



Research article

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 dischargeable after treated in activated sludge for two days. In summary, the fully biodegradable soy sizes had potential to substitute PVA for sustainable textile processing.

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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 unsustainable. For decades, industry and academia are actively seeking 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). Therefore, Molecularly, proteins have the potential to replace PVA in sizing. Since 1940s, gelatin from swine skin was successful in coating wool before weaving (Trowell, 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

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

On the other hand, it is more 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., 2013, 2014). 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; 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 (Mohr 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 h. 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 h. 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 × 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 h 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 h. 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,

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