



Modified soy protein to substitute non-degradable petrochemicals for slashing industry



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ABSTRACT

Additives with multiple hydroxyl groups, nonlinear molecular structure and electric charge, like triethanolamine (TEA), could modify soy protein into effective sizes for high speed weaving of cotton fabrics. Poly(vinyl alcohol) (PVA) sizes are known as the best sizing agent for cotton. However, PVA is poorly biodegradable and is a major contributor to high chemical oxygen demand in textile effluents. Starch sizes have escalating prices and also could not provide cotton yarns with enough protection in high speed weaving or weaving of high-count cotton fabrics as PVA does. Soy protein, extracted from bio-diesel or edible oil byproducts such as soymeal, is highly available, low cost, water soluble, biodegradable, and has limited industrial applications. The major disadvantage of using soy protein as warp sizes is their formation of films with low flexibility, leading to poor size performance and weaving efficiency. In this paper, adding triethanolamine (TEA) substantially improves tensile properties of soy protein films. Industrial weaving results showed TEA-soy protein (TEA-soy) had 36% and 12% higher weaving efficiency for cotton fabrics than modified starch and PVA sizes. In addition, TEA-soy sizes had a 5-day biochemical oxygen demand/chemical oxygen demand ratio of 0.44 compared to 0.03 for PVA indicating that TEA-soy sizes were easily biodegradable in activated sludge. To replace starch and PVA sizes, about 1.2 million tons of soymeal could be used to produce TEA-soy for high quality and high speed weaving, benefiting agriculture, textiles, and environment.

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1. Introduction

Warp sizing or slashing imparts protection to yarns to withstand friction during weaving, and thus determines the performance of textile weaving processes and the qualities of textiles. Currently, sizing chemicals share a major part of the \$19 billion annual world textile chemical market (Chen et al., 2013a). However, textile sizing is facing considerable challenges due to concerns on price and availability of sizing agents and increasing environmental restrictions (Yang and Reddy, 2013).

Starch based sizes constitute nearly 75% of the sizing agents used in the textile industry throughout the world because starch has low cost, high adhesion to cotton fibers and biodegradability

(Hebeish et al., 2005, 2008; El-Sheikh, 2010). However, the price of starch is escalating recently as demand increases much faster than production in food and biofuel industries (Yang and Reddy, 2013). In addition, using starch as a sizing agent has drawbacks. The drawbacks include: the inability of starch to dissolve evenly due to changes in viscosity when heated; enzymes are needed when desizing starch sizes; the starch films with low tensile properties are unable to protect the yarn while weaving (Zhu and Cao, 2004; Zhu et al., 2009; Guettler et al., 2013). Chemical modifications such as oxidation, hydrolysis, esterification, grafting of acrylates on to starch, and adding synthetic polymers have been applied to enhance stability of sizes viscosity and flexibility of size films (Whistler et al., 1984; Khalil et al., 1993; Meshram et al., 2009; Li et al., 2011; Shen et al., 2011). However, most of modified starch still could not provide cotton yarns with enough protection in high speed weaving or weaving of high-count cotton fabrics as PVA does, and eventually affect productivity and quality of cotton fabrics (Shi, 2009). Furthermore, grafting and chemical modification increase cost of starch based sizes and decrease their biodegradability (Lu et al., 2009; Chen et al., 2013a,b).

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Poly(vinyl alcohol) (PVA) is the best sizing agent for cotton slashing due to high weaving efficiency of fabrics. However, petroleum based PVA is high cost and poorly biodegradable, leading to high chemical oxygen demand (COD) in textile effluent (Larking et al., 1999; Bisschops and Spanjers, 2003; Reddy et al., 2013). It is reported PVA could only be degraded 15–25% after degradation of around 300 days (Chiellini et al., 2003) and has been banned by some European countries. Therefore, the global textile industry, companies manufacturing textile chemicals and national environmental administrations are endorsing the need for biodegradable and low cost sizing chemicals to replace starch and PVA.

Oil production byproducts like soy meal are highly available, low cost and biodegradable (Zhang et al., 2001). In the US, about 25 million metric tons of soy meal at \$0.18–0.25 per lb is produced as a co-product from edible oil and bio-diesel production (Moreau et al., 2014). Unlike starch, which is mainly used in food and biofuel (Yang and Reddy, 2013), soy meals are usually used for animal feed and have abundant surplus annually. Soy protein, extracted from soy meal, has been found to have good biodegradability (Zhu et al., 2013), film forming properties and potential of being sizes in our previous study (Chen et al., 2013b). However, soy protein films are too brittle to protect cotton yarns during high speed weaving. When the harness rubs the sized yarns at high speed, soy protein films on yarns are easily broken and shed, strength and hairiness of rubbed yarns would be decreased and increased respectively, leading to yarn breakage.

Adding additives could improve plasticity of protein films (Sessa et al., 2006). Amines could serve as eco-friendly additives and used for protein films or composites prepared by hot compression-molding techniques (West and Gonsior, 1996). Irissin-Mangata reported that plasticizing films of wheat gluten protein with amino compounds induced significant modifications to their mechanical properties (Irissin-Mangata et al., 2001). Tian showed that 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 proteins. (Tian et al., 2009) However, there is no study reporting the characteristics of additives that could improve size performance of soy protein for high speed weaving. In this study, tensile properties of soy protein films modified by triethanolamine (TEA), diethanolamine, ethanolamine, propanolamine, butanolamine and glycerol were compared. Size performances of soy protein with TEA and traditional glycerol were further studied. In addition, industrial-scale weaving tests were carried out to verify the potential of using TEA-soy protein (TEA-soy) as warp sizing agents for high speed weaving. Use of TEA-soy as cotton sizing agents for high speed weaving would lead to value addition to soy meal, and elimination of non-biodegradable PVA to benefit agriculture, textiles and environment.

2. Materials and methods

2.1. Materials

Soy protein used for the study was kindly supplied by Ceres Technology Group Co., Ltd. Cotton rovings and cotton yarns (32 Ne) were supplied by Nantong Su Textile Co., Ltd. (Shanghai, China). The average length of cotton fibers was of 29 mm. Sodium hydroxide was purchased from Sinopharm Chemical Reagent Co., Ltd. (Zhejiang, 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. Commercially available modified starch 130 sizes (esterified starch sizes) were kindly supplied by Luthai Textile Co., LTD. (Shandong, China). Other chem-

icals used in this study were purchased from National Chemicals Inc. (Winona, Minnesota).

2.2. Film preparation and properties

TEA-soy or glycerol soy sizes were respectively prepared by heating 6 wt.% soy protein solutions which contained 0–30 wt.% TEA or 0–30 wt.% 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 acetic acid. Then the solution was cast onto Teflon coated glass plated and allowed to dry at 20 °C and 65% humidity for about 35–40 h. PVA (6 wt.%) and modified starch 130 (6 wt.%) dispersed in water was respectively heated to 90 °C, then cast to form films. Films formed were tested for tensile properties according to ASTM Standard D822 (ASTM, 2012). Film samples measuring 10 × 1 cm were cut and tested using a gauge length of 10 cm and crosshead speed of 50 mm/min.

2.3. Sizing

Soy protein was pretreated by adding different types and contents of additives in alkali solution or distilled water. After pretreatment, the pH of the solution was adjusted to pH 7 by adding acetic acid into the solution. The rovings wound on frames were immersed in the sizing solution at 90 °C for 5 min. After sizing, rovings were air-dried and later heated in an oven at 105 °C to determine the dry weights. As for the yarns, sizing was conducted on a ASS3000 sample sizing machine (Tianjin, China) with an oven temperature of 75 °C, slurry tank temperature of 60 °C, running speed of 18 m/min. Cotton yarns and rovings were also sized by commercial sizes (PVA and starch 130) using the same conditions as soy protein. Differences in the dry weights before and after sizing were used to calculate the amount of sizes (wt.% add-on) on the materials. As for the yarns, differences in the dry weights before and after desizing were used to calculate the amount of sizes (wt.% add-on) on the yarns. Both sized rovings and yarns were conditioned at 65% relative humidity and 21 °C until a constant weight was obtained before testing.

2.4. Characterization

2.4.1. Intrinsic viscosity of sizing solution

The intrinsic viscosities of the additive-free soy protein, TEA-soy, diethanolamine soy protein, ethanolamine soy protein, propanolamine soy protein, butanolamine soy protein and glycerol soy protein were determined according to ASTM standard D2857 (ASTM, 2007) at a temperature of 25 ± 1 °C.

2.4.2. Tensile properties of rovings

Properties of the sized rovings were determined by their strength and elongation as an indication of cohesiveness of the TEA-soy and glycerol soy protein to the fibers in the rovings. Tensile properties of the rovings were tested on a Universal Material Tester H5K-S (Hounsfield, UK) using a gauge length of 10 cm and a crosshead speed of 50 mm/min. At least 10 samples were tested for each condition and the experiments were repeated three times to report average and standard errors.

2.4.3. Hairiness

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 (Shanxi, China) using a gauge length of 10 m and test speed of 30 m/min. The numbers of hairs with more than 2 mm length were calculated. Hairiness results of each sample were collected from 10 m of yarns. At least 10

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