Industrial trial of high-quality all green sizes composed of soy-derived protein and glycerol

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Abstract

All-green textile sizes with satisfactory weaving performance and biodegradability were developed from soy protein and glycerol, two major byproducts from soy-based biodiesel production. Polyvinyl alcohol has long dominated textile sizing chemical market due to its excellent sizing performance, despite its non-biodegradability. Efforts have been devoted to replace polyvinyl alcohol for a more sustainable textile industry. Recently, substituting size developed from soy protein after using high amount of petro-based triethanolamine showed acceptable sizing properties. However, triethanolamine was not an eco-friendly additive, due to its petroleum origin and non-biodegradability. In this research, glycerol was used to plasticize soy protein to develop all-green soy size. Glycerol interrupted hydrogen bonds in the soy globulin, allowing them to extend in the films. Resultantly, the soy size films possessed high stretchability and work of rupture. Lab-scale experiments and industrial weaving proved that the all-green soy size had similar or better weaving performance and remarkably better degradability than polyvinyl alcohol and triethanolamine plasticized soy protein size. For the first time, a possible logarithmic relationship was found between work of rupture of the size film and relative weaving efficiency.

Keywords: Soy protein; Polyvinyl alcohol; Biodegradable; Glycerol; Industrial trial; Biodiesel.

1. Introduction

To mitigate environmental problems caused by non-biodegradable synthetic polymers, using natural macromolecules as replacements is a feasible approach. In textile industry, sizing is an indispensable procedure to endow warp yarns with resistance to abrasion and tension during weaving. Polyvinyl alcohol (PVA) is the non-degradable synthetic polymer that dominates sizing chemical market with a 2.5% global share, and leads to severe pollution (Freedoniagroup, 2008; Printing, 2012). PVA contributes to about 40% of COD (chemical oxygen demand) in effluents generated in textile processes (Shaw, Carliell et al., 2002). Treating the textile effluent in anaerobic sludge for 300 days might still leave up to 85% of PVA intact (Chiellini, Corti et al., 2003). Release of the PVA-containing effluent could cause a series of ecological issues, such as, disturbing biological activities of aerobic microorganisms in water and soil (Hamad, Mehrvar et al., 2014), and immobilizing heavy metals (Zheng and Wang, 2010). Hoque et al. suggested to use low BOD (biological oxygen demand) synthetic sizes to replace the current sizes (Hoque and Clarke, 2013), while Hasanbeigi and Price proposed to use specialty surfactants to simultaneously remove sizes and scour the fabric to avoid use of enzyme (Hasanbeigi and Price, 2015). Comparing to these methods, elimination of PVA for sizing might be the best approach to fundamentally solve the environmental problem.

Proteins could be suitable alternatives for PVA sizes with multiple advantages. Similar to PVA, proteins readily form films, and contain both hydrophobic and hydrophilic domains, and thus could have good adhesion to both hydrophilic natural fibers and hydrophobic synthetic fibers (Xu, Jiang et al., 2011; Xu and Yang, 2014). Nevertheless, unlike PVA, proteins are readily biodegraded in nature (Dastidar and Netravali, 2013). Currently, soy protein, wheat gluten (Chen, Reddy et al., 2013a), feather keratin (Chen, Reddy et al., 2013b) and corn protein

showed good potential for textile sizing applications in lab-scale experiments (Reddy, Zhang et al., 2013). These proteins are byproducts with abundance and low cost from production of edible oil, meat or starch, and thus, have good potential for large-scale textile utilization.

Among all the proteins, soy protein, which was widely investigated for packaging applications (Garrido, Etxabide et al. 2014, Guerrero, Arana et al. 2015), and could be readily composted (Leceta, Etxabide et al. 2014), showed the best sizing performance. After plasticized with high amount of triethanolamine (TEA), soy protein size could demonstrate similar or better protection to yarns, comparing to PVA size in industrial weaving trials (Zhao, Zhao et al., 2015; Zhao, Zhao et al., 2015). However, TEA with BOD₅/COD (5-days biological oxygen demand/chemical oxygen demand) ratio, the standard determines biodegradability, of less than 0.01 is regarded as non-biodegradable (Mohr, 2010). Non-renewability and high cost of TEA could also hinder the industrial utilization of soy protein based sizes. Currently, TEA is derived from non-renewable petroleum, and sold at prices higher than \$1300/ton (Zaubas, 2015).

With remarkably lower cost, better renewability, better health, safety and degradation profiles, glycerol, the polyol that could be derived from soy, has the potential to replace TEA in developing all-green soy sizes (Shen, Xu et al., 2015; Xu, Canisag et al., 2015). Glycerol with BOD₅/COD ratio of 0.87, which is higher than 0.5, is considered completely biodegradable (Hardesty, 2008). As the main byproduct accounts for up to 20% of biodiesel production, the current selling price for glycerol is around \$50/ton (Quispe, Coronado et al., 2013). Due to rapid expansion of biodiesel industry, the price of glycerol could be further decreased. Moreover, glycerol with HMIS (Hazardous Materials Identification System) health, flammability and reactivity ratings of 1, 0, 0 is safer and more convenient to handle and use, comparing to TEA with relevant ratings of 2, 1, 1 (Hardesty, 2008; Spectrum, 2015).

In this research, potential of using all-green soy size composed of soy protein and glycerol to replace PVA for textile sizing was evaluated via lab-scale characterizations and industrial-scale sizing and weaving experiments. Tensile properties of the size films and add-on were measured and correlated with the relevant weaving efficiencies. Desizing and degradation properties of the all-green soy sizes were evaluated and compared with TEA plasticized soy size and commercial PVA size.

2. Experimental

2.1. Materials

Polyester yarns (11s), soy protein isolate and commercial PVA size were used. Chemicals including glycerol, NaOH and triethanolamine (TEA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). JFC was purchased from Demei Chemical, Wuxi, China. Defoamer was supplied by Shengshi Chemical, Wuhan, China. The commercial PVA size were composed of 80% of polyvinyl alcohol, 12% of starch and other additives.

2.2. Preparation of all-soy size solution and films

Soy protein was dispersed in NaOH solution at concentrations varying from 4 wt% to 10 wt%. The concentration of NaOH was in the range of 0.5 wt% and 1.5 wt%. Glycerol was added into the dispersion at different ratios (15 wt%-35 wt%) based on the weight of soy protein. The mixture was heated under 100 °C for 30 min with stir.

2.3. Viscosity of all-soy size solution

Penetration of sizing solution into the yarns also played an important role during sizing process, thereby viscosity of the sizing solution needed to be analyzed. The concentration of soy protein was controlled at 6 wt%. Apparent viscosity of the obtained all-soy size solution was

measured on a NDJ-79 rotary viscometer (Changji Geological Equipment, Shanghai, China) at 90 °C with shear rate of 750 r/min.

2.4. Tensile properties of all-soy size films

Solution of all-soy sizes (6 wt%) prepared under different conditions were poured in Teflon coated plates, and air dried to obtain films. Before testing, the films were balanced under standard condition (65 % Relative Humidity, 21 °C) for at least 24 hours. Tensile properties, including tensile strength, % elongation and work of rupture, of size films were measured on a tensile testing machine (HD026NS, Hongda Textile Machinery, Nantong, China) according to ASTM standard D882. The dimension of the films was 1 cm × 10 cm and the crosshead speed was 50 mm/min. For each condition, more than 20 samples obtained from at least three different films were measured. Thickness of each piece of film was measured with a thickness gauge (Changzhou No.2 Textile Machinery, Changzhou, China) at three different spots.

2.5. Lab-scale sizing

The yarns were padded through the 90 °C sizing solution with one-dip-one-nip method on a lab-scale sizing machine (GA 392, Jiangyin Tongyuan Machinery, Wuxi, China) and wound onto a spindle at 30 m/min. The padding pressure was adjusted to the highest level. The sized yarns were heated under 80 °C for 7 min. The sized yarns were balanced under standard condition (65 % Relative Humidity, 21 °C) for at least 24 hours. The add-on% was calculated based on weight of yarns before and after sizing as below in Equation 1.

$$\% \text{ add - on of size} = \frac{\text{mass of sized yarn} - \text{mass of unsized yarn}}{\text{mass of unsized yarn}} \times 100\% \quad \text{Eqn (1)}$$

2.6. Observation of cross section of sized and unsized PET yarns

A Hitachi SU1510 Scanning Electron Microscope (SEM, Tokyo, Japan) was used to observe the distribution of cross sections of sized and unsized PET yarns. The samples were

mounted on conductive adhesive tape, sputter coated with gold palladium and observed under a voltage of 5 kV. The magnification was 250x.

2.7. Abrasion resistance of sized yarns

Abrasion resistance of balanced sized and unsized yarns was measured on an abrasion testing machine (G552, Zweigle Instruments, Sonnenbergstrasse, Switzerland). The % add-on was controlled to $\pm 0.5\%$ for fair comparison. At least 20 yarns (each with length of 1 m) were tested for each sizing condition.

2.8. Industrial sizing and weaving trial

Selected conditions were used to prepare all-soy sizing solution with protein concentration of 10 wt%. The warped polyester yarns was sized in the solution at 90 °C with a double-dip-double-nip method. The sized yarns were heated under 140 °C at a winding rate of 45 m/min. The dried sized yarns were balanced under standard condition for 12 hours and then loaded for weaving on air jet looms (Mythos 230, Somet Machinery, Florence, Italy). The weaving speed was set at 630 rpm, which equivalents to insertion of 630 weft yarns each minute. For each sizing condition, about 1000 m of yarns was woven in several shifts. Each shift took 8 hours, generating one data point of weaving efficiency using Equation 2. Weaving efficiency of the first 8 hours was not included in the calculation as the weaving process might be still unstable.

$$\text{Weaving efficiency \%} = \frac{\text{Actual length of fabrics after weaving for 8 hours}}{\text{Theoretical length of fabrics after weaving for 8 hours}} \times 100\% \quad \text{Eqn (2)}$$

2.9. Desizing

Based on a report issued by DL Testing (Shanghai, China), PVA was not detected on the un-desized fabrics sized with all-soy size, as seen in supplementary material.

The obtained fabrics were considered completely desized after boiled in water at a weight ratio of 50:1 for 30 min, when the fabric weight became constant. Weighing of the sized and desized fabrics were conducted after heated under 105 °C for 4 hours. Percent add-on of size on the woven fabric was calculated based on Equation 1.

The woven fabrics with known add-on% were rinsed using water at temperatures of 90 °C, 80 °C and 70 °C for up to 3 cycles, each lasted for 10 min. The water-to-fabric weight ratio was 5:1. The desizing efficiency % was calculated based on the following Equation 3.

$$\text{Desizing efficiency \%} = \frac{\text{Weight of fabric after rinse} - \text{Weight of desized fabrics}}{\text{Weight of fabric before desizing} \times \% \text{ add-on of size}} \times 100\% \quad \text{Eqn (3)}$$

2.10. Biodegradation (Chemical oxygen demand)

To determine the biodegradability of soy protein sizes and commercial size, activated sludge obtained from Shuofang Sewage Treatment Plant, Wuxi, China, was used to degrade the sizing solution for up to 5 days (Ghaly, Ananthashankar et al. 2014). The concentration of sizing solution was adjusted to 300 ppm based on the standards for fair comparison.

Chemical oxygen demand (COD) in the sizing effluent was tested according to U.S. Environmental Protection Agency method 8000 using a COD digest apparatus (5B-1F(V8), Lianhua Environmental Instruments, Lanzhou, China) and a Vis/UV spectrophotometer (JH722, Jinghua Instruments, Shanghai, China). A high range (20–1500 ppm) test kit TNT822e was purchased from Hach Company. 2 mL of sample was collected from the activated sludge each 24 hr and added to the vial of TNT 822e COD testing kit, and then heated at 150 °C for 2 hr on a heating block (Hach DRB 200). The sample was cooled before the absorbance of the solution inside was measured on a spectrophotometer (Hach DR 3900) at 620 nm. The reading of the spectrophotometer represented the COD of the solution in ppm.

Third-party measurement of COD was conducted to confirm biodegradability of the soy protein sizes by SGS International (Shanghai, China).

Fig. 1.

Here is a flow chart (Fig. 1) demonstrating the whole process of development and application of soy protein sizes.

2.11. Statistics

For each condition, at least three samples were tested to obtain a mean value and a standard deviation. Data was analyzed using Tukey's multiple-pair wise comparison in SAS program (SAS Institute, Raleigh, NC). A significance level of $\alpha = 0.05$ was regarded as statistically significant. Data points with significant differences were marked with different letters, numbers or symbols.

3. Results and discussion

3.1. Morphologies of sized and unsized yarns

Fig. 2.

As shown in Fig. 2, loose and compact fibers were found in Fig. 2a and Fig. 2b. The fibers at the edge of sized yarn were stuck together by soy protein yarns, as demonstrated in Fig. 2c and Fig. 2d. The fibers in the center of the yarn were not as heavily coated with size as those on the edge. The uneven distribution of size in yarns could not only facilitate sizing process, but also reduce the utilization of sizing agents.

3.2. Tensile properties

Tensile properties of size films are critical characteristics as they substantially influence abrasion resistance of sized yarns. To obtain satisfactory films from soy protein which is water insoluble (Xu, Cai et al., 2014), NaOH was used to hydrolyze soy protein, and glycerol was used

to decrease the intermolecular force among the polypeptides to improve flexibility of the films. However, excessive hydrolysis and plasticization could decrease robustness of the films. The two effects should be investigated to produce all-green soy size films with both good strength and flexibility.

Fig. 3.

Effects of NaOH and glycerol on tensile properties of all-green soy size films are shown in Fig. 3. Tensile strength decreased and tensile elongation increased constantly as the concentration of NaOH increased from 0.5% to 1.25%, and became unchanged when more NaOH was used. However, for samples with glycerol concentrations between 20% and 30%, the work of rupture first increased as the NaOH concentration increased from 0.5% to 1%, and then decreased as the NaOH concentration further increased to 1.25%. The films had the highest work of rupture when the glycerol concentration was 25%, though the relevant tensile strength and tensile elongation were medium. However, the highest work of rupture of soy protein (NaOH 1%, Glycerol 25%) was still about 50% lower than that of commercial PVA size film. Under this condition, the soy protein film had about tensile elongation 59% higher and tensile strength 80% lower than commercial PVA film. For the soy protein film plasticized with 35% of glycerol, tensile strength was similarly low, and tensile elongation increased very slowly as more NaOH was used. Surprisingly, the work of rupture decreased very slowly as the NaOH concentration increased.

NaOH hydrolyzed the backbones of soy protein as well as breaking the disulfide bonds between the polypeptides, creating more linear molecules that could dissolve in aqueous solution. Increasing NaOH concentration generated more short polypeptides, which could function as plasticizers, and thus increased the film extension. Also due to the reduced molecular length, the

tensile strength of the soy protein film was reduced. On the other hand, glycerol interrupted the intermolecular interaction, and thus rendered them to slide with each other more easily.

Therefore, increasing glycerol concentration decreased tensile strength and increased tensile elongation. Work of rupture, which was affected by both strength and extension of the film, reached a maximum when the film had moderate strength and strain. For the film treated with 35% of glycerol, the intermolecular force was remarkably reduced, and thus resulted in poor tensile strength, even when the NaOH concentration was low.

The influence of glycerol on tensile properties of soy protein films could also be observed from the stress-strain curves as shown in Fig. 3b. The higher the concentration of glycerol was, the higher the tensile strain was, and the lower the tensile stress was. Breakage of film either under tension or under abrasion consumed energy to disrupt intermolecular force among soy protein polypeptides. Therefore, tensile properties of films could primarily reflect their abrasion properties, which determined their sizing performance.

3.3. Viscosity

In addition to the tensile properties of size films, viscosity of sizing solution was also important as it directly affected the penetration and distribution of size in the yarns, and ultimately, adhesion between sizes and fibers.

Fig. 4.

Fig. 4a shows that as the concentration of glycerol increased from 0 to 30%, the viscosity of both 1.25% and 1% NaOH treated soy protein sizing solution increased in a close manner until reached the viscosity of glycerol itself. Increasing glycerol concentration to 35% did not further increase their viscosity. Fig. 4b shows that as concentrations of soy protein and PVA increased, the viscosity of PVA increased much faster than the all-green soy size. Industrial

weaving used 6% PVA, at which concentration the viscosity of PVA was similar to that of soy protein size at concentration as high as 10%, inferring that the soy protein with 30% of glycerol still could have similar penetrating behavior. It could be inferred that, the viscosity of all-green soy size was acceptable for sizing applications. Glycerol interrupted hydrogen bonds in the soy polypeptides, allowing them to extend in the sizing solution. The increasing trend of viscosity of soy protein sizing solution indicated that expansion of soy protein molecules increased friction among the molecules.

3.4. Abrasion resistance of sized yarns

Abrasion is the main force the sized yarns need to withstand during weaving. Both tensile properties of size film and penetration of size in the yarns will affect the abrasion resistance and subsequently the breakage of yarns during weaving.

Fig. 5.

Fig. 5 demonstrates that with increased % add-on of sizes, the abrasion resistance of sized yarns increased faster for the commercial PVA size than the all-green soy sizes, though both in linear patterns. With the same % add-on, commercial PVA sizes showed higher abrasion resistance than the all-green soy sizes. The difference could be attributed to the much better tensile properties of the commercial PVA size film comparing to the all-green soy film, as discussed in Fig. 3. However, by increasing the % add-on of all-green soy sizes, the abrasion behavior of the sized yarns could be improved to a level comparable to commercial PVA size. For example, the yarns sized by 6.5% of commercial PVA size could withstand about 800 cycles of abrasion, which could be achieved using 7.4% of all-green soy size.

In addition, between the soy protein sizes plasticized with 25% and 30% of glycerol, the abrasion resistance of sized yarns did not differ significantly. Since glycerol (\$50/ton) was much

cheaper than soy protein isolate (\$3000/ton), cost of all-green soy size could be further decreased without compromising the sizing performances by increasing glycerol concentration from 25% to 30%.

Based on the results of Fig. 5, 30% could be a good percentage for glycerol and 7.5% might be a lowest % add-on for all-green soy size to achieve similar weaving efficiency.

However, the friction rate of the abrasion tester was much slower than that in real weaving process, the lab-scale tests might not reflect the real performance difference of the all-green soy sizes. Thus, industrial weaving trials were conducted.

3.5. Weaving efficiency obtained from industrial trial

3.5.1. Effect of add-on

Fig. 6.

Add-on is a critical parameter that determines the sizing results and cost. As shown in Fig. 6, the relative weaving efficiency increased in a logarithmic manner as the add-on of soy size increased. Under the same high pressure, add-on increasing meant even increase of the amount of size inside and outside the yarns, forming more uniform sizing films with less weak spots, and thus endowed the yarns with higher resistance to abrasion. At the same add-on, PVA size showed higher weaving efficiency than soy protein size, due to its much better film properties, as shown in Fig. 3. However, by increasing the add-on to 10%, all-green soy size could obtain weaving efficiency similar to commercial PVA size. Logarithmic fitting was possible as increasing size on yarns with low add-on had a more important impact on abrasion resistance of sized yarns comparing to yarns with high add-on. In the latter case, size was usually coated on the yarns, therefore could not improve bonding of fibers in the yarns to resist abrasion.

Comparing to TEA plasticized soy protein size, glycerol plasticization endowed all-green soy size with better sizing results at the same add-on. However, the cost of glycerol was only about 1/6 the cost of the TEA, and glycerol showed much better degradability and environmental friendliness. The results inferred high economical and technical feasibility of replacing PVA size and TEA plasticized soy protein size with all-green soy size.

3.5.2. Effect of size film properties

Fig. 7.

Tensile properties of size films substantially affected the weaving performance of sized yarns. However, till now, no research has been conducted to compare the importance of the tensile strength, tensile strain and work of rupture, to the weaving performance of relevantly sized yarns. Fig. 7 compares the change of tensile strength, tensile strain, work of rupture and weaving efficiency, as the concentration of glycerol varied. As the concentration of glycerol increased, the relative weaving efficiency and work of rupture of the size film first increased and then decreased (Fig. 7a), meanwhile, the tensile strength decreased almost linearly while the tensile elongation increased (Fig. 7b). Therefore, work of rupture, which was affected by both tensile strength and strain, might highly correlate to the weaving efficiency. As demonstrated in Fig. 7c, there was probably a logarithmic relationship between work of rupture and weaving efficiency with an r^2 of 0.9145.

This was the first time that tensile properties of size film was correlated with real weaving performance of size. It could be inferred that, to evaluate the potential of a polymer or macromolecule for sizing applications, work of rupture should be a more important parameter to be investigated, comparing to tensile strength and strain.

3.5.3. Desizing property

Fig. 8.

Fig. 8 shows that, under 70 °C after 3 rinse cycles, about 98%, 94% and 88% of glycerol plasticized protein sizes, TEA plasticized protein sizes and PVA could be removed, respectively. Increasing temperature by 10 °C could remove 100%, 98% and 90% of glycerol plasticized protein sizes, TEA plasticized protein sizes and PVA could be removed, respectively. The desizing efficiency of soy protein sizes remarkably increased as the number of rinse cycle increased, but did not change as the water temperature increased, indicating that the desizing of soy protein could be conducted under much lower temperature than PVA. Significantly less amount of water and lower temperature were required to desize the yarns sized with soy protein sizes comparing to those sized with PVA, inferring much less generation of desizing effluent and consumption of energy.

Comparing the glycerol and TEA plasticized soy protein sizes, the glycerol treated one demonstrated slightly better desizability than the TEA group. TEA has solubility of 149 g L⁻¹ in water while glycerol is miscible with water, therefore, dissolution of glycerol could be easier than TEA. In addition, the best weaving performance was obtained using 25% of glycerol and 20% of TEA plasticized soy protein sizes, respectively. The higher concentration of glycerol could further accelerate the dissolution process of glycerol plasticized soy protein size film.

Desizing efficiency substantially affects consumption of water, energy and chemicals, and subsequently, the sustainability of textile processes. It is reported that about 200 kg of water is consumed to produce 1 kg of textiles (Ghaly, Ananthashankar et al. 2014). Using the all-green soy size, substantially less water and chemicals need to be used for desizing, resulting in generation of much less desizing wastewater.

3.5.4. Biodegradation

Fig. 9.

Fig. 9 demonstrates that, the all-green soy size had moderately and substantially better degradability than the TEA plasticized soy protein size and commercial PVA size, respectively, though they did not show significant difference among CODs before degradation. Regarding the all-green soy size, degradation in activated sludge decreased its COD to lower than 120 ppm (the grade II discharge standard of wastewater) by 1 day, and to lower than 60 ppm (the grade I discharge standard of wastewater) by 2 days, respectively. However, it took TEA plasticized soy protein 3 days to reach the grade II discharge standard, though the amount of TEA was already 20% less than glycerol. The comparison was in accordance with the well documented complete biodegradability of glycerol and non-biodegradability of TEA (Hardesty, 2008; Quispe, et al., 2013). In terms of the commercial PVA size, after 5 days of degradation, its COD demonstrated marginal decrease from 325 ppm to a plateau value of 245 ppm, rendering it un-dischargeable, as has been proved multiple times. The results from third-party testing of COD of all-green soy size (15-06363.001-15-06363.006 were samples of day 0 to day 5) were in good accordance with the above results (supplementary material). In general, the all-green soy size composed of soy protein and glycerol illustrated fast and complete degradability under municipal wastewater treatment conditions, and thus could satisfactorily fulfill the requirements for sustainable development of textile processes.

Poor degradability of PVA sizes, which contribute to 40% of COD in the effluent from the entire textile process, is the ultimate reason for tremendous efforts devoted in seeking biodegradable substitutes (Shaw, Carliell et al., 2002). The all-green soy sizes satisfactorily met the requirement with much better desizability and substantially improved biodegradability, comparing to PVA. Either high temperature, or enzymes, or harsh chemicals needed to be used

to desize or degrade all-green soy size. Though more soy size should be used to achieve performance similar to PVA, the overall environmental impact of textile sizing process could be remarkably abated due to its milder desizing condition and fast degradation in activated sludge. Consequently, substitution of PVA with the all-green soy size could render textile wet processing cleaner and the overall textile processes more sustainable.

Current barriers of all-green soy size were the high prices of soy protein isolate and the immature size formulations. Soy protein size might be developed from less expensive resources, such as soy meal. The formulation could be improved as more industrial sizing trials were conducted. High-speed weaving, for which PVA outperformed all other sizes, should be done to evaluate the potential of all-green soy size.

4. Conclusions

All-green textile size with satisfactory sizing performance properties could be developed from soy protein and glycerol, both byproducts from soy-based biodiesel production. The tensile properties of the all-green soy size film were poorer than the commercial PVA size film. However, with higher % add-on, the all-green soy size could endow the yarns with abrasion resistance close to or higher than the commercial PVA sizes. The optimum % of glycerol, 25%, and optimum % of NaOH, 1.25%, were selected to prepare soy protein size for weaving trial, due to the highest work of rupture, proper viscosity and good abrasion resistance. The industrial weaving trials of soy protein size obtained using optimum % of glycerol of 25% and optimum % of NaOH of 1.25% confirmed that, under higher % add-on, the weaving efficiency of the soy protein sized yarns could be higher than or similar to the PVA sized ones. Even with higher % add-on, the all-green soy sizes were remarkably easier to be desized, and easier and faster to be biodegraded, comparing to PVA sizes. In conclusion, with similarly good performance, less

water and chemical needed for desizing, and better degradability, sustainability of textile industry could be improved via replacement of PVA with all-green soy sizes.

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Figure Captions

Fig. 1. Flow chart of the experimental arrangements

Fig. 2. SEM of the cross-sections of, a) unsized yarn; b) yarn sized with 10 wt% soy protein size; c) enlarged view of area 1 in b); d) enlarged view of area 2 in b), under magnification of 250x.

Fig. 3. a) Effects of concentrations of NaOH and glycerol on the tensile properties of all-soy size films; b) Tensile stress-strain curves of soy size films plasticized with different concentrations (20%, 25%, 30% and 35%) of glycerol with NaOH % of 1.25%. (Commercial PVA size film: tensile elongation $147.50\% \pm 6.60\%$, tensile strength 20.83 ± 1.05 MPa, work of rupture 0.73 ± 0.03 J.)

Fig. 4. Influence of concentrations of (a) glycerol, and (b) soy protein or PVA sizes, on viscosity of sizing solutions under sizing temperature of 90 °C. (a: 1.25% and 1% of NaOH based on the weight of soy protein, 10 wt% soy protein in solution; dash line: the viscosity of pure glycerol under 90 °C; b: 1.25% of NaOH and 30% of glycerol based on the weight of soy protein; 10 wt% soy protein in solution)

Fig. 5. Abrasion resistance of yarns sized with different amounts of commercial PVA size and soy protein dissolved under different conditions (glycerol: 25% and 30%, NaOH: 1% and 1.25%, both based on the weight of soy protein).

Fig. 6. Effect of % add-on of all-green soy size (SP-Gly) size on the relative weaving efficiency and their comparison with TEA plasticized soy protein (SP-TEA) and commercial PVA sizes. (NaOH and glycerol at concentrations of 1.25% and 25% based on the weight of soy protein were used. Soy protein, NaOH and glycerol were dispersed in water with a soy protein-to-water weight ratio of 1:9, and then heated at 90 °C for 30 min before sizing. 20% of TEA based on the weight of soy protein was used for SP-TEA sample.)

Fig. 7. Correlation of tensile properties of all-green soy protein size films and relative weaving efficiency. a) Effect of glycerol concentration on the relative weaving efficiency of sized yarns and work of rupture of the size films; b) Effect of glycerol concentration on the tensile strength and elongation of soy protein size films; c) The relationship between work of rupture of size film and relevant relative weaving efficiency. The % add-on of soy protein size on yarns was 10.5%, 10.9%, 10.4% and 10.8%, respectively. (NaOH at concentration of 1.25% based on the weight of soy protein was used to dissolve soy protein. Soy protein, NaOH and glycerol were dispersed in water with a soy protein-to-water weight ratio of 1:9, and then heated at 90 °C for 30 min before sizing. Concentration of plasticizer was determined based on the weight of soy protein.)

Fig. 8. Desizing efficiency of glycerol plasticized soy protein size (SP-Gly), TEA plasticized soy protein size (SP-TEA) and commercial PVA sizes (PVA) under 70 °C, 80 °C and 90 °C for up to 3 rinse cycles in water.

Fig. 9. COD of all-green soy size (SP-Gly, soy protein sizes plasticized with glycerol) and soy protein sizes plasticized with TEA (SP-TEA), commercial PVA size after degraded in activated sludge for 5 days. The purple and red dash lines indicating COD of 120 ppm and 60 ppm, represent the grade II and grade I discharge standard, respectively, according to the National Standard of the People's Republic of China Integrated Wastewater Discharge Standard GB 8978-2002. (Conditions: SP-Gly and SP-TEA, 25% of glycerol and 20% of TEA based on the weight of soy protein, respectively)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical Abstract