Biodegradable sizing agents from soy protein via controlled hydrolysis and dis-entanglement for remediation of textile effluents

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Abstract: Fully biodegradable textile sizes with satisfactory performance properties were developed from soy protein with controlled hydrolysis and dis-entanglement to tackle the intractable environmental issues associated with the non-biodegradable polyvinyl alcohol (PVA) in textile effluents. PVA derived from petroleum is the primary sizing agent due to its excellent sizing performance on polyester-containing yarns, especially in increasingly prevailing high-speed weaving. However, due to the poor biodegradability, PVA causes serious environmental pollution, and thus, should be substituted with more environmentally friendly polymers. Soy protein treated with high amount of triethanolamine was found with acceptable sizing properties. However, triethanolamine is also non-biodegradable and originated from petroleum, therefore, is not an ideal additive. In this research, soy sizes were developed from soy protein treated with glycerol, the biodegradable triol that could also be obtained from soy. The soy sizes had good film properties, adhesion to polyester and abrasion resistance close to PVA, rendering them qualified for sizing applications. Regarding desizing, consumption of water and energy for removal of soy size could be remarkably decreased, comparing to removal of PVA. Moreover, with satisfactory degradability, the wastewater containing soy sizes was readily dischargable after treated in activated sludge for two days. In summary, the fully biodegradable soy sizes had potential to substitute PVA for sustainable textile processing.

Keywords: soy protein; polyvinyl alcohol; biodegradable size; green plasticizer; sustainable textiles.

1. Introduction

Diverse petroleum-derived chemicals are utilized in textile processing, leading to severe environmental pollution. Among all the chemicals, polyvinyl alcohol (PVA) contributes to 40% of chemical oxygen demand (COD) in textile wastewater (Shaw et al., 2002). PVA is used in textile sizing process, which endows the warp yarns with strength and abrasion resistance to stand friction during weaving. Due to its excellent performance, PVA has been the best textile sizing agent for polyester yarns as well as for high-speed weaving (Zhao et al., 2015a). However, the non-biodegradability of PVA rendered conventional textile sizing processes un-sustainable. For decades, industry and academia are actively seeking for substitution of PVA (Tong, 2013).

Among the multiple PVA substitutes, protein has its unique advantages over other biodegradable macromolecules. Proteins contain hydrophilic and hydrophobic portions in their backbones (Xu et al., 2011), thus, have affinity to both hydrophilic cotton fibers and hydrophobic polyester fibers (Chen et al., 2013). In addition, proteins have good film forming properties (Liu et al., 2015; Shen et al., 2015). Molecularly, proteins have the potential to replace PVA in sizing. Since 1940s, gelatin from swine skin was successful in coating wool before weaving (Trowell et al., 1941). However, their unsatisfied performance prevented its wide application. Inexpensive and abundant proteins resources are needed for large-scale industrial utilization.

Proteins, including soy proteins, wheat protein, corn protein and poultry keratin, are low in cost and large in availability to meet the requirements, since they are byproducts or wastes from production of edible oils, biodiesel, starch and poultry industries. These proteins have been studied for different applications. For example, Yang et al. used soy protein (Xu et al., 2014a) and keratin (Xu and Yang, 2014) for fiber fabrication, and Zhao et al. developed textile auxiliaries and biomedical scaffolds from them (Zhao et al., 2016a and 2016b; Xu et

al., 2014b; Xu et al., 2016). However, the complicated fabrication process of fibers and limited market demand for scaffolds restricted the industrialization of proteins.

On the other hand, it is most feasible to utilize these proteins for sizing in industry. In the last 5 years, Yang et al. started research on sizing applications of various agricultural proteins (Reddy et al., 2014; Reddy et al., 2013). Via industrial and lab experiments, it could be observed that soy protein size had similar to better sizing properties comparing to PVA (Zhao et al., 2015a and 2015b). However, currently, a large amount of triethanolamine (TEA) should be used in the soy protein sizes. TEA with BOD₅/COD ratio of less than 0.01 is regarded as non-biodegradable (Thomas et al., 2010). Non-renewability and high cost could also hinder the industrial utilization of soy protein-TEA sizes. Currently, TEA is derived from non-renewable petroleum, and sold at prices higher than \$1300/ton (Zaubas, 2015).

Glycerol is a polyol that could be derived from soy with the potential to replace TEA in developing new soy protein sizes (Shen et al., 2015; Xu et al., 2015). Glycerol has a BOD₅/COD ratio of 0.87, and thus, is considered completely biodegradable (Hardesty, 2008). The current selling price for glycerol is around \$50/ton (Quispe et al., 2013), as it is the main byproduct accounts for up to 20% of biodiesel production. Rapid expansion of biodiesel industry could help further decrease the price of glycerol. 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 (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. Materials and methods

2.1. Materials

Polyester yarns (16s), commercial PVA size and soy protein isolate were used. Chemicals including glycerol, sodium hydroxide and triethanolamine (TEA) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). JFC, a common non-ionic surfactant used in textile wet processing, was purchased from Demei Chemical, Wuxi, China. The commercial PVA size was composed of 80% of polyvinyl alcohol, 12% of starch and other additives. The commercial modified starch was composed of modified starch and additives.

2.2. Preparation of soy protein size solution and films

Soy protein isolate (4 wt% to 10 wt% based on the weight of liquid) was dispersed in NaOH solution with concentrations 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 isolate. The mixture was heated under 100 °C for 30 min with stir.

2.3. Tensile properties of soy films

Solution of soy size (6 wt%) prepared under different conditions were poured in Teflon coated plates, air dried to obtain films, and then balanced in standard condition (65 % Relative Humidity, 21 °C) for 48 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. Films of 1 cm × 10 cm and crosshead speed of 50 mm/min were used. Thickness of each piece of film was measured with a thickness gauge (Changzhou No.2 Textile Machinery, Changzhou, China) at three different spots. More than 20 samples obtained from at least three different films were measured for each condition.

2.4. Lab-scale sizing

On a lab-scale sizing machine (GA 392, Jiangyin Tongyuan Machinery, Wuxi, China), the yarns were padded through the 90 °C sizing solution (one-dip-one-nip) and wound onto a roll at 30 m/min. The sized yarns were heated under 80 °C for 7 min. The sized yarns were balanced in the standard condition (65 % Relative Humidity, 21 °C) for 48 hours. The add-on% was calculated based on the weights of yarns before and after sizing using Equation 1.

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

2.5. Adhesion between yarns and sizes

Adhesion of sizes to polyester fabrics were evaluated via peeling test. Two layers of polyester fabrics, each with dimension of 5 cm x 16 cm, were immersed in sizing solution at 90 °C and padded to control the pick-up to around 100%. The add-on of size on the fabrics was controlled by changing the concentration of sizing solution. The fabrics were dried under standard condition for 48 hours until the weight became constant. Peel force of the two fabrics was measured on the tensile testing machine (HD026NS, Hongda Textile Machinery, Nantong, China) based on the standard ASTM D1876-08. For each condition, 20 sets of samples were tested and max value of each testing was recorded for calculation.

2.6. Abrasion resistance of sized yarns

Abrasion resistance of balanced sized and unsized 16s PET yarns was measured on an abrasion testing machine (G552, Zweigle Instruments, Sonnenbergstrasse, Switzerland). At least 20 yarns (each with length of 1 m) were tested for each sizing condition.

2.7. Desizing properties

The sizing solution was used to immerse 100% PET fabrics, which were then padded to control the pick-up of 100%. The fabrics were dried to constant weight in the standard condition. The sized fabrics were then 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 Equation 2.

$$\text{Desizing efficiency \%} = \frac{\text{Weight of fabric after rinse} - \text{Weight of desized fabrics}}{\text{Weight of fabric before desizing} \times \% \text{ add-on of size}} \times 100\% \quad (2)$$

2.8. Biodegradation (COD)

To determine the biodegradability of soy protein size, activated sludge obtained from Shuofang Sewage Treatment Plant, Wuxi, China, was used to degrade the sizing solutions for up to 15 days. The estimated size concentration in real wastewater was around 0.03 wt% (Zhao et al., 2015a), and was used to compare degradability of soy protein size and commercial PVA size used in the industrial weaving trials.

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, Hach, Loveland, CO). The sample was cooled before the absorbance of the solution inside was measured on a spectrophotometer (Hach DR 3900, Hach, Loveland, CO).

2.9. 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, USA). 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. Tensile properties of soy size films

Fig. 1. Effects of concentrations of glycerol and NaOH on the tensile properties of all-soy size films. (Tensile property of commercial PVA size film: elongation $147.50\% \pm 6.60\%$, strength 20.83 ± 1.05 MPa, work of rupture 0.73 ± 0.03 J.)

Effects of glycerol and NaOH on tensile properties of soy size films are shown in Fig. 1. Tensile strength decreased and tensile elongation increased constantly, as the concentration of glycerol increased from 15% to 35%, or as the concentration of NaOH increased from 0.75% to 1.5%. However, the work of rupture first increased as the glycerol concentration increased from 15% to 25%, and then decreased as the glycerol concentration further increased to 35%. When the glycerol concentration was lower than 25%, the work of rupture of films obtained with 1% and 1.25% of NaOH was higher than the films obtained with 0.75% and 1.5%. However, further increasing the glycerol concentration, the work of rupture of the four types of soy protein films did not change following the previous pattern.

Overall, the films had the highest work of rupture when the NaOH concentration was 1% and 1.25%, though the relevant tensile strength and tensile elongation of soy protein films obtained under these two concentrations were medium. The optimal soy protein film obtained using 1% NaOH and 25% glycerol had work of rupture 49% lower, tensile elongation 59% higher and tensile strength 80% lower, than PVA size film, respectively.

NaOH hydrolyzed the backbones of soy protein as well as breaking the disulfide bonds between the protein backbones, thus, created more polar end groups and shorter polypeptides, rendering the soy protein water soluble. The amount of short polypeptides, which could function as internal plasticizers, increased as NaOH concentration increased, and thus increased the film extensibility. However, as the molecular length decreased, tensile strength of the soy protein film decreased too. In terms of the external plasticizer, glycerol interrupted the intermolecular interaction via breaking the hydrogen bonds, 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. 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.

3.2. Sizing properties

3.2.1. Adhesion between polyester and sizes

Fig. 2. Adhesion between 100% polyester fabric and commercial PVA size and soy protein size (20%, 25%, 30% and 35% of glycerol based on the weight of soy protein, 1.25% of NaOH based on the weight of soy protein), respectively.

Fig. 2 demonstrates that, PVA sizes showed higher adhesion to polyester comparing to soy protein sizes in general. However, by adding the amount of size on polyester yarns, the adhesion strength between the polyester fabrics glued together by 25% glycerol plasticized soy size could increase to a value similar to that sized by PVA. Among the soy sizes, the adhesion strength decreased as the glycerol concentration increased.

The hydrophobic backbones endowed PVA with good affinity to hydrophobic polyester fibers. The adhesion between soy protein and polyester might be weaker than that between PVA and polyester due to the differences in backbones and side chains. Regarding the backbones, hydrophilic amide groups as the connecting units made the backbones of

proteins more polar than PVA connected by carbon-carbon bonds. Regarding the side chains, soy proteins contain about 59 to 77 wt% of amino acids with hydrophilic side groups (Sohn et al., 1994), rendering the proteins overall hydrophilic. Regarding the comparison among different soy protein sizes, glycerol played a major role. Glycerol had high hydrophilicity with three hydroxyl groups in one molecule, and thus had poor affinity to polyester itself. However, disentanglement of polypeptides could expose the hydrophobic portions of soy protein to increase its affinity to polyester. Thus, the two effects might influence the affinity of soy size to polyester oppositely. Resultantly, the soy size treated with 20% and 25% of glycerol did not have significant differences, while further increase in glycerol concentration decreased the affinity to polyester in a faster manner. Based on the tensile properties of size film and adhesion results, soy sizes plasticized with 25% and 30% of glycerol, respectively, will be selected for further study.

3.2.2. Tensile properties of sized yarns

Fig. 3. Tensile properties of yarns sized with commercial PVA, soy protein size obtained with 1.25% NaOH and plasticized with 25% and 30% glycerol, represented by “Soy-25% Gly” and “Soy-30% Gly”, respectively.

Tension or stretching is the force that yarns are directly subjected to during weaving. Fig. 3 shows that, after treated with soy sizes and commercial PVA size, the tensile strength of 16s polyester yarns increased while the tensile strain did not change significantly. Linear regression indicated that PVA provided the fastest increase in tensile strength as the add-on increased, followed with 25% glycerol and 30% glycerol plasticized soy size, respectively. The strength of sized yarns could be affected by both size film properties and affinity between soy size and PET fibers. From Fig. 2 and Fig. 3, it could be observed that PVA had better film tensile properties and higher affinity to polyester than soy protein. However, by applying 29 wt% more 25% glycerol plasticized soy size, the strength of yarn could be not significantly

different from the PVA sized ones. One purpose of sizing is to increase the strength and retain the elongation of yarns to stand friction during weaving. Thus, the soy size could fulfill the target, though not as efficiently as PVA.

3.2.3. Abrasion resistance of sized yarns

Fig. 4. Abrasion resistance of yarns sized with different amounts of commercial PVA size and soy protein dissolved under different conditions (glycerol: 25%, NaOH: 1.25%, both based on the weight of soy protein).

Abrasion is the other force that yarns are directly subjected to during weaving. Fig. 4 demonstrates that with increased % add-on of sizes, the abrasion resistance of sized yarns increased faster for the commercial PVA size than the soy sizes. Based on the linear patterns, the commercial PVA sizes showed higher efficiency to improve abrasion resistance, comparing to soy sizes. The difference could be attributed to the much better film tensile properties and higher affinity of commercial PVA size, comparing to the soy film, as discussed in Fig 2 and Fig 3. However, by increasing the % add-on of all-green soy sizes, the abrasion resistant behavior of the yarns sized with soy size could be improved to a level close to commercial PVA size. For example, the yarns sized with 18% of soy size could withstand about 720 cycles of abrasion, which was achieved by using 15% of commercial PVA size.

Based on the results in Fig. 3 and Fig. 4, it could be seen that, soy size could perform as well as PVA size to make yarns sufficiently strong to stand the tension and friction during weaving, as long as adequate sizing materials were applied.

3.2.4. Desizing properties

Fig. 5. Desizing efficiency of commercial PVA size and glycerol-soy protein size on 100% PET fabrics under 70 °C, 80 °C and 90 °C for up to 3 rinse cycles.

Fig. 5 shows that, under 70 °C after 3 rinse cycles, about 98% and 88% of soy protein sizes and PVA could be removed, respectively. Increasing temperature by 10 °C could increase the desizing efficiency to 100% and 90% of soy protein sizes and PVA, respectively. The desizing efficiency of soy protein sizes remarkably increased as the number of rinse cycle increased, but did not change significantly as the water temperature increased. It could be inferred that the desizing of soy protein could be conducted under much lower temperature than PVA. Based on these results, substantially less amount of water and lower temperature were required to desize the yarns sized with soy protein comparing to those sized with PVA. Therefore, much less generation of desizing effluent and consumption of energy could be achieved.

3.3. Degradation of soy protein sizes

Fig. 6. COD of soy protein size plasticized with glycerol and commercial PVA size degraded in activated sludge for 5 days (concentration: 0.03 wt%). The red and green dot lines indicating 120 and 60 ppm COD represents the grade II and I discharge standards, respectively.

Fig. 6 demonstrates that, glycerol-soy protein size had substantially better degradability than the commercial PVA size. Regarding the glycerol plasticized soy protein, degradation for nearly 1 day in activated sludge decreased its COD to lower than 120 ppm, which represented the grade II discharge standard of wastewater (State Technology Supervision Bureau, 2002). Prolonging the degradation for one more day, COD of soy size contained wastewater could be further reduced to lower than 60 ppm, which was the grade I discharge standard of wastewater. It could be deducted that, the soy protein size could be easily disintegrated in municipal wastewater treatment plant. The difficulty and cost for treating textile wastewater could be effectively reduced, subsequently. However, 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. It was in consistence with the report that PVA could be degraded 15–25% after degradation of around 300 days and could not meet the requirement for effluent releasing (Chiellini et al., 2003). The

poor degradability caused PVA unfavorable to be used as sizes, despite all the excellent sizing performances.

4. Conclusions

Degradable textile size with satisfactory sizing performance properties could be developed from soy protein after been plasticized with glycerol, a low-cost biobased chemical. Tensile properties of soy protein sizes optimized by adjusting NaOH and glycerol concentrations were poorer than the PVA sizes. Adhesion between soy protein size and polyester was lower comparing to that between PVA and polyester. However, with higher % add-on, soy protein size could endow polyester yarns with similar capability to stand the tension and friction during weaving. However, even with higher % add-on, the soy protein sizes were remarkably easier to be desized or degraded, comparing to PVA sizes. In general, due to its satisfactory sizing properties, desizability, degradability and renewability, glycerol plasticized soy protein had great potential to replace PVA for sustainable development of textile industry.

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Figure legends

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