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A Sustainable Slashing Industry Using Biodegradable Sizes from Modified Soy Protein To Replace Petro-Based Poly(Vinyl Alcohol)

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S Supporting Information

ABSTRACT: Biodegradable sizing agents from triethanolamine (TEA) modified soy protein could substitute poly(vinyl alcohol)(PVA) sizes for high-speed weaving of polyester and polyester/cotton yarns to substantially decrease environmental pollution and impel sustainability of textile industry. Non-biodegradable PVA sizes are widely used and mainly contribute to high chemical oxygen demand (COD) in textile effluents. It has not been possible to effectively degrade, reuse or replace PVA sizes so far. Soy protein with good biodegradability showed potential as warp sizes in our previous studies. However, soy protein sizes lacked film flexibility and adhesion for required high-speed weaving. Additives with multiple hydroxyl groups, nonlinear molecule, and electric charge could physically modify secondary structure of soy protein and lead to about 23.6% and 43.3% improvement in size adhesion and ability of hair coverage comparing to unmodified soy protein. Industrial weaving results showed TEA-soy protein had relative weaving efficiency 3% and 10% higher than PVA and chemically modified starch sizes on polyester/cotton fabrics, and had relative weaving efficiency similar to PVA on polyester fabrics, although with 3–6% lower add-on. In addition, TEA-soy sizes had a BOD₅/COD ratio of 0.44, much higher than 0.03 for PVA, indicating that TEA-soy sizes were easily biodegradable in activated sludge.



INTRODUCTION

Textile industries consume large volume of water, non-degradable or toxic chemicals, and become a major contributor to worldwide water pollution. Petroleum-based chemicals like poly(vinyl alcohol) (PVA) in textile desizing effluent result in a high wastewater load and amount to a COD of 40–80% of the entire load from a textile finishing industry.¹ Also, PVA has been found to be refractory pollutants in textile effluent.² Studies have shown that only 15–25% of PVA was degraded in anaerobic sludge after around 300 days.³ Discharged PVA effluent affects both the water quality, the microbial, and aquatic flora. In addition, PVA has the ability to mobilize heavy metals from sediments in water streams and lakes and caused severe environmental problems.^{4,5} Currently, some European countries have enacted several regulations to limit the industrial use of PVA sizes.

A considerable amount of studies on the degradation, reuse and substitution of PVA have been carried out. Most of the degradation studies focused on chemical and photochemical oxidation,^{6–9} enzyme biodegradation,³ and photocatalytic degradation.¹⁰ Approaches, such as coagulation,^{11,12} adsorp-

tion,¹³ and ultrafiltration¹⁴ were also developed to reuse PVA. However, these methods had fatal drawbacks, including long operation time and high costs, and therefore have not been used for real industrial applications.⁶ On the other hand, various types of chemically modified starch have been explored to replace PVA.^{15,16} Unfortunately, the properties of starch-based sizes were not comparable to PVA on polyesters and their blends. The price of starch is escalating recently as its demand increases much faster than production in food and biofuel industries.¹⁷ In addition, some chemical modifications could decrease the biodegradability of starch and increase the price, making modified starch unattractive as a slashing chemical compared to PVA.

Soy protein, wheat gluten and keratin, have been found to have good biodegradability, film forming properties and potential of being as textile sizes in our previous lab-scale

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study.^{18–20} However, without modification, these proteins formed brittle films and showed low adhesion to polyester and polyester/cotton yarns, therefore failed to protect yarns during high-speed weaving.

Many studies of additives have been done to improve flexibility of proteins films. Polyols and amines have been used as good plasticizers for protein-based materials due to their ability to reduce intermolecular hydrogen bonding to increase intermolecular spacing.^{21,22} Small molecules containing amino, imino group, or hydroxyl group were capable of plasticizing proteins due to their excellent compatibility and disruption of intermolecular hydrogen bonding between and within proteins.^{23,24} However, there is no study reporting the molecular characteristics of additives that could improve size performances of proteins for high-speed weaving without decreasing their biodegradability.

In this study, low-cost soy protein, extracted from soy meal, the byproducts from production of edible oil and biodiesel, were physically modified by specific additives, including triethanolamine (TEA), diethanolamine, ethanolamine, propanolamine, butanolamine, and glycerol. Conformational change of soy protein was induced and found highly relevant to their final sizing performance. Tensile properties of TEA soy proteins (TEA-soy) films, adhesion properties, ability to cover hair, desizing properties and biodegradability were tested. Industrial-scale weaving trials were also carried out to verify the potential of using TEA-soy to size polyester and polyester/cotton for high-speed weaving. Use of TEA-soy to replace nonbiodegradable PVA sizes for high-speed weaving would remediate environmental pollution and promote sustainability of textile industry.

■ EXPERIMENTAL SECTION

Materials. Soy protein used for the study was kindly supplied by Ceres Technology Group Co., Ltd. The 100% polyester rovings were supplied by Shuford Yarns LLC, Hickory, NC. The polyester/cotton (65/35) rovings (70s Hank) used in the study were supplied by Mount Vernon Mills. The 100% polyester yarns (45s) were supplied by Nantong Textile Co., Ltd., Nantong, China. The polyester/cotton (30/70) yarns (45s) and commercially available modified starch 130 sizes (esterified starch sizes) were kindly supplied by Luthai Textile Co., LTD, Shandong, China. Commercially available PVA based sizes were purchased from Japan Kuraray Company, Tokyo, Japan. Viscosity of the PVA 205MB was 3.9–4.2 mPa·s at 3% solid content under 20 °C and pH of the solution was between 5 and 7. Other chemicals used in this study were purchased from National Chemicals Inc., Minnesota, USA.

Film Preparation and Tensile Properties. Modified soy protein sizes were respectively prepared by heating 10 wt % soy protein solutions which contained 20 wt % TEA, diethanolamine, ethanolamine, propanolamine, butanolamine, and glycerol (base on weight of soy protein) at pH 10 and 90 °C for 30 min pH was adjusted by 10 wt % sodium hydroxide. After heating, the pH of the solution was adjusted to 7 using diluted acetic acid. Then the solution was cast onto Teflon coated glass plated and allowed to dry at 20 °C and 65% humidity for about 35 to 40 h. PVA and modified starch 130 dispersed in water was respectively heated at 90 °C for 30 min, and cast to form films. Films formed were tested on a MTS tensile tester QTest 10 (MTS Systems Corporation) for tensile properties according to ASTM Standard 822e. According to the standard, film samples with size of 8 × 1.5 cm were prepared

and tested using a gauge length of 2 in. and crosshead speed of 10 mm/min.

Intrinsic Viscosity of Sizing Solutions. The intrinsic viscosities of the additive-free soy protein, TEA-soy, diethanolamine-soy, ethanolamine-soy, propanolamine-soy, butanolamine-soy, and glycerol-soy solutions were determined according to ASTM standard D 2857 at a temperature of 25 ± 1 °C. An Ubbelohde capillary viscometer, size: 68b, capillary diameter: 0.55 mm, (Zhejiang Jiaojiang glassware factory, China) was used. The solvents were 1.2 wt % additives solutions.

Circular Dichroism (CD). Soy protein (10 wt %) was dissolved in TEA-distilled water solution containing 0, 10, 20, and 30 wt % TEA (base on weight of soy protein) under 90 °C for 30 min. The solution was diluted with distilled water to 5 mg/L before CD measurement. Each solution in a cuvette with a path length of 0.1 mm was continuously scanned over the wavelength range of 190–250 nm at a rate of 50 nm/min on a Jasco model J-815 spectropolarimeter (Jasco, JP)

Tensile Properties of Rovings. Soy protein (10 wt %) were pretreated by adding different types and contents of additives (0 wt % to 30 wt % TEA or glycerol) in distilled water under 90 °C for 30 min. Before heating, the pH of solutions were adjusted to pH 10 by 10 wt % sodium hydroxide. After pretreatment, the pH of the solution was adjusted to pH 7 by adding acetic acid. The rovings wound on frames were immersed in the sizing solution at 90 °C for 5 min. Without sizing, the roving had almost no strength since the roving was a loose assembly of fibers. Sizing agent adhered to the fibers and provided cohesion leading to improved strength. Therefore, property of the sized roving was determined by their strength as an indication of adhesion of the sizes to the fibers in the rovings.

Industrial-Scale Weaving Trial. The weaving trial was carried out in Luthai Textile Co., Ltd. Before weaving, yarns usually experience processes of winding, warping, sizing, reeding, and healing. After winding and warping, polyester/cotton and polyester yarns were sized on a factory sizing machine with an oven temperature of 75 °C, slurry tank temperature of 90 °C, running speed of 50 m/min, and roller pressure of 1.8 kN. Polyester/cotton and polyester yarns were also sized by commercial sizes (PVA and starch 130) using the same conditions as soy protein. After going through drier, sized yarns were coiled and ready for reeding and healing. Finally, warp yarns were woven on Picanol (plus OMNI 800) air jet looms (Picanol, China) at a weaving rate of 750 r/min at 25 °C and 75% humidity.

Hairiness of Yarns. All samples for hairiness testing were conditioned at 21 °C and 65% relative humidity for 35–40 h before testing. Hairiness tests were performed on YG 172 type hairiness tester (Changling Textiles, China) with test speed of 30 m/min. The numbers of hair with more than 2 mm length were calculated. Hairiness results of each sample were collected from 10 m of yarns. At least 10 samples were tested for each condition and the experiments were repeated three times to report average and standard errors.

Desizing. The woven fabrics with a known amount of percent add-ons were desized to determine the efficiency of removal of the TEA-soy sizes, PVA sizes and modified starch sizes from the woven fabrics. Desizing was done by treating the sized fabrics in water with different rinse times at 5:1 wash and rinse ratio under 90 °C. After desizing, the fabrics were dried in an oven and weighed. The fabrics were weighed before and

after desizing, and the loss in weight was calculated to determine desizing efficiency.

Biodegradation. To determine the biodegradation of the sizing solutions, wastewater sludge from Songjiang sewage treatment plant, Shanghai, China, was used. The concentration of sizes in the textile mill is 300 mg/L.²⁵ COD in desizing effluent was measured according to U.S. Environmental Protection Agency method 8000 using digital reactor block DRB 200 (HACH, DE). Five-day biochemical oxygen demand (BOD₅) was determined according to American Public Health Association guidelines in the standard methods for the examination of wastewater using optical dissolved oxygen meter HQ440d (HACH, DE). Total nitrogen of the soy protein sizes in the sludge was measured by UV/vis spectrophotometer DU 720 (Beckman Coulter) and calculated based on the alkaline persulfate oxidation digestion method. Ammonia nitrogen was measured by the same spectrophotometer and calculated using salicylate and hypochlorite in an alkaline phosphate buffer.²⁶

Statistical Analysis. Data generated was analyzed using Tukey's multiple-pair wise comparison using SAS program (SAS Institute, Raleigh, NC). A significance level of $\alpha = 0.05$ was considered as statistically significant. In each figure, data points with significant differences were marked with different letters, numbers or symbols.

RESULTS AND DISCUSSION

Influence of Additives on Unfolding of Soy Protein and Tensile Properties of Soy Protein Films. Hydroamine with multiple hydroxyl groups, nonlinear molecular structure, and electric charge played a critical role in disentanglement of soy protein to enhance unfolding and alignment of molecules in solution, and thus improve tensile properties of the casting films. Soy protein mainly contains coiled 11s globulins which have small intermolecular contact area, leading to limited intermolecular slippage before film breakage.²⁷ Therefore, soy protein films have poor capability of elongation. One approach of improving flexibility with minor decline in tensile strength of soy protein films is to decrease intramolecular interaction while slightly decrease intermolecular interaction of soy protein through increasing their disentanglement and alignment.

Small molecules with multiple hydroxyl groups, nonlinear molecular structure, and electric charge, like TEA, could disentangle and enhance alignment of soy protein. In the solution of pH 7, soy protein carried negative charge as its isoelectric point was at around pH 4.5.²⁸ Thus, TEA with positive charge could adhere onto molecules of soy protein via electrostatic attraction. Some of the attached TEA could disrupt intermolecular hydrogen bonds while some could interact with hydrophobic domains in soy protein coils due to hydrophobic interaction with CH₂CH₂. The volume of coils could be enlarged by bulky TEA molecules, and intramolecular hydrogen bonds of folded proteins could be disrupted by TEA. In addition, attached TEA could decrease negative charges on soy protein. Thus, unfolded soy protein with reduced repulsion among each other facilitates intermolecular interaction, which improved the strength of films.

To compare capability of different additives of unfolding soy protein, intrinsic viscosity of soy protein solution and tensile properties of soy protein films with various additives are shown in Table 1. Soy proteins with unfolded structure had higher intrinsic viscosity of solution, film flexibility and strength. Soy protein films were too brittle to be tested and had low intrinsic

Table 1. Effect of Additives on Intrinsic Viscosities of Soy Protein and Tensile Properties of Soy Protein Films

soy protein with/ without additives ^a	intrinsic viscosity, dL/g	tensile properties of films	
		strength, MPa	elongation, %
soy protein	4.8 ± 0.5 ^a		
TEA-soy ^b	8.8 ± 0.2 ^b	9.9 ± 0.3 ¹	165.0 ± 5.1 ^A
diethanolamine-soy	6.6 ± 0.3 ^c	2.0 ± 0.2 ²	126.3 ± 9.5 ^B
ethanolamine-soy	5.4 ± 0.3 ^d	1.2 ± 0.2 ³	38.0 ± 4.5 ^C
propanolamine-soy	5.6 ± 0.3 ^d	1.2 ± 0.3 ³	52.5 ± 1.6 ^D
butanolamine-soy	6.1 ± 0.4 ^{cd}	1.6 ± 0.4 ^{2,3}	74.6 ± 10.3 ^E
glycerol-soy	6.8 ± 0.3 ^c	4.9 ± 0.3 ⁴	90.0 ± 1.8 ^F

^aAdditive concentration is 20 wt % (based on protein weight). Data points with different numbers or letters indicate statistically significant difference. ^bTEA-soy is the abbreviation of TEA soy protein.

viscosity, which was in accordance with several reports.^{29,30}

Addition of additives enhanced flexibility of the soy protein films. From ethanolamine, diethanolamine to TEA, the numbers of hydroxyl groups, degree of nonlinearity and electric charge gradually increased. Correspondingly, a substantial increase in tensile strength (8.2 times) and elongation (4.3 times) of modified soy protein films and intrinsic viscosity (1.6 times) of modified soy protein was showed. By adding ethanolamine, propanolamine and butanolamine, modified soy protein films had 33.3% and 94.7% improvement in strength and elongation, while 13.0% increase in intrinsic viscosity. Compared to glycerol, TEA with bulky structure and electric charge could easily break intramolecular hydrogen bonds of soy protein and enhance diameters of micellae. As a result, TEA-soy had obviously higher intrinsic viscosity and tensile properties than glycerol-soy. Changes in terms of intrinsic viscosity, tensile strength, and elongation among TEA-soy, diethanolamine-soy, ethanolamine-soy, propanolamine-soy, butanolamine-soy, and glycerol-soy demonstrated additives with multihydroxyl groups, nonlinear molecular structure and electric charge endowed high tensile properties to soy protein films. TEA-soy films had lower strength than PVA (24.8 ± 3.4 MPa), but higher flexibility than PVA (155.1% ± 7.5%). Compared to the modified starch films, which were too brittle to be tested, TEA-soy films had better tensile properties.

Influence of Concentrations of TEA and Glycerol on Tensile Properties of Soy Protein Films. Figure 1 depicts the effect of TEA and glycerol concentration on tensile properties of soy protein films. Increasing concentration of TEA and glycerol from 10 wt % to 30 wt % increased 38.4 and 14.4 times of elongation, but decreased 1.9 as well as 5.1 times of strength of soy protein films, respectively. TEA could provide higher tensile properties to soy protein films than glycerol. It was probably because TEA had ability to slightly decrease intermolecular interaction of soy protein while substantially decrease interaction within protein molecules. Glycerol had comparatively lower potential to weaken intramolecular interaction of soy protein, and thus disrupted intermolecular hydrogen bonds of soy protein. Therefore, TEA is a promising additive to improve size performances of soy protein.

Influence of TEA on Conformation of Soy Protein. As TEA concentration increased, the orderedness of the secondary structures of soy protein was gradually enhanced. As shown in Figure 2, all the spectra indicated unordered conformation of soy protein with a deep negative peak at around 208 nm.³¹ The

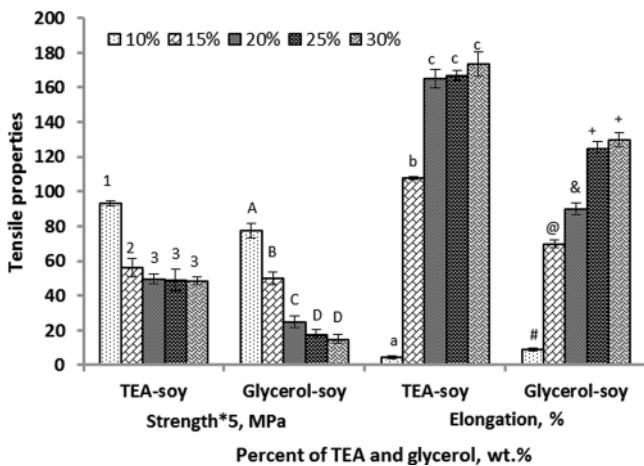


Figure 1. Effect of TEA and glycerol concentration on tensile strength and elongation of soy protein films. 0 wt % to 30 wt % (based on protein weight) TEA or glycerol were added for preparation of TEA soy protein or glycerol soy protein. Data points with different numbers, letters, or symbols indicate statistically significant difference.

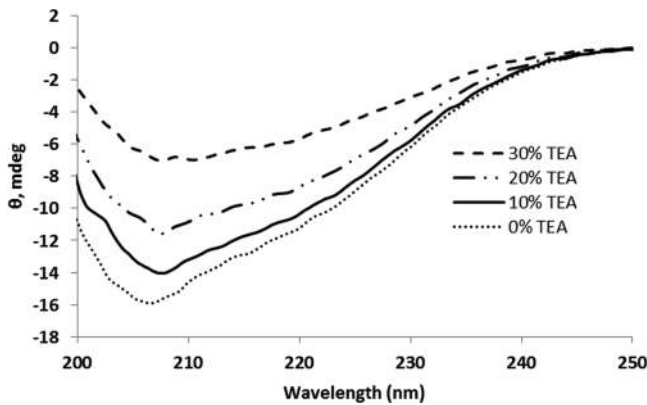


Figure 2. CD spectra of soy protein solution with 0, 10, 20, and 30 wt % TEA, respectively.

peaks gradually weakened as TEA concentrations increased from 0% to 30%, indicating less unordered coils in soy protein. At higher concentration of TEA, more TEA molecules attached onto the surface of soy protein, embedded into hydrophobic domains of soy protein, and thus disrupted intramolecular hydrogen bonds of coiled protein. As a result, soy protein unfolded and had less random conformation, which was in accordance with increased intrinsic viscosity of soy protein with TEA.

Influence of TEA Concentration on Adhesion of Soy Protein Sizes to Polyester/Cotton and Polyester Fibers.

Weaving efficiency is also highly influenced by adhesion properties of sizing agents.^{26,32} Figure 3 showed the effect of TEA concentration on adhesion properties of soy protein sizes to polyester/cotton and polyester fibers. Increasing TEA concentration from 0 wt % to 20 wt % increased 23.6% and 15.2% tensile strength of polyester and polyester/cotton rovings respectively, indicating adhesion of soy protein sizing agents were improved. This was probably because soy protein molecules became liberating and stretching when increasing TEA concentration. Increasing contact area between proteins and fibers contributed to high adhesion. Continuously increasing TEA concentration to 30 wt % decreased tensile strength of both sized rovings. At the same add-on, rovings had

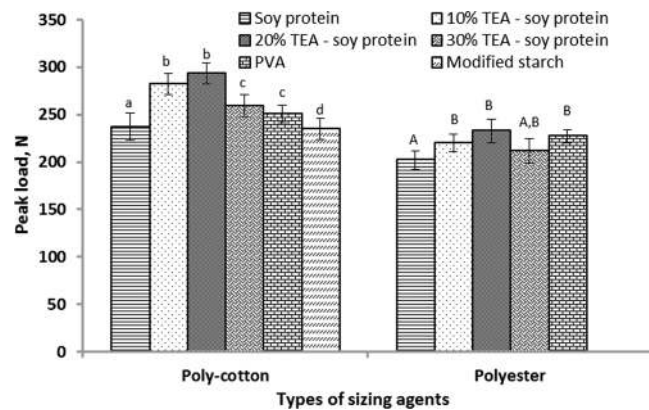


Figure 3. Effect of TEA concentration on the tensile strength of sized polyester/cotton and polyester rovings. 0 wt % to 30 wt % (based on protein weight) TEA were added for preparation of TEA soy protein sizes. All sizing was done at 90 °C for 5 min. Percent of add-on is 15 wt % (based on weight of rovings). Data points with different letters indicate statistically significant difference.

decreased amount of soy proteins when increasing weight percent of additives. Thus, soy protein sizes had low adhesion to fibers. TEA-soy had 17.2% and 24.8% higher adhesion to polyester/cotton than PVA and modified starch, respectively, but had adhesion similar to PVA on polyester. This was probably because unfolded soy protein contained hydrophilic and hydrophobic domains, and had good adhesion to both cotton and polyester. PVA had hydrophobic carbon backbones, which placed good adhesion to hydrophobic polyester but poor to cotton. Modified starch with esterification contained curly molecules,³³ and had small contact area with fibers, and therefore had lower adhesion to fibers.

Influence of TEA Concentration on the Ability of Soy Protein Sizes to Decrease Hairiness.

Staple yarns of polyester fibers or polyester/cotton should be sized before weaving in order to reduce the yarn surface friction.³⁴ Thus, short hair is expected to be bonded onto the yarn surface tightly by slashing. Figure 4 showed the effect of TEA concentration on the ability of soy protein sizes to decrease yarns hairiness of polyester/cotton and polyester.

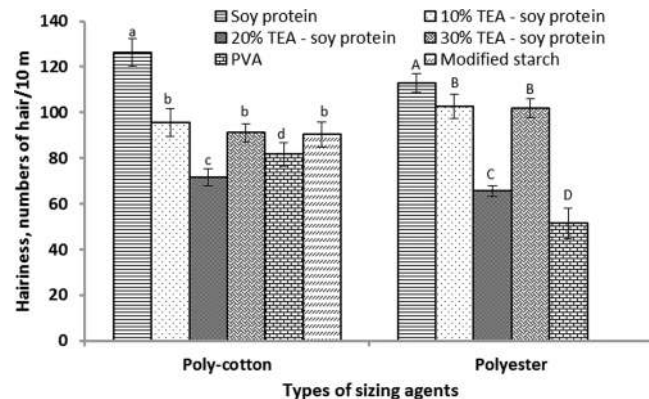


Figure 4. Influence of TEA concentration on the hairiness of sized polyester/cotton and polyester yarns. 0 wt % to 30 wt % TEA (based on protein weight) were added for preparation of TEA soy protein sizes. All sizing was done at 90 °C using slashing equipment. The numbers of hair with more than 2 mm length were calculated from 10 m of yarns. Data points with different letters indicate statistically significant difference.

and polyester yarns had average 976 ± 2.07 numbers of hair/10 m and 603 ± 6.35 numbers of hair/10 m. Soy protein sizes without additives could decrease yarns hairiness of polyester/cotton and polyester at 6% add-on. Increasing TEA concentration from 0 wt % to 20 wt % decreased 43.3% and 41.9% more yarns hairiness of polyester/cotton and polyester yarns, respectively. Further increasing additives concentration to 30 wt % increased hairiness again, which was similar to the effect of 10% additives. Increasing TEA percent increased affinity between the soy protein and fibers. However, 30 wt % TEA-soy sized yarns were sticky due to higher moisture absorption, and therefore had increased hair during warp preparation. With 20 wt % TEA, soy protein sized polyester yarns had 27.4% higher hairiness than that of PVA. But the polyester/cotton yarns sized by soy protein with 20 wt % TEA had 12.3% and 20.7% lower hairiness compared to PVA and modified starch, respectively. Since 20 wt % TEA endowed comparatively higher size performances to soy protein (adhesion properties, and ability of hair coverage), industrial-scale weaving trial would be carried out to verify the feasibility of substituting PVA with TEA-soy.

Industrial-Scale Weaving Trial. A comparison of TEA-soy sizes with PVA and modified starch sizes, in terms of relative weaving efficiency, was displayed in Table 2. At 6% and 3%

Table 2. Comparison of the Relative Weaving Efficiency of Polyester and Polyester/Cotton Yarns Sized with TEA-soy, PVA, and Modified Starch

sizing agent	add-on (warp yarns), %	relative weaving efficiency ^a , %	
		polyester/cotton	polyester
TEA-soy ^b	11	100	97
PVA	17	97	100
modified starch	14	90	

^aFor each type of yarns, the sizing agent with highest real weaving efficiency was regarded as having 100% relative weaving efficiency. Real weaving efficiency is the ratio of actual weaving length to the theoretical weaving length in 8 h. ^bTEA-soy is the abbreviation of TEA soy protein.

lower add-on, TEA-soy still showed 3% and 10% higher relative weaving efficiency for polyester/cotton fabrics than PVA and modified starch, respectively. Also, at 6% lower add-on, TEA-soy had slightly lower relative weaving efficiency (3%) for polyester fabrics compared to PVA. Compared to PVA, TEA-soy had similar or better adhesion to polyester and polyester/cotton, higher ability to decrease hairiness of polyester/cotton yarns, and higher flexibility of films. Compared to the modified starch, TEA-soy had better films properties, adhesion, and ability of hair coverage of polyester/cotton, and therefore showed much higher weaving performances. Unmodified soy protein sized polyester/cotton and polyester yarns failed to be woven on the high-speed weaving machine in this industrial-scale trial, due to their poor sizes properties. Therefore, TEA-soy sizes are promising as warp sizing agents for high-speed weaving of polyester/cotton and polyester fabrics to replace PVA and modified starch sizes.

Desizing. Desizing efficiency mainly influenced water consumption during fabrics production. Efficient removal of sizes from fabrics using less water will promote sustainability of textile industry. In Table 3, more than 90% TEA-soy sizes could be removed from polyester and polyester/cotton fabrics after twice rinse in 90 °C water bath. At the same desizing condition,

Table 3. Comparison of the Desizeability (Percent Size Removed) for TEA Soy Protein, PVA and Modified Starch Treated Polyester/Cotton and Polyester Fabrics at Various Desizing Conditions^a

type of yarns	rinse times	% size removed		
		TEA-soy	PVA	modified starch
polyester/cotton	1	76.3 ± 0.87	72.4 ± 2.7	58.9 ± 4.7
	2	91.0 ± 1.3	79.7 ± 4.9	62.3 ± 5.3
	3	100	98.4 ± 2.0	65.0 ± 4.9
polyester	1	73.0 ± 4.9	68.5 ± 2.8	
	2	93.3 ± 5.7	79.8 ± 5.1	
	3	100	95.6 ± 3.0	

^aAdd-on of woven fabric is 5.5 wt % to 8.5 wt % (only warp yarns were sized). Desizing temperature is 90 °C. Both of wash ratio and rinse ratio (liquor to fabrics) are 5:1.

only 80% of PVA were removed from polyester and polyester/cotton, while 62% modified starch were removed from polyester/cotton fabrics. After rinsing 3 times, more than 95% PVA could be desized from both fabrics, while only 65% modified starch sizes were removed from polyester/cotton fabrics. Usually, enzymes are needed when doing starch based desizing, which consumes additional chemicals and increases cost of fabric production. It has been reported almost 3 tons of water are used when producing 100 m fabrics (15 kg/100 m).²⁵ Desizing effluent is one of the major contributors of textile wastewater. Easy removal of sizes fabrics without chemicals indicated that the TEA-soy would not affect further processing of the fabrics and would save more water and energy for textiles production.

Biodegradation. COD and BOD₅. Figure 5a and b showed a comparison of TEA-soy sizes in terms of COD and BOD₅ values with PVA and modified starch. At 0 day, samples of TEA-soy and PVA sizes had similar COD, but starch samples contained slightly lower COD. After 2 days, soy protein and modified starch as nutrients for micro-organisms were largely (>50%) deduced in the sludge, whereas only 8.1% of COD was decreased for PVA samples from the original value. This was because, as seen in Figure 5b, TEA-soy and modified starch samples had substantially higher BOD₅ value than PVA samples before sludge treatment. Further prolonging days of treatment decreased COD of TEA-soy and modified starch samples to 109.5 ± 6.2 mg/L and 105.9 ± 2.8 mg/L on the fifth day, respectively, both of which were less than the allowable concentration (110 mg/L) when effluent was discharged. However, PVA showed very slow decrease in COD during 5 days treatment. Even after 5 days, COD of PVA size decreased 23%, and did not decrease further. Based on low BOD₅ value of 2.5 ± 0.5 mg/L and high COD value of 398.3 ± 8.4 mg/L on the fifth day, PVA sizes were determined not degradable. On the contrary, TEA-soy had low COD and comparatively high BOD₅ on fifth day, indicating it can be degraded further if necessary.

Total and Ammonium Nitrogen. Protein contains certain amount of nitrogen, and thus may posed risk to environment by inducing eutrophication in water body. Figure 6 showed the amount of total and ammonia nitrogen released from the TEA-soy during 5 days of treatment in activated sludge. There was a sharp decline in the total nitrogen after treating in the activated sludge for 1 day. A corresponding increase in ammonia

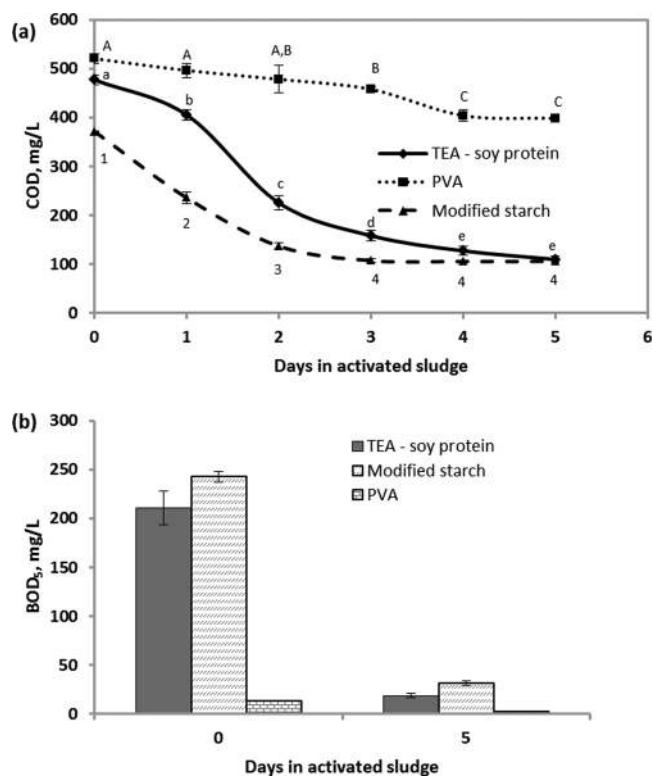


Figure 5. (a) Changes in the chemical oxygen demand (COD) of TEA soy protein, modified starch and PVA sizes after treating in activated sludge for 0–5 days. Letters or numbers represent statistically significant differences. (b) Five-day biochemical oxygen demand (BOD₅) of TEA soy protein, modified starch and PVA sizes treated in activated sludge for 0 and 5 days.

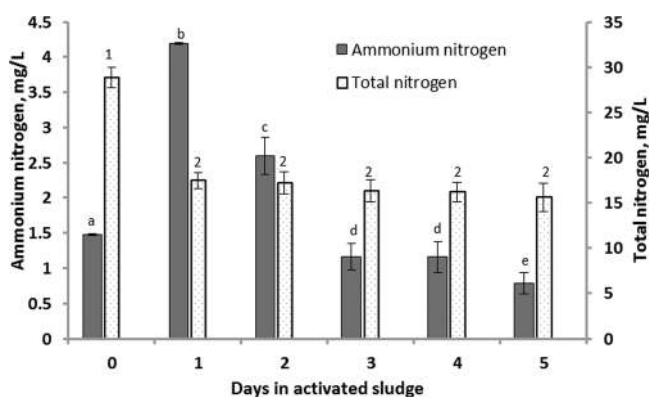


Figure 6. Total and ammonium nitrogen of TEA soy protein sizes treated in activated sludge up to 5 days. Letters or numbers represent statistically significant differences.

nitrogen was seen until day 1 and then the ammonia nitrogen released from TEA-soy decreased rapidly. Aerobic bacteria in the activated sludge would use proteins as their nutrition or could turn the proteins into nitrates, resulting in decline in total nitrogen. The low levels of total and ammonia nitrogen released from TEA-soy after 5 days of treatment in activated sludge demonstrated that TEA-soy had low possibility to arouse water eutrophication and affect the operation of the effluent treatment plants.

Based on the degradation study, almost 72.6% COD would be decreased in textile desizing effluent, if TEA-soy was used to substitute nonbiodegradable PVA sizes for slashing of polyester

and polyester/cotton yarns. TEA-soy had similar biodegradation to modified starch but considerably better than PVA, according to the changes in COD, BOD₅, and total and ammonia nitrogen from the study of activated sludge treatment. Therefore, substituting PVA with TEA-soy for slashing would decrease sizing related pollution from wastewater, and impel sustainability of the textile industry.

Biodegradable sizing agents from TEA-soy could substitute PVA sizes for high-speed weaving of polyester and polyester/cotton fabrics. Lab-scale study of size performance and industrial-scale high-speed weaving tests on polyester/cotton and polyester yarns showed additives with multiple hydroxyl groups, nonlinear molecular structure and electric charge, such as TEA, could effectively modify soy protein into high performance sizes for high-speed weaving. The overall size performances of TEA-soy were better than soy protein and glycerol-soy. Film flexibility and ability of hair coverage of soy protein were enhanced after addition of TEA, although tensile strength of soy protein films was slightly decreased. At the same add-on as PVA on polyester and polyester/cotton materials, TEA-soy showed similar or better adhesion properties, ability of hair coverage and desizing properties. The industrial-scale weaving study verified that even at 6% and 3% lower add-ons, TEA-soy could provide 3% and 10% higher relative weaving efficiency for polyester/cotton than PVA and modified starch sizes, and provided 3% lower relative weaving efficiency than PVA sizes for polyester fabrics. In addition, TEA-soy had biodegradability similar to modified starch and much higher than PVA. Therefore, TEA-soy has ability to substitute PVA for slashing industry, and benefit textiles and environment.

■ ASSOCIATED CONTENT

📄 Supporting Information

Detailed processes of testing tensile properties of rovings, intrinsic viscosity of sizing solutions, industrial-scale weaving efficiency, and biodegradation are shown. Cost calculations of TEA-soy protein and prices of the raw materials and chemicals are shown in the files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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