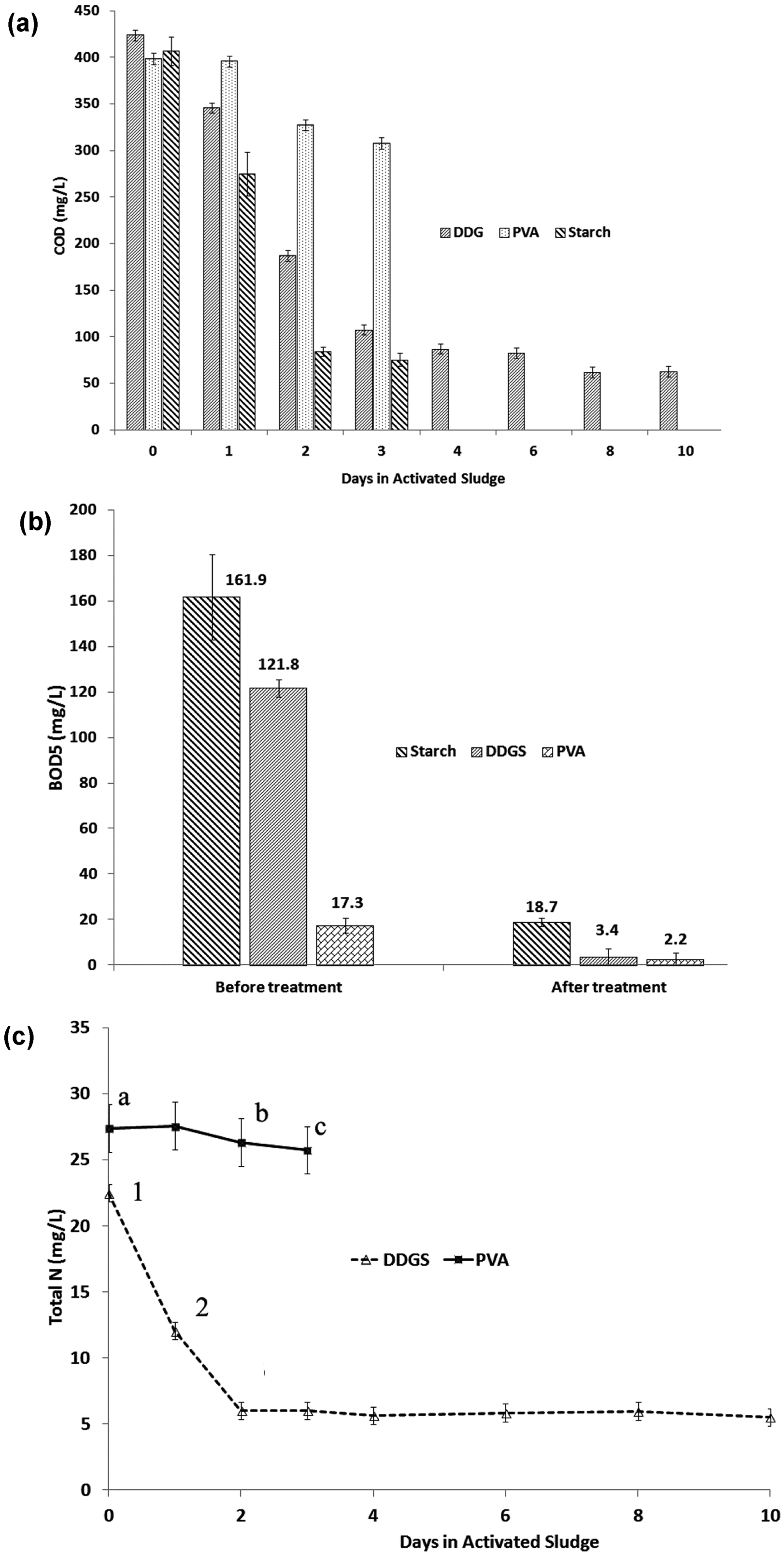


Figure 6. (a) Changes in the chemical oxygen demand (COD) of DDG, PVA, and starch size after treating in activated sludge for 0 to 10 days. (b) Changes in the BOD_5 of DDG, PVA, and starch size after treating in activated sludge. (c) Comparison of the decrease in total nitrogen for the DDG and PVA size after treating in activated sludge up to 10 days. Letters or numbers on the curves represent statistically significant differences.

and PVA. COD for DDG decreased to 187 mg/L after the third day of treatment compared to 424 mg/L before treatment. The COD for DDG continued to decrease further and was less than 100 g/L (allowable limit in released effluent) after 4 days of treatment. Although the COD for PVA decreased to 308 mg/L from 399 mg/L after 3 days of treatment, there was no further significant decrease in the COD values indicating that PVA was not degradable. We did not continue the degradation of PVA beyond 3 days because the BOD_5 values indicated that the PVA did not contain biodegradable materials. The DDG size showed much higher degradability than PVA and was similar to that of starch, suggesting that DDG would not pose a burden on the wastewater treatment plants.

5-Day Biochemical Oxygen Demand (BOD_5). Figure 6b shows the BOD_5 values for the three sizes compared in this study. As seen from the figure, DDG and starch contain much higher amount of biodegradable material compared to PVA. After treating in the activated sludge for 3 days (until the COD was less than 100 mg/L), the BOD_5 values for starch decreased by 89% and nearly 99% for DDG compared to their initial BOD content. The BOD_5/COD values are 0.4 for starch, 0.3 for DDG and only 0.04 for PVA suggesting that PVA was considerably less degradable. Presence of cellulose, lignin and other substances in the DDG size solution that are difficult to degrade should be the reason for the slightly lower biodegradability of DDG compared to starch.

Total and Ammonia Nitrogen. Proteins are considered to affect the operations of effluent treatment plants due to the release of excess amounts of nitrogen. The DDG size consisted of up to 40% proteins that could be a concern when DDG was desized and released into the effluent water. Total nitrogen in the DDG size was similar to that in PVA before the degradation. The amount of nitrogen in the wastewater containing DDG decreased sharply after 1 and 2 days of treatment as shown in Figure 6c, suggesting that the DDG proteins were easily digested. Although PVA by itself does not release nitrogen, the commercial PVA size consists of several additives such as plasticizers and preservatives that should be responsible for the total nitrogen in PVA. The components that contributed to the nitrogen in PVA showed very low degradability, and the levels of total nitrogen in PVA size were high even after 3 days of degradation. Ammonia nitrogen released was negligible, less than 0.01 mg/L for DDG and less than 0.3 mg/L for PVA. Overall, the DDG size had excellent biodegradability, similar to starch and much better than that of PVA.

CONCLUSIONS

Distillers dried grains show similar sizing performance and have the potential to replace PVA and starch for textile warp sizing. Low cost, large availability, easy biodegradability, and simple preparation methods make DDG an attractive sizing agent. The DDG sizing solution was composed of about 40% proteins, and films from the extracted DDG had considerably lower strength and elongation than PVA films. However, the proteins and carbohydrates have better affinity to polyester and cotton fibers and therefore provide good sizing performance. Abrasion resistance of fabrics and peak load for rovings sized with DDG were similar to that of PVA and starch. DDG is easily degraded in activated sludge, and there was no excess release of ammonia that could affect the degradation. In addition, DDG was readily removed (desized) from the fabrics even at room temperature using low amounts of water. At a price of about $0.05 per lb and the ability to provide good sizing performance, ease of degradation in effluent treatment plants, and ease of removal from fabrics make DDG a highly attractive sizing agent to replace PVA.

AUTHOR INFORMATION

Corresponding Author

*Phone: 402-472-5197. Fax: 402-472-0640. E-mail: yyang2@unl.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Agricultural Research Division at the University of Nebraska-Lincoln and U.S. Department of Agriculture (Hatch Act and Multi-State Project S1054 (NEB 37-037)) for their financial support to complete this research.

REFERENCES

(1) Bisschops, I.; Spanjers, H. Literature review on textile wastewater characterization. *Environ. Technol.* **2003**, *24*, 1399−1411.

(2) Huda, S.; Reddy, N.; Karst, D.; Xu, W.; Yang, W.; Yang, Y. Nontraditional biofibers for a new textile industry. *J. Biobased Mater. Bioenergy* **2007**, *1* (2), 177−190.

(3) Reddy, N.; Yang, Y. Novel protein fibers from wheat gluten. *Biomacromolecules* **2007**, *8* (2), 638−643.

(4) Reddy, N.; Yang, Y. Soyprotein fibers with high strength and water stability for potential medical applications. *Biotechnol. Prog.* **2009**, *25* (6), 1796−1802.

(5) Ren, X. Development of environmental performance indicators for textile process and product. *J. Cleaner Prod.* **2000**, *8*, 473−481.

(6) Irina-Isabella, S.; Butnaru, R. Wastewater characteristics in textile finishing mills. *Environ. Eng. Manage. J.* **2008**, *7* (6), 859−864.

(7) Zhu, Z.; Cao, S. Modifications to improve the adhesion of crosslinked starch sizes to fiber substrates. *Text. Res. J.* **2004**, *74* (3), 253−258.

(8) Meshram, M. W.; Patil, V. V.; Mhaske, S. T.; Thorat, B. N. Graft copolymers of starch and its application in textiles. *Carbohydr. Polym.* **2009**, *75*, 71−78.

(9) Chen, L.; Reddy, N.; Yang, Y. Remediation of environmental pollution by substituting poly(vinyl alcohol) with biodegradable warp size from wheat gluten. *Environ. Sci. Technol.* **2013**, *47*, 4505−4511.

(10) Chen, L.; Reddy, N.; Yang, Y. Soyproteins as environmentally friendly sizing agents to replace poly(vinyl alcohol). *Environ. Sci. Pollut. Res.* **2013**, *20* (9), 6085−6095.

(11) Yang, Y.; Reddy, N. Potential of using plant proteins and chicken feathers for cotton warp sizing. *Cellulose* **2013**, *20*, 2163−2174.

(12) Xu, W.; Reddy, N.; Yang, Y. An acidic method of zein extraction from DDGS. *J. Agric. Food Chem.* **2007**, *55* (15), 6279−6284.

(13) Xu, W.; Reddy, N.; Yang, Y. Extraction, characterization and potential applications of cellulose in corn kernels and distillers dried grains with solubles (DDGS). *Carbohydr. Polym.* **2009**, *76* (4), 521−528.

(14) Reddy, N.; Hu, C.; Yan, Y.; Yang, Y. Acetylation of polysaccharides in corn distillers dried grains for thermoplastic applications. *Appl. Energy* **2011**, *88* (5), 1664−1670.

(15) Hu, C.; Reddy, N.; Yan, K.; Yang, Y. Synthesis and characterization of highly flexible thermoplastic films from cyanoethylated corn distillers dried grains with solubles. *J. Agric. Food Chem.* **2011**, *59*, 1723−1728.

(16) Hebeish, A.; Aly, A. A.; El-Shafei, A. M.; Zaghloul, S. Innovative starch derivatives as textile auxiliaries for application in sizing, finishing and flocculation. *Starch* **2008**, *60*, 97−109.

(17) Goswami, B. C.; Anandjiwala, A. D.; Hall, D. M. *Textile Sizing*; Marcel Dekker, Inc.: New York, 1994.

(18) El-Sheikh, M. A. Carboxymethylation of maize starch at mild conditions. *Carbohydr. Polym.* **2010**, *79* (4), 875−881.