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Environmentally Friendly Sizing Agent from Corn Distillers Dried Grains

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**ENVIRONMENTALLY FRIENDLY SIZING AGENT
FROM CORN DISTILLERS DRIED GRAINS**

By

Yue Zhang

A THESIS

Presented to the Faculty of

The Graduate College at the University of Nebraska

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Lincoln, Nebraska

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ENVIRONMENTALLY FRIENDLY SIZING AGENT FROM CORN DISTILLERS DRIED GRAINS

Yue Zhang, MS

University of Nebraska, 2013

Advisor: Yiqi Yang

Distillers dried grains (DDGS), the coproducts of corn ethanol production, were used as a textile sizing agent on cotton, polyester and polyester/cotton blends in an effort to find inexpensive and biodegradable alternatives to sizing agents such as poly(vinyl alcohol) that are currently used. Although DDGS is an inexpensive, biodegradable and abundant co-product, it has limited industrial applications. DDGS is a mixture of carbohydrates, proteins and oil which are used as sizing agents or as size additives. The effects of DDGS extraction conditions on sizing evaluation parameters such as fiber adhesion, film properties, viscosity and fabric abrasion were studied in comparison with commercially available PVA or starch based size. Among the various conditions studied, DDGS that was extracted in 0.5% alkali concentration solution for 1 hour was most suitable for textiles sizing, based on the improvement in the strength and elongation of rovings and fabric abrasion resistance. The Chemical Oxygen Demand (COD) of DDGS size decreased 80% in 3 days compared to 25% for PVA demonstrating that DDGS was easily biodegradable in activated sludge. Although DDGS contains up to 30% protein, the total nitrogen and ammonia released from

DDGS sizing agent had negligible effect on biodegradability. Good sizing performance and easy biodegradability demonstrate that DDGS based sizes have potential to serve as an environmentally friendly sizing agent.

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CHAPTER 1: INTRODUCTION

Textile industry world-wide is facing considerable challenges due to concerns on price and availability of raw materials, increasing environmental restrictions and lack of technological breakthroughs that can reduce cost and/or develop new products. Heavy dependence on non-renewable petroleum resources, energy and labor-intensive processes, environmental regulations and competitions from developing countries have made commodity textile production almost extinct from the United States. However, the United States still has major textile chemical manufacturers and specialty textile producers. Reducing the use of non-renewable resources and relying on indigenously available raw materials, developing environmentally friendly processes are some of the approaches that could make textile production competitive in the United States.

United States is the largest agricultural producer in the world. Agricultural production in the United States generates considerable amounts of byproducts and coproducts that are low-cost, available in large quantities and are renewable resources. The agricultural byproducts such as corn stover, wheat and soybean straw can be used to produce inexpensive and environmentally friendly natural cellulose fibers. Synthetic fibers that are biodegradable have been developed using renewable resources such as corn, soyproteins. Industry applications of agricultural coproducts should be extended. In addition to developing new products, textile processing should also be made sustainable and environmentally friendly in the long run. Textile

processes such as sizing and desizing, bleaching and dyeing consume considerable amounts of water and energy and are also the primary sources of pollution. Considerable efforts are being made to find alternative approaches to the traditional textile processing and making the textile industry more environmentally friendly.

1.1 Textile Warp Yarn Sizing

In textile processing, except for filament yarns, most warp yarns need to be sized before weaving. During weaving, warp yarns experience 3000-5000 times repeated stretching, inflection and abrasion and as a consequence are susceptible to breakage. Breaking of warp yarns during weaving causes loom stoppages, decreased productivity and creates fabric defects. Therefore, sizing, a process of coating yarns, is done to reduce or eliminate yarn breakage, provide lubrication to the yarns so that they can resist the abrasive forces when moving through heald shafts on the loom, decrease electro-static problems and hairiness.

A typical sizing process is depicted in Figure 1. Warp yarns wound on a beam, dipped in a size solution, squeezed between rollers to a predetermined pickup and then dried and the size film cured on steam drying cans (Lord and Mohamed, 1982).

An ideal sizing process should form a film on the surface, protect the fibers on the surface and must not penetrate into the center of the yarns to enable easy removal after weaving. Figure 2 shows after sizing, yarns have a thin film of size on them with some size penetration (Goswami et al., 2004).

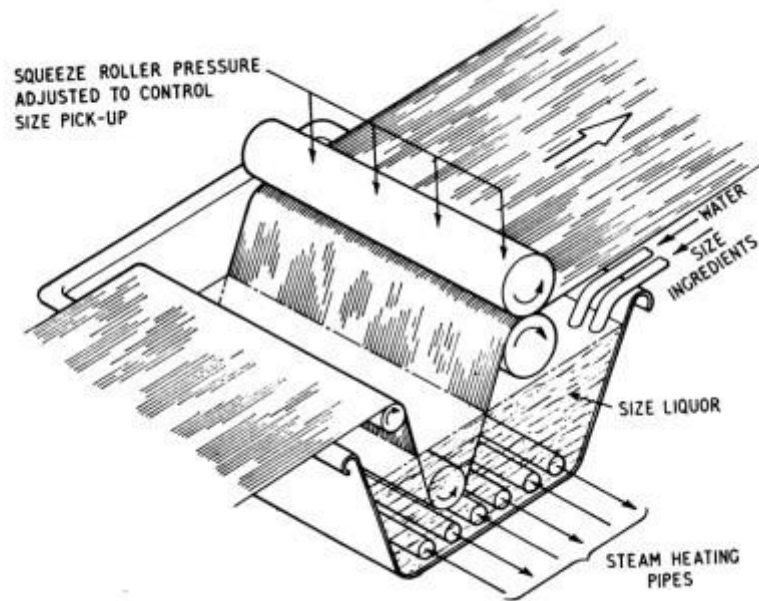


Figure 1 Section of Size Box (Lord and Mohamed, 1982)

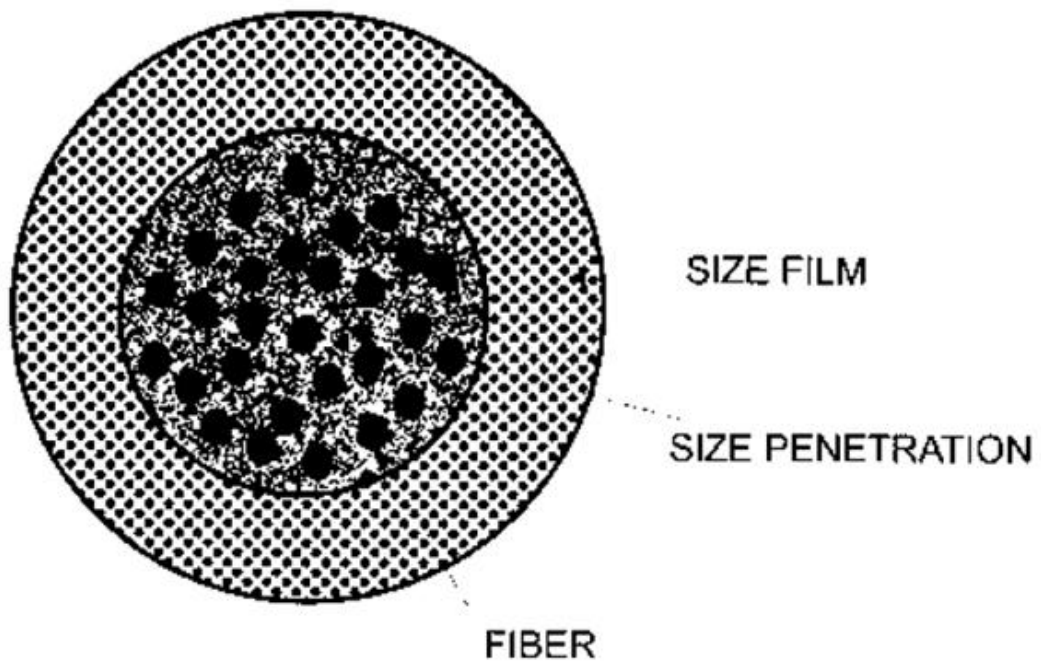


Figure 2 Fiber-size binding in a yarn (Goswami et al., 2004)

1.1.1 Sizing Agents

Sizing agents are derived from both natural and synthetic polymers. Starch and starch derivatives are the most common natural sizing agents and PVA is the most common synthetic polymer used for sizing. Sizing agents are selected on the basis of type of yarn, viscosity, environmental friendliness, ease of removal (desizing) and cost considerations, etc. Some of the common sizing agents and their characteristics are discussed below.

Starch

Starch has a long history of being used as a sizing agent in the textile industry. Natural starch and its derivatives still constitute nearly 75% of the sizing agents used in the textile industry throughout the world and could remain the predominant ingredient in most types of sizes (Zhu and Gao, 2008). Starch can be derived from renewable resources, is abundantly available, inexpensive and forms excellent films making it a preferred sizing agent.

In the United States, the endosperm portion of the kernels of the hybrid yellow dent corn (which is about 90% starch) provides the major source of starch used in textile applications. (Goswami et al., 2004) In starch molecule, every glucose unit contains three hydroxyl groups, which provides adhesive capacity to cellulosic fibers. However, the cyclic structure and numerous hydroxyls make starch brittle and rigid. For this reason, starch films are inflexible and the adhesion to fibers, especially

polyester, is poor and starch is not useful as a sizing agent for synthetic fibers and their blends.

Although starch is inexpensive and provides good sizing performance, native starch has poor viscosity stability and gels upon cooling. In addition, yarns sized with native starch are unable to be processed on the high speed weaving machines. Several approaches have been used to modify starch and make it more convenient for sizing and applicable for synthetic fibers and their blends.

Modified Starches

Chemical, physical and biological means have been used to modify starch. The purposes of starch modification are to change the properties of natural starch paste, such as gelatinization point, viscosity stability, freeze-thaw stability, transparency, adhesion force, and film properties, like flexibility (Rutenberg and Solanek, 1984). Some of the common starch modification methods are:

- (1) Physical modification including: gamma ray irradiations, ultra-high frequency modification, mechanical lapping, heat-moisture treatment, etc.
- (2) chemical reagent treated modified starch could separate into two parts, methods of chemical modification such as acidified starch and oxidized starch reduces the relative molecular weight of starch; and the other increases the relative molecular weight of starch, alter their structure , like crosslinked starch, esterified starch, etherified starch and grafted starch, etc.

- (3) Compound modification: modified starch obtained using more than one treatment methods, for instance, Oxidized and cross-linked starch and esterified and cross-linked starch.

Polyvinyl alcohols (PVA)

Polyvinyl alcohol (PVA) has been one of the most versatile size materials available for warp sizing formulations since it was commercialized as a textile warp sizing agent sometime around 1965 (Goswami et al., 2004). PVA is the product obtained from the alcoholysis using polyvinyl acetate under the effect of the sodium methoxide process in methanol. Alcoholysis products have total alcohoysised and partially alcohoysised. The sizing properties influenced by the degree of polymerization and degree of alcoholysis of polyvinyl alcohol. Polyvinyl alcohol size has shown excellent water-solubility, adhesiveness to the fiber, especially hydrophobic fibers. PVA films have superior elasticity, abrasion, high tensile-strength and elongation. The mixtures of polyvinyl alcohol and modified starches could also provide good protection to warp yarns (Zhu and Gao, 2008).

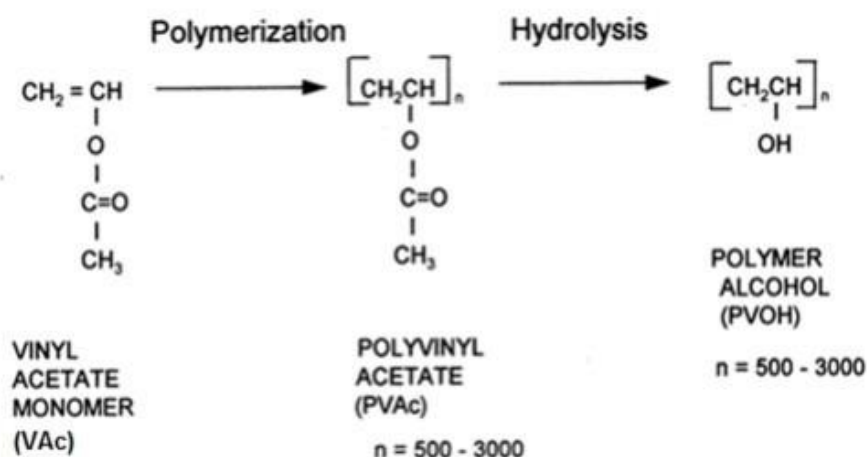


Figure 3 Chemistry of Polyvinyl Alcohol Manufacturing (Robinson, 1996)

Acrylic monomers

Acrylic monomers are another class of synthetic polymers that have been widely studied for sizing applications. In some cases the acrylic size is used alone as the primary film former or as binder component of the size to improve the adhesion between a primary base sizing agent (film former) and the yarn (Zhu and Gao, 2008). Low cost, ability to dissolve easily and be removed during desizing is some of the benefits of using acrylic monomers for sizing. More than two dozen sizing agents based on acrylic monomers are commercially available for sizing. Some of the common acrylic monomers used for sizing are:

The acrylic sizes can be broadly divided into two classes, namely, water or alkali soluble or water insoluble. The alkali soluble types will have acrylic acid or its ammonia or sodium salt or other water-soluble derivative (such as acrylamides) as a major component of the polymer chain. The insoluble size materials contain acrylic

esters or acrylonitrile derivatives. The copolymers can vary widely in composition to give a large family of “acrylic” polymers useful as sizing materials (Goswami et al., 2004).

1.1.2 Environmental Problems of Sizing

After weaving process, size on the fabrics should be removed, in order to ensure the quality of finishing and dyeing processes. About 40-50% of waste water released from textile plants is related to desizing. Most of the size removed during desizing is released as effluent and causes environmental problems, especially when non-biodegradable sizes such as PVA are used. PVA is reported to remain in water for up to 900 days. Though PVA is not toxic, it has a great surface activity, and can form large amounts of foam in the water, which affect the oxygen content in water body, thereby inhibit or even undermine the respiratory activity of aquatic organisms (Zhang et al., 2005).

As a common refractory organic matter, one gram of PVA is an equivalent of 0.016 biochemical oxygen demand (BOD₅) or 1.6 chemical oxygen demand (COD); its BOD/COD is low to 0.01, indicating the poor biodegradability (Matsumura et al., 1993; Yu et al., 1996). As a consequence, discharging PVA containing wastewater directly into streams would cause serious environmental problems.

1.1.3 DDGS

Distillers Grains are coproducts obtained during the distillation process to produce ethanol from corn. There are two main sources of DDG. Wet Distillers Grains (WDG) that contain primarily unfermented grain residues (protein, fibre, fat and up to 70% moisture. Dried Distillers Grains with Solubles (DDGS) is WDG that has been dried with the concentrated thin stillage to 10-12 per cent moisture. (Wikipedia, 2012)

The use of corn as the major source of ethanol in the United States generates considerable amounts of co-products generally called DDGS which is inexpensive (about \$100-\$130 per ton), available in large quantities but with limited industrial applications. For instance, a gallon of ethanol produced from corn kernels generates about 7.4 pounds DDGS (Pimentel, 2003). The distiller's grains production in the US which is the largest producer of grain ethanol in the world, has increased more than ten

Table 1. Historic Distillers Grains Production from U.S. Ethanol Biorefineries

(Renewable Fuels Association, 2011)

Year	Million Metric Tons
2000	2.7
2001	3.1
2002	3.6
2003	5.8
2004	7.3
2005	9.0
2006	12.0
2007	14.6
2008	23
2009	30.5
2010	32.5

times during the 2000 – 2010 period from 2.7 to 32.5 million metric tons (Table 1) (Renewable Fuels Association, 2011). DDGS contains oil (8–11%), proteins (about 25–30%, with about 50% zein), cellulose (9–16%) and other carbohydrates(Loy and Wright, 2003). Due to the high protein content of DDGS, DDGS is widely used as a protein feed material.

However, DDGS used as animal feed is reported to cause health problems in animals that could restrict the use of DDGS as animal feed. (Wu and Munkvold, 2008) Therefore, it will be imperative to find new applications for DDGS to help reduce the cost of producing ethanol.

The low cost, biodegradability and combination of carbohydrates, proteins and oil in DDGS make it an attractive sizing agent. However, it is necessary to dissolve the components in DDGS and understand the performance of DDGS as a sizing agent.

CHAPTER 2 OBJECTIVS

The main objective of this research is to develop a biodegradable, low price and effective sizing agent that can replace PVA for textile warp sizing. DDGS as a coproduct with large availability and low cost and containing up to 30% proteins could be an ideal candidate to substitute PVA. The properties of DDGS as a sizing agent for cotton, polyester and polyester blends will be studied in comparison to commercially available sizing agents.

CHAPTER 3 REVIEW OF LITERATURE

3.1 Development of new sizing agents

Developing alternative sizing agents and technologies that can reduce or eliminate the environmental problems associated with textile sizing is of vital importance for the long-term sustainability for the textile industry. Studies to make sizing more environmentally friendly are mainly based on two approaches. First, to develop new textile sizing agents which provide superior sizing properties and are at the same time also biodegradable. Second approach is to increase the biodegradability of PVA in textile effluent treatment plants.

Currently, many materials, such as modified starch, acrylate, and polyester and so on, have been developed as environmentally friendly size, with attempts to substitute PVA partly or completely, and solve the environmental problems of textiles industry.

Starch, the most common sizing agent has been chemically modified to make starch suitable for sizing synthetic fibers and their blends. Grafting is one of the approaches used to make starch suitable for sizing polyester and its blends. Although grafting provides desired properties to starch for sizing synthetic fibers, grafting makes starch considerably expensive and also less biodegradable. Increasing the grafting efficiency is an effective way of improving the properties of starch graft copolymers and reducing their preparation costs (Nguyen et al., 1992; Nguyen et al.,

1991). To enhance the grafting efficiency of starch graft copolymers, previous investigators have tried to obtain reasonable technological parameters for the copolymerization (Reyes et al., 1996; Athawale and Vidyagauri, 1998). Mostafa and El-Sanabary reported that sizing properties of starch could be evidently improved through the grafting of a quantity of acrylic acid onto starch (Mostafa and El-Sanabary, 2004).

Starch was pretreated with allyl etherification to enhance the grafting efficiency of the copolymerization of granular starch with acrylic acid and to improve the properties of starch-g-poly(acrylic acid) used as a warp sizing agent (Zhu, 2009).

γ -irradiation improved the behavior of MS/PVA maize starch (MS)/poly(vinyl alcohol) (PVA) blends and their composites with GY or GP as a sizing material for cotton fabrics. Films of different composites based essentially on maize starch (MS)/poly(vinyl alcohol) (PVA) blends were prepared by the solution-casting technique and subjected to various doses (20–100 kGy) of γ -radiation. The MS/PVA blends were modified by the addition of glycerol (GY) and a graft copolymer (GP) of MS with acrylamide separately or together with the polymer blend solutions before casting (El-Naggar et al., 2004).

Sun W &, Tian J treated the PVA-containing wastewater using gamma irradiation as a pretreatment strategy to improve its biodegradability. The results showed that the biodegradability of PVA-containing wastewater with low initial concentration (e.g., 327.8 mg/l) could be improved greatly with increasing irradiation

dose. However, PVA gel formation was observed at higher initial PVA concentration (e.g., 3,341.6 mg/l) and higher irradiation dose, which inhibited PVA degradation by aerobic microorganisms. However, the formed gel could be separated by microfiltration, which led to more than 90% total organic carbon (TOC) removal (Sun et al., 2012).

Although researchers have developed new textile sizes and/or attempt to solve or decrease the environmental problems associated with sizing and desizing an ideal approach has so far not been achieved. For example, although starch derivatives or modified starch are more suitable to size synthetic fibers and their blends compared to native starch, modified starches do not have the performance properties and/or cost advantages to substitute PVA. Acrylic sizing agents still had the problems of thickness after moisture absorption. Similarly, methods to degrade PVA in textile effluent treatment plants are not practical and/or too expensive. So neither of the two ways solves the environmental problem, so developing biodegradable textile sizing agent is of practical importance.

3.2 DDGS application

3.2.1 DDGS Composites

Distillers' dried grains with solubles (DDGS) have been studied in biocomposites and green composites use. One of the very first studies reports the incorporation of DDGS, up to 30 wt%, into polyolefin polymers, e.g. polypropylene (PP) and polyethylene (PE) (Julson et al., 2004). Wu and Mohanty (Wu and Mohanty,

2007) investigated the DDGS incorporation into polymerized polyurethane. They have reported the production of PU/DDGS compositions having 20 to 90% by weight of DDGS. Also, biopolymer blends have been used as the polymeric matrix in DDGS composites (Zarrinbakhsh et al., 2011). Polylactide (PLA) and DDGS-based composites have also been studied by Li and Sun (Li and Sun, 2011). There are reports on using phenolic resin as a binder between DDGS particles (Tatara et al., 2007; Tatara et al., 2009; Cheesbrough, 2008).

The incorporation of biomass-derived biofiber and crop-derived bioplastics into the composite materials in designing green composites poses immense opportunities in transportation parts, construction panels and packaging uses (Mohanty, 2002).

Attempts have also been made to develop composites and other products from DDG. The potential of developing biodegradable thermoplastics by chemically modifying (carboxymethylation, glutaration, maleiation) DDG was studied by Schilling (Schilling et al., 2004). DDG was also used as reinforcement in composites by mixing DDG with phenolic resin and wood glue (Cheesborough et al., 2008). DDGS acetylated using alkaline and acidic conditions to obtain composites (Reddy et al., 2011).

Distillers' dry grain (DDG) was derivatized either by carboxymethylation, glutaration, maleiation, phthallation, or succination in order to produce anionic materials suitable for complexation with soy protein isolate (Schilling et al., 2004).

DDGS has the potential to be used in resin glue-based composites to both

improve flexural strength and improve potential biodegradability. Resin glue proved to be far better suited to composite formation, yielding products that cured more uniformly, were stronger, and experienced less deterioration than those formed from glue. High DDGS content was essential for the formation of glue composites; a moderate amount of DDGS resulted in an increased maximum fiber stress, but decreased Modulus of Elasticity in the resin glue trials (Cheesborough et al., 2008).

Oil-and-zein-free DDG was acetylated using alkaline and acidic conditions. Acetylation using acidic catalysts provided substantially higher acetyl content and intrinsic viscosity at low ratios of anhydride and catalyst concentrations compared to alkaline catalysis of the carbohydrates and proteins in DDGS. DDGS acetates obtained using acid catalyst also had lower melting temperature and higher melting enthalpy resulting in more transparent thermoplastics than the DDGS acetates obtained using alkaline catalysts (Reddy et al., 2011).

3.2.2 DDGS components extraction

Researchers extract the components in DDGS such as oil, proteins and carbohydrates and try to develop various products. The oil in DDGS has similar properties to the commercially available corn oil and could be used either in the food industry or as a biofuel (Xu et al., 2007). Zein, the major protein in corn, is suitable for various applications such as films, binders in paints and also for fibers (Lawton, 2002). Obtaining oil and zein from DDGS would be more economical than from corn kernels but the normal process of extracting zein from corn kernels are not suitable for

extracting zein from DDGS. Cellulose obtained from DDGS may be used for applications such as films, composites, paper, water absorbents, lubricant and nutritional supplements (Xu et al., 2009).

A novel process of using acidic conditions in the presence of a reducing agent has been optimized to obtain high quality zein with about 90% proteins and a yield of about 44% of the proteins in DDGS. The zein obtained in this research has higher viscosity and is whiter than commercially available zein. In addition to the zein, about 17% oil similar in composition to commercially available corn oil has also been obtained. The zein obtained also has high phosphorus content, which may provide the proteins with relatively high flame resistance (Xu et al., 2007).

Cellulose has been purified from DDGS and corn kernels using alkali and enzymes with purity up to 81% and 72%, respectively. The cellulose obtained from DDGS has higher DP than cellulose from corn kernels but both the celluloses have similar % crystallinity. The presence of chemically linked hemicellulose in the crude cellulose obtained makes it possible to form films just using water without any chemicals. Cellulose obtained from DDGS may be used for applications such as films, composites, paper, water absorbents, lubricant and nutritional supplements (Xu et al., 2009).

CHAPTER 4 MATERIALS AND METHODS

The experiments start from the extraction of DDGS. Use the extracted DDGS solution to study the sizing conditions, including sizing temperature and add-on %. Then desizing conditions, how to remove the sizing agent, were studied. At last, environmental performances (BOD, COD, total nitrogen and ammonia nitrogen) of DDGS were determined. The general experimental design was shown in table 2.

Table 2 General experimental design

	Parameters under investigation	
Extraction	NaOH concentration (%)	extraction Time (hour)
	0.5,1,2	1,2,3
Sizing	temperature (°C)	Add-on (%)
	20, 90	2-20
Desizing	Rinse liquid ratio	Wash liquid ratio
	1:5,1:10,1:20	1:5,1:10,1:20
Environmental performance	COD, BOD5, total and ammonia nitrogen	
	0-3 day	

4.1 Materials

DDGS was supplied by Abengoa Bio Energy Corporation, York, NE. Polyvinyl alcohol (PVA) based commercially available size Penflex Plus 527 provided by PhilChem company, Greer, SC, and starch were used to compare the sizing performance of DDGS. Polyester/cotton (40/60) roving and fabric were supplied by Jiangnan Enterprises Group Co.,Ltd (Wuhan, Hubei, China) and 100% cotton roving were supplied by Mount Vernon Mills, Inc. (Mauldin, SC, USA)

The 100% polyester rovings were supplied by Shuford Yarns LLC, Hickory, NC. Fabrics used (cotton type 400, P/C type 7435 and 100% polyester type Dacron 54) were purchased from test fabrics Inc, West Pittston, PA). Before sizing, fabrics were washed with detergent in a washing machine to remove any finishing chemicals on the surface.

Hydrochloric acid, sodium hydroxide were used to adjust the pH of DDGS solutions. Potassium sodium tartrate, salicylic acid, sodium nitroferricyanide, ammonium chloride, sodium hypochlorite were used in biodegradability evaluation. All other chemicals used were purchased from VWR international.

Activated Sludge was supplied by City of Lincoln Wastewater and Solid Waste Operations Plant.

4.2 Methods

4.2.1 Extraction of DDGS

The goal of this experiment was to observe the effect of sodium hydroxide concentration and extraction time on fiber adhesion and resistance to abrasion on cotton, polyester and polyester /cotton blends. The film properties and viscosity of DDGS base on various extraction conditions were also evaluated.

DDGS was dried below 105 °C in an oven for 4 hours and the amount of moisture in DDGS was calculated water ratio of DDGS is in equation (1).

$$\text{DDGS \%} = \frac{W_0 - W_1}{W_1} \times 100 \quad (1)$$

Where W0 and W1 are the weight of DDGS before and after drying, respectively. The dried DDGS was added into water at a liquid ratio of 1:20, and pre-treated in various concentrations of sodium hydroxide (2%, 1%, and 0.5%) at 90 °C for 1 hour, 2 hours and 3 hours. Concentrations of sodium hydroxide lower than 0.5% had considerable low yield and were therefore not studied in this research. After the pre-treatment, the pH of the solution was adjusted to 7 by adding 37% hydrochloric acid. The extracted DDGS was centrifuged at 8000 rpm for 10 min and the supernatant obtained was used for sizing. The solid portion obtained after centrifuging were discarded but could potentially be used for animal feed or other applications after appropriate washing and neutralization.

The amount of solids extracted in the supernatant obtained was measured to

determine the yield. The yields of DDGS extraction were measured in the following way: wash the precipitate, dry it in 105 °C until the weight doesn't change. The yield of DDGS was calculated in equation (2).

$$\frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

Where W1 and W2 are weight of DDGS (dry) and precipitate after centrifuge (dry).

4.2.2 Sizing

The cotton, polyester and polyester/cotton blended rovings and fabrics were sized with the DDGS extracted at various extraction conditions. To size the rovings, the rovings were wound onto a frame and immersed in the sizing solution. The extraction and sizing conditions studied are listed in table 2.

For comparison, cotton fibers and fabrics were sized with starch and polyester and P/C blends were sized with the commercially available sizing agent under the manufacturers recommended conditions. For fabric sizing, the samples were immersed in the sizing solution at 90 ° for 5 minutes, later squeezed in a padder to help the size spread evenly on the fabrics. The % wet-pick up was determined to ensure that the fabrics had the desired % add-on.

After sizing, the rovings and fabrics were conditioned at 21 °C and 65% relative humidity. All tests were performed on the conditioned samples.

4.2.3 Desizing

The sizing agent on the fabrics after weaving has to be removed before the next textile production process. Ability of the size to be removed (desized) is an important index to evaluate sizing performance. Common sizing agents such as PVA and starch are desized using hot water (more than 80 °C) but desizing at room temperature would save energy and water. For comparison, PVA and starch sized fabrics were also desized under the same conditions. The loss in fabric weight before and after desizing was calculated to determine the % desizing.

The loss in the fabric weight after washing is called size removal, and it is determined as following equation (3).

$$\text{Size removal (\%)} = \frac{W_1 - W_2}{W_1 - W_0} \times 100 \quad (3)$$

Where W₀, W₁ and W₂ are the fabric weight before sizing, fabric weight before and after washing, respectively.

4.2.4 Biodegradation

Biodegradation of the sizing solutions were determined in terms of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD₅) and changes in total nitrogen and ammonia nitrogen. To determine the biodegradation of the sizing solutions, waste water sludge from the local waste water treatment plant was used. The sludge was first diluted and then aerated in the laboratory for 2 days to acclimatize the microorganisms.

The sizing solutions were added into the sludge at a concentration of 300 ppm which is higher than the typical concentration of size in textile effluent treatment plants. When processing 100 meters of fabric, 2.5~4.0 tons of waste water are produced (Standard Preparation Group, 2007). 100 meters of fabric normally weights 10.01~26.00 kg (Ministry of Industry and Information Technology of the People's Republic of China, 2010). Fabric weight of 15kg/100m, which is the medium fabric weight, was selected, so 3.0 tons of waste water was producing during the manufacturing. While only warp yarns (60% of the total fabric weight) need to be sized, and the weight of size is always the 10% of the warp yarn weight. So 300 mg/L size will be in the textile mill waste water.

The DDGS size was added into the activated sludge and aerated for up to COD value below 100 mg/L. Solution at the top of the aerated sludge was collected and used to analyze the changes in COD, BOD5 and total and ammonia nitrogen. Commercial PVA size was also determined for the comparison.

4.3 Measurement

4.3.1 Measurement of adhesion

The rovings were used to determine the adhesiveness of the size to the fibers using the impregnated roving method.

The sized rovings were tested to determine their tensile strength and elongation as a measure of the adhesion of the sizing agent to the fibers. Testing was performed on a MTS tensile tester (Model: QTest 10) using a gauge length of 10 cm and

crosshead speed of 50 mm/min. Twenty tests were conducted for each sizing condition and each experimental condition was repeated at least three times.

4.3.2 Measurement of abrasion resistance

The cotton and polyester/cotton blended and polyester fabrics sized with DDGS were tested for abrasion resistance.

A QM Universal Wear Tester (Model # CS-ZZC) was used to determine the abrasion resistance of a fabric samples measuring 4 3/16" in diameter. The abradant used was grade emery paper and the type of abrasion was unique directional. The load used for the cotton, poly/cotton and polyester fabrics are 1/2, 1/2 and 1 pound respectively. The sample was placed over a diaphragm the QM Universal Wear Tester. The diaphragm inflated with 28 kPa subsequently bringing the sample in contact with the abrasion surface. The abrasion surface moved in a multidirectional pattern until the sample was abraded to form a hole in the fabric. The number of cycles it took to completely abrade the sample was observed and recorder. The abradant paper was changed every test. The evaluation abrasion resistance adhered to ASTM D 3886 test method.

4.3.3 Viscosity

A rheometer (Brookfield, Model R/S plus) was used to determine the apparent viscosity and viscosity stability of sizing solutions. DDGS samples and PVA size samples were suspended in distilled water to form 6% (w/w) dispersion. A CC-25 cup

and about 70 g of solution was used for each test. The apparent viscosity was measured at 90 °C for 1 hour.

4.3.4 Film preparation and properties

Films were prepared from DDGS that was extracted at various sodium hydroxide concentration and pre-treatment time. The solution was cast on Teflon coated glass plates and allowed to dry at 50 °C in the oven. After the films were dried, they were washed with distilled water three times to remove the salt formed during neutralization with acid. Films were later placed in 21 °C and 65% relative humidity for 24 hours and collected. Commercial PVA films were formed for the comparison. But starch film was too brittle to test, so it wasn't formed.

Tensile properties of the films were tested according to ASTM D822 on an MTS (Qtest 10) tensile tester using a gauge length of 2 inches and traverse speed of 10mm/min, using samples with dimensions of 1.5 mm×8 mm. Ten samples obtained from every film casted were tested and each experimental condition had samples from three separately casted films.

4.3.5 Biodegradation

Once sizing waste water was discharged into water body, they can cause serious damage to the environment. The biodegradability of DDGS, with commercial PVA sizes were measured.

COD

The Chemical Oxygen Demand (COD) test measures the oxygen equivalent consumed by organic matter in a sample during strong chemical oxidation. The strong chemical oxidation conditions are provided by the reagents used in the analysis. Potassium dichromate is used as the oxygen source with concentrated sulfuric acid added to yield a strong acid medium. Several reagents are added during the set up of the analysis to drive the oxidation reaction to completion and also to remove any possible interference. Specifically, these reagents are mercuric sulfate, silver sulfate and sulfuric acid. Mercuric sulfate is added to remove complex chloride ions present in the sample.

Add 2 ml sample into Chemical Oxygen Demand (COD) Reagent TNT 822, with high range (20-1500 mg/L), purchased from Hach Company, digest the sample in Hach DRB 200 reactor at 150 °C for 2 hours, then cool the sample down to room temperature, inset the test tube in to sample cell module of Hach DR 3900 Benchtop Spectrophotometer at a wavelength of 620 nm.

BOD

The 5 day BOD test was performed according to the Standard Methods for the Examination of Water and Waste Water published by the American Public Health Association. The oxygen levels in the water with and without sludge and before and after treatment were measured using a dissolved oxygen probe (Hach Company, HQ

440D multi). Samples were appropriately seeded and the water used for the test confirmed to the standard and had an oxygen depletion of less than 0.2 mg/L in five days.

Aerate dilution water for 15 minutes, in order to provide adequate oxygen in water, and add Hach Company nutrient buffer pillows to a selected volume. Shake the container of dilution water for about 1 minute to dissolve the slurry and to saturate the water with oxygen. Place the dilution water in the constant temperature chamber to maintain a temperature of 20 °C until sample dilutions and analyses begin. Place the sample container in the constant-temperature chamber or water bath to begin warming the sample to 20 °C \pm 1 °C.

At the end of 5 days \pm 4 hours, remove the BOD bottles from the incubator, remove the overcap, pour off the water seal, remove the ground-glass stopper, and measure the final DO concentration (D2). The calculation for BOD₅ is in equation (4).

$$\text{BOD}_5 = \frac{D_1 - D_2}{P} \quad (4)$$

Where D1=initial sample dissolved-oxygen (DO) concentration (in mg/L), D2=sample DO (in mg/L) after 5 days, P=decimal volumetric fraction of sample used.

Total Nitrogen

Nitrogen compounds are oxidized to nitrogen in alkaline persulfate spontaneously when the media is autoclaved under 120°C.

Take 10 ml of testing sample and 5 ml of alkaline potassium persulfate solution (15 g/L NaOH, 40 g/L K₂S₂O₈) into digestion tube. Place the digestion tube in 120 °C digesting for 40 minutes. Cool down the digestion tube, add 1 ml hydrochloric acid and distilled water into total volume of 25 ml. Distills water serve as blanks for quality control. The total nitrogen concentrations in the sample solutions were measured on the spectrophotometer at 220 nm and 275 nm. A calibration curve Area was obtained according to difference potassium nitrate concentration prior the test ($R^2 > 0.999$). Ar, absorbance difference between sample and blank, was calculated in the following equations (5), (6) and (7).

$$Ab = Ab_{220} - 2Ab_{275} \quad (5)$$

$$As = As_{220} - 2As_{275} \quad (6)$$

$$Ar = As - Ab \quad (7)$$

where A_{b220} : absorbance of blank at 220 nm; A_{b275} : absorbance of blank at 275 nm; A_{s220} : absorbance of sample at 220 nm; A_{s275} : absorbance of sample at 275 nm.

The total nitrogen ρ (mg/L) was calculated for the equation (8):

$$\rho = \frac{Ar - a}{bV} \times f \quad (8)$$

where ρ is the concentration of total nitrogen, mg/L; A_r : the absorbance difference between sample and blank; a: intercept of the calibration curve; b: slope of the calibration curve; v: volume of sample; f: dilution factor of sample.

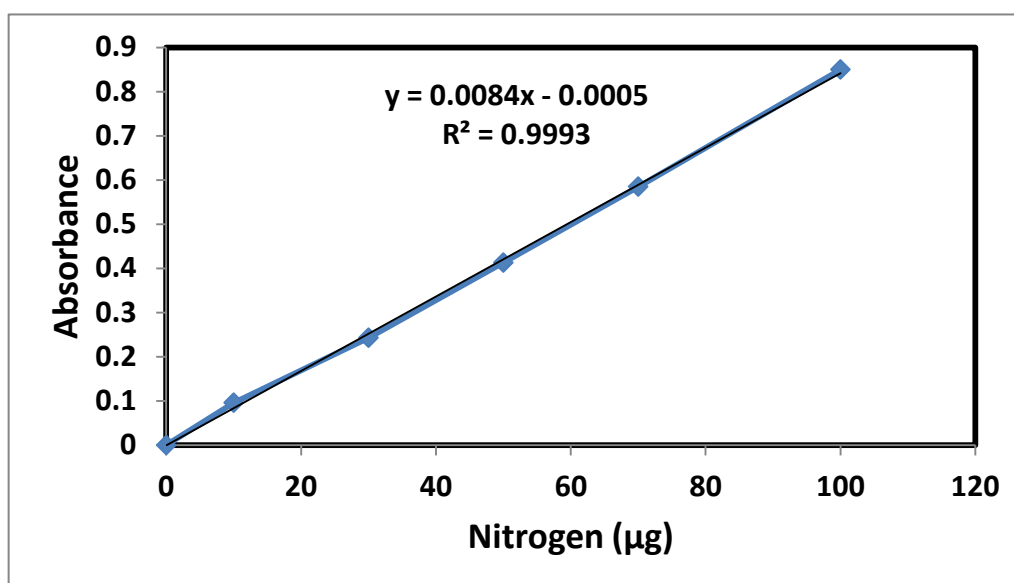


Figure 4 Calibration curves of total nitrogen

The linear regression equation of calibration curve for total nitrogen is shown in figure 4.

Ammonia

When ammonia is digested with salicylate and hypochlorite in an alkaline phosphate buffer, an emerald green color is produced which is proportional to the ammonia concentration.

Take 8.00 ml test sample into the tube, add 1 ml visualization reagent [50 g/L $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$, 50 g/L $\text{KNaC}_4\text{H}_6\text{O}_6$], 2 drops of 10g/L sodium nitroferricyanide solution, 2 drops of sodium hypochlorite solution (3.5 g/L active chlorine, 0.75mol/L free alkali). Shake it well, and place it for 1 hour before measure the ammonia concentrations. The sample solutions were measured on the spectrophotometer at 697 nm. These samples serve as blanks for quality control. A

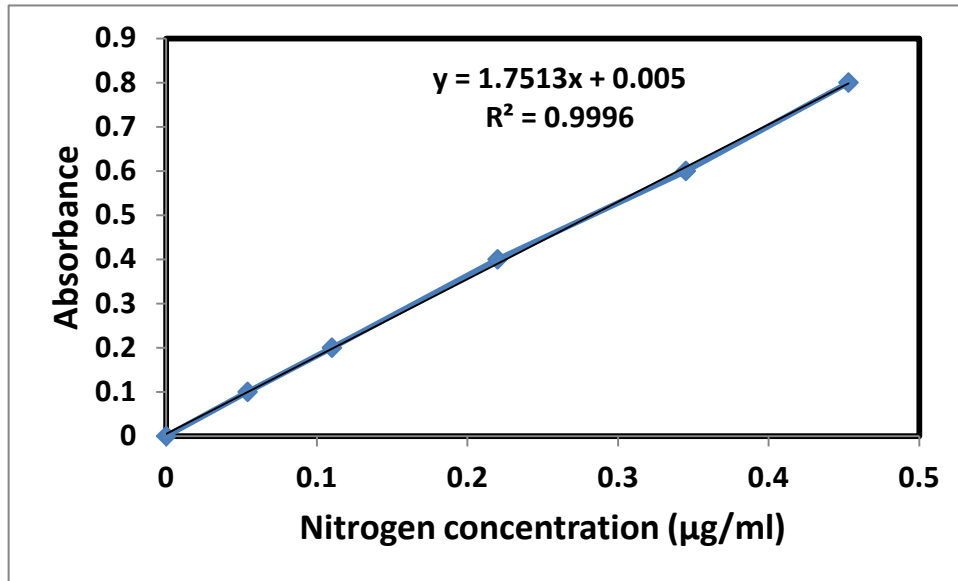


Figure 5 Calibration curves of ammonia

calibration curve, obtained according to difference ammonium chloride concentration prior the test ($R^2 > 0.999$), was shown in figure 5. The ammonia concentration ρ_N (mg/L) is determined as equation (9)

$$\rho_N = \frac{A_s - A_b - a}{b \times V} \quad (9)$$

where A_s : the absorbance of tested sample; A_b : the absorbance of blank; a : intercept of the calibration curve; b : slope of the calibration curve; v : volume of sample; f : dilution factor of sample.

4.3.6 Statistical analyses

All the data obtained were analyzed by the multi-way analysis of variance with comparison. A p value smaller than 0.05 was considered to be a statistically significant difference. The data in the figures labeled with different numbers or characters indicated significant differences among the data. Standard errors were

shown by the error bars in figures.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 Yield of DDGS at different extraction conditions

The influence of sodium hydroxide concentration and extraction time on the yield of DDGS is shown in Figure 6. Prior to the extraction study, DDGS was pre-treated with alkali concentration of 0.25% for 3 hours. Comparing to 0.5% alkali cooking in the time, for polyester roving, it has similar tensile properties, for cotton roving, it has 50% lower peak load on both poly/cotton and cotton roving. And the yield of this low alkali condition is only 30%, but double the alkali concentration; the yield could reach 70%. So we select hydroxide concentration starting from 0.5%.

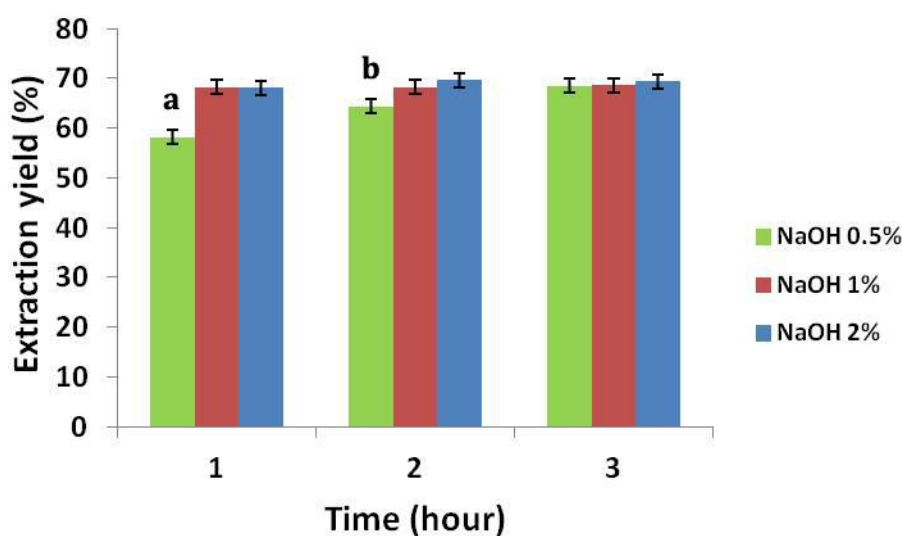


Figure 6 Effect of sodium hydroxide concentration and pre-treatment time on the yield from DDGS. DDGS was pre-treated at 90 °C with an alkali solution.

Statistical analysis using a linear model was shown in equation 10.

$$Y_{ijk} = \mu + \text{time}_i + \text{NaOH}_j + (\text{time} \times \text{NaOH})_{ij} + \varepsilon_{ijk} \quad (10)$$

Where, Y_{ijk} is the yield of DDGS after treatment; μ is the overall mean yield; time_i is the additional yield when extraction time i is used; NaOH_j is the additional yield when sodium hydroxide concentration j is used; $(\text{time} \times \text{NaOH})_{ij}$ is the additional yield when using extraction time i with sodium hydroxide concentration j together; ε_{ijk} is the error.

The SAS program result showed that the interaction ($p = 0.0007$) between the variables is significant and therefore the simple effects of the interaction were examined. Except for the DDGS extracted with 0.5% sodium hydroxide at 1 and 2 hours which had a relatively low yield of 58% and 64%, other extraction conditions did not have a significant effect on the yield of DDGS.

The quadratic and liner relation of sodium hydroxide concentration, extraction time and yield was obtained in equation 11:

$$\begin{aligned} \text{Yield} = & 28.555 + (59.4359 * \text{NaOH}) - (20.0066 * \text{NaOH} * \text{NaOH}) + \\ & (13.7385 * \text{time}) - (20.5507 * \text{NaOH} * \text{time}) + (7.0038 * \text{NaOH} * \text{NaOH} * \\ & \text{time}) \end{aligned} \quad (11)$$

There's quadratic sodium hydroxide by time effect on yield, but the liner relation of time and sodium hydroxide are overwhelming. The regression figure was shown in

figure 7. When DDGS extracted in 0.5% sodium hydroxide solution, extraction time affects the yield. Increased the time, more DDGS yield will obtained.

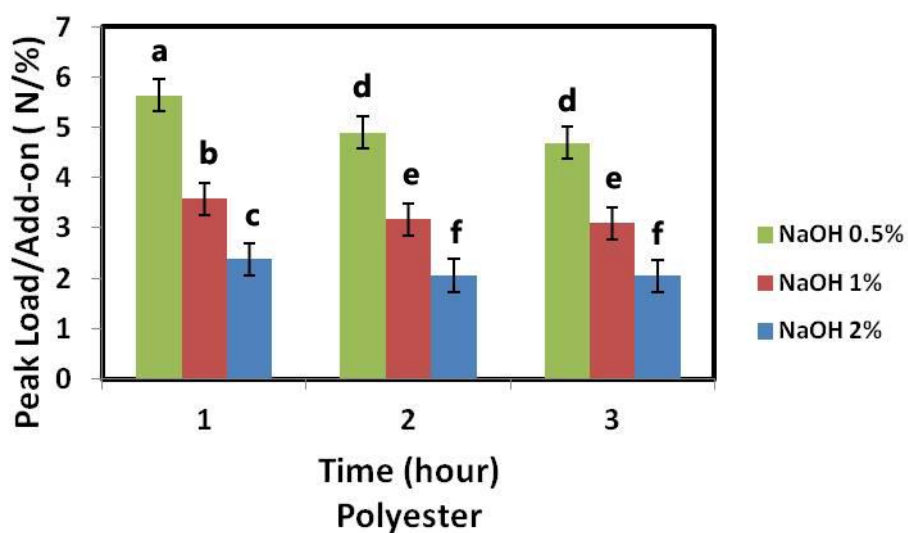
Low concentration and shorter extraction times are unable to extract the carbohydrates and proteins and therefore there is lower yield. Although higher concentrations may provide higher yield, the proteins in DDGS could be damaged. Also, the ratio of carbohydrates and proteins will be different under different extraction conditions and it is necessary to understand the influence of the composition of size on the properties of the sized materials. Therefore, the most optimum condition for extraction should not only be decided on the yield but also on the composition and characteristics of the extracted components.

5.2 Effect of extraction conditions on adhesion of fibers

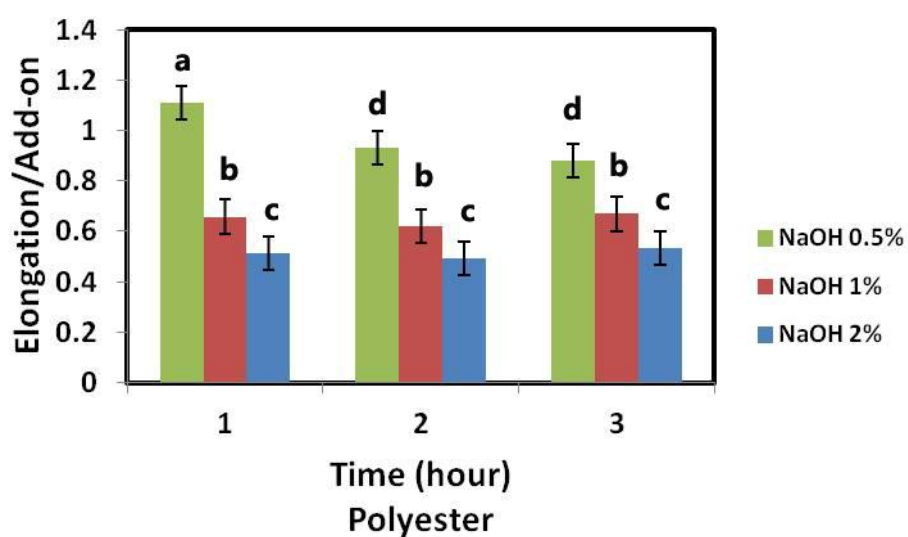
For cotton, the linear model would be the equation (12).

$$Y_{ijk} = \mu + \text{time}_i + \text{NaOH}_j + (\text{time} \times \text{NaOH})_{ij} + \epsilon_{ijk} \quad (12)$$

It has interaction effect on extraction time and sodium hydroxide concentration, while for polyester and poly/cotton blends, the interaction term was dropped. Therefore, we examine the simple effects of cotton roving and main effects of polyester and poly/cotton blends roving.

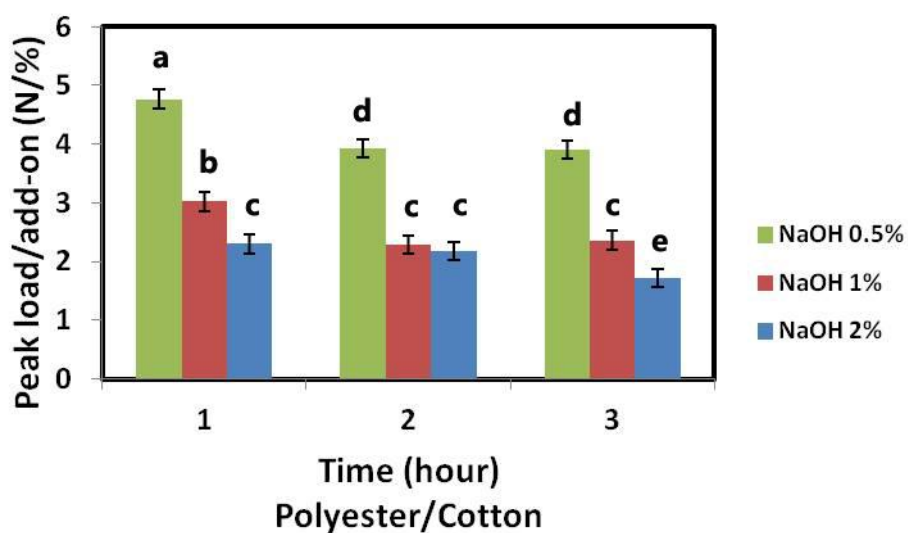


(a)

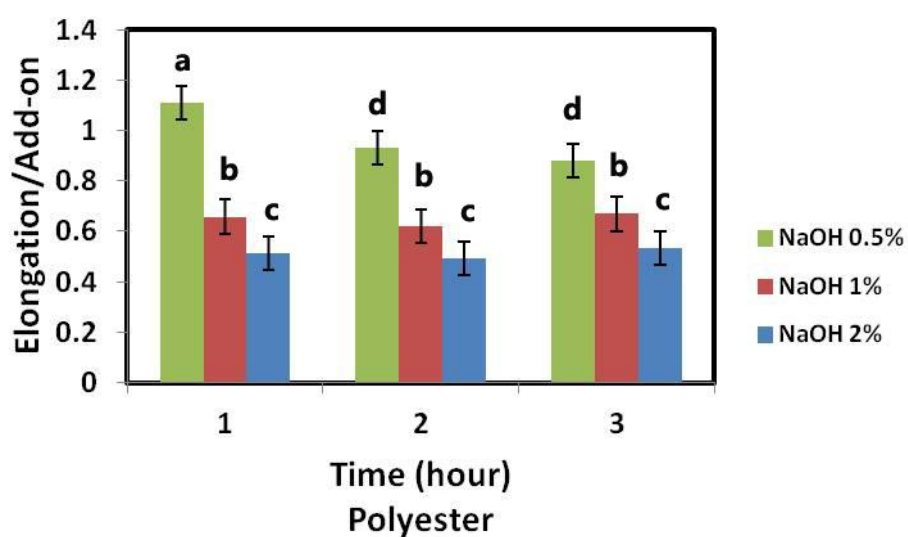


(b)

Figure 7.1 Peak load (a) and elongation (b) of polyester rovings sized using DDGS extracted under different extraction conditions. Sizing was done was 90 °C and the 10% add-on on the polyester.

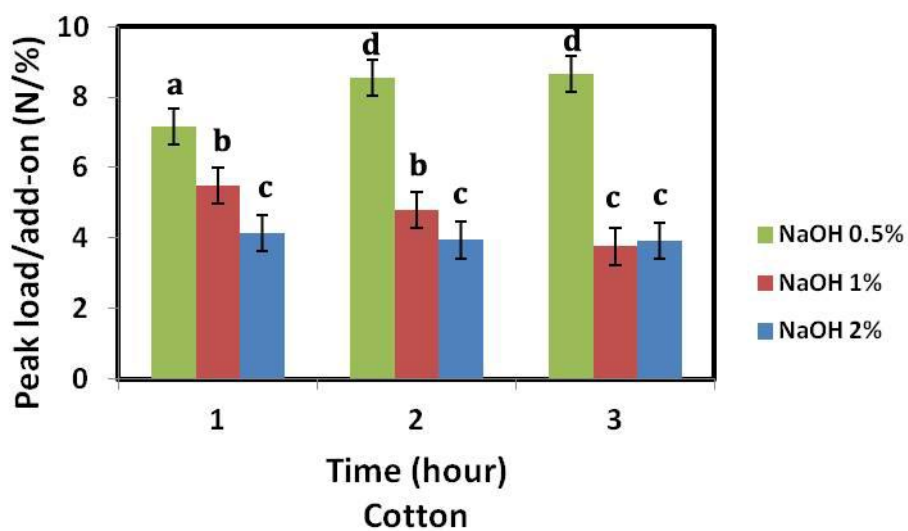


(a)

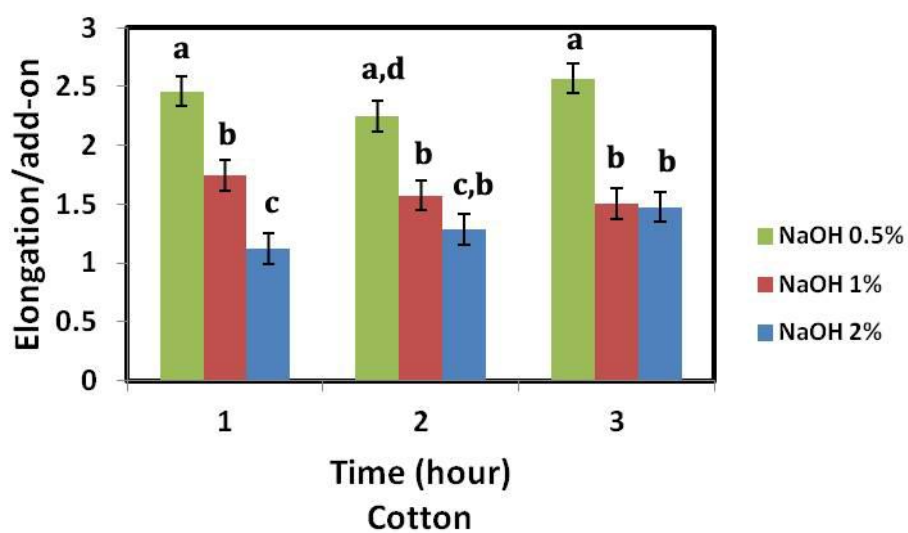


(b)

Figure 7.2 Peak load (a) and elongation (b) of poly/cotton rovings sized using DDGS extracted under different extraction conditions. Sizing was done was 90 °C and the 10% add-on on the polyester.



(a)



(b)

Figure 7.3 Peak load (a) and elongation (b) of cotton rovings sized using DDGS extracted under different extraction conditions. Sizing was done was 90 °C and the 6% add-on on the cotton.

The tensile properties of polyester, poly/cotton and cotton roving sized by DDGS on the effect of extraction time and sodium hydroxide concentration was shown in figure 7. Effect of increasing alkali concentration from 0.5 to 2% on the tensile strength and elongation of polyester, P/C and cotton rovings is shown in Figure 7. Both strength and elongation of the three kinds of rovings were significantly higher when low concentration of alkali was used. At the lowest alkali concentration (0.5%), the strength decrease with longer extraction time on polyester and P/C roving, but increased on cotton roving. At alkali concentration of 1% and 2%, the elongation and peak load was mainly affected by the concentration of alkali and a statistically minor effect of time was observed. Elongation of cotton rovings was enhanced when treated with longer extraction time at the alkali concentration of 2%, which is opposite to other conditions. Pre-treating the DDGS at high alkali concentrations and long extraction time hydrolyzed the proteins and therefore decreased the tensile strength with increasing concentration of alkali.

5.3 Effect of Extraction Conditions on Viscosity of the size solution

The regression equation 13 of DDGS Viscosity was shown below. It has sodium hydroxide by time effect, but sodium hydroxide plays more important role.

$$\text{Viscosity} = 2.8611 + 0.5933 * \text{NaOH} + 0.7306 * \text{time} - 1.1150 * \text{NaOH} * \text{time} - 0.2978 * \text{NaOH} * \text{NaOH} * 0.3544 * \text{NaOH} * \text{NaOH} * \text{time} \quad (13)$$

Effect of Extraction Conditions on Viscosity of the size solution was shown in

figure 8. Extraction time and sodium hydroxide concentration have interaction effect on viscosity of DDGS solution. The increase in the cooking time and alkali concentration lead to the decrease in the viscosity mainly of the decrease in molecular weights of the proteins and carbohydrates when excessive concentrations of sodium hydroxide are used. Using the slice option in SAS program, we examined the influence of alkali concentration and extraction time on each other on viscosity at all the conditions studied. The slice analysis showed that varying the alkali concentration at the same extraction time had significant difference on the viscosity. However, changing the pre-treatment time at different concentrations of alkali showed a statistically significant difference only at low (0.5%) alkali concentration. Sufficient alkali is necessary to separate the proteins and carbohydrates in DDGS and make them soluble in water. At low alkali concentrations, extraction time of up to 3 hours

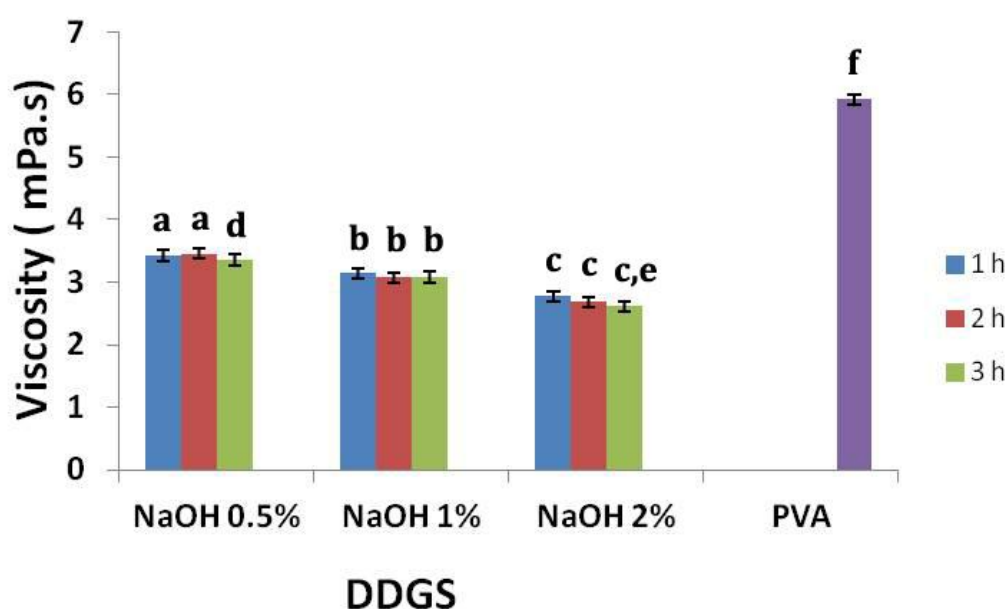


Figure 8 Viscosity of DDGS on different extraction conditions

was insufficient to extract the proteins and carbohydrates and therefore there was no major change in viscosity. Overall, DDGS had lower viscosity (3.4 mPas) compared to 5.9 mPas for PVA suggesting that DDGS size would penetrate more easily into the fabrics and probably form a thinner film on the surface which could affect both the adhesion and the abrasion resistance.

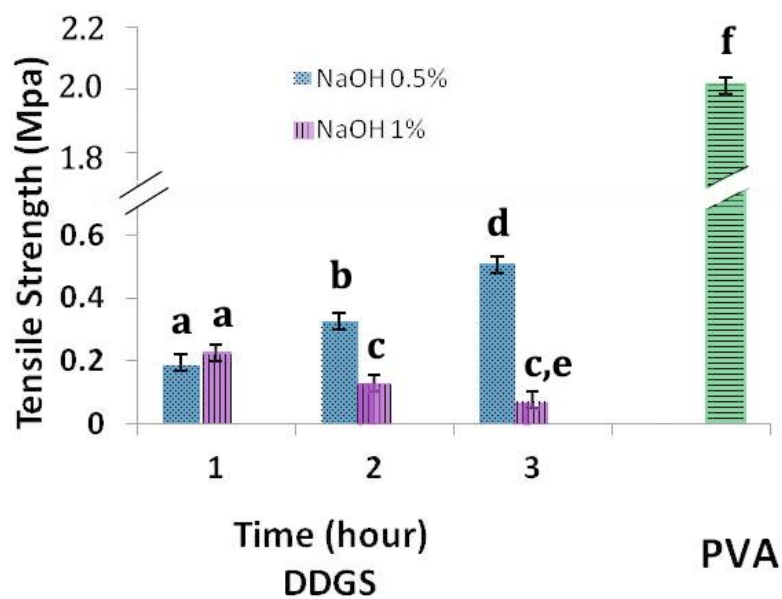
5.4 Effect of Extraction Conditions on Film properties

The regression equation of elongation (14) and tensile strength (15) of DDGS film was shown below. Both of them have sodium hydroxide by time effect.

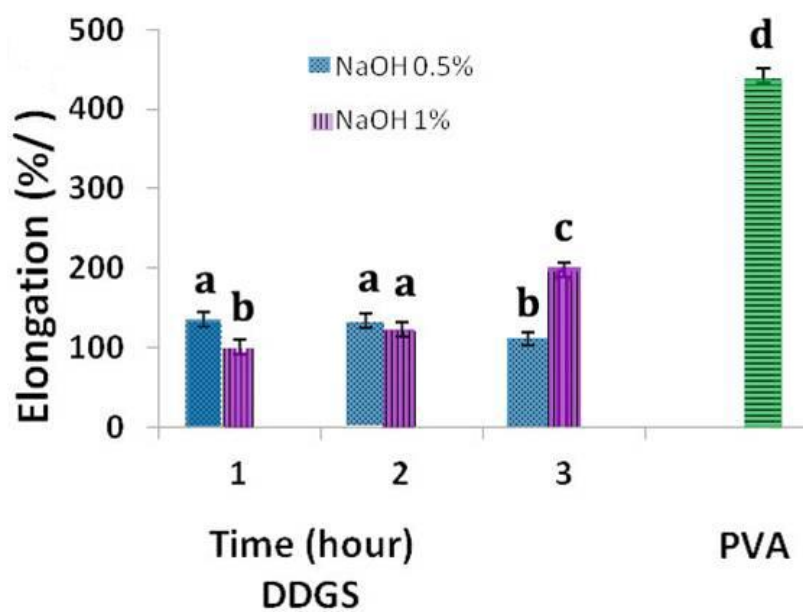
$$\text{Elongation} = 258.98 - 214.60 * \text{NaOH} - 72.7787 * \text{time} + 120.94 * \text{NaOH} * \text{time} \quad (14)$$

$$\text{Tensile strength} = -0.2324 + 0.5251 * \text{NaOH} + 0.3848 * \text{time} - 0.4590 * \text{NaOH} * \text{time} \quad (15)$$

The film properties of DDGS with different extraction conditions comparing with PVA commercial sized were indicated in figure 9. When extracted with 0.5% alkali solution, the tensile strength of DDGS sizing film increased with increasing extraction time, whereas an opposite trend was observed when the DDGS was extracted with 1% alkali solution,. The elongations of films obtained from DDGS treated with 0.5% 1 hour and 2 hours were similar and the films extracted for 3 hours had a marginal decrease in elongation. At low concentrations of alkali, the carbohydrates and proteins have limited hydrolysis and therefore the films have good properties. Increasing extraction time at low concentration extracts proteins and carbohydrates with higher molecular weights and therefore the strength of the films extracted at 3 hours is higher



(a)



(b)

Figure 9 Tensile strength (a) and elongation (b) of DDGS films cast after different extraction conditions.

than those extracted at 1 and 2 hours. On the contrary, longer extraction times at higher concentration of alkali destroyed the DDGS components leading to poor film strength. Films obtained from the DDGS extracted with 2% alkali even for 1 hour had very low strength which substantiates the claim of damage to the proteins and carbohydrates when high concentration and longer extraction times are used.

5.5 Effect of Extraction Conditions on Abrasion resistance

Abrasion resistance of fabrics treated with DDGS and commercial size (PVA and Starch) on polyester, poly/cotton and cotton fabrics are shown in figure 10, with the size add-on of about 5%. The roving adhesion tests, viscosity and film properties measurements showed that extraction time had a less important role compared to alkali concentration. We therefore only examined the effect of alkali concentration fabric abrasion resistance.

For all the fabrics, lower sodium hydroxide concentration provided higher abrasion resistance Polyester and poly/cotton fabric's abrasion resistance when sized with DDGS extracted at three alkali concentration were significantly different to each other, whereas poly/cotton fabrics did not show any major difference when sized with 0.5% or 1% alkali but decreased when the sodium hydroxide concentration increased into 2%, Abrasion resistance of the fabrics is generally higher when low concentrations of alkali are used because of the better quality film formed at low alkali concentration as seen from the film properties discussed above.

Roving strength increase is predominantly influenced by cohesion between fibers whereas abrasion resistance is mostly related to the surface film on the fabrics. DDGS would have better cohesion for cotton than polyester and therefore the P/C roving had higher strength increase than polyester rovings. Repulsion between the hydrophobic polyester and hydrophilic DDGS probably results in the formation of a denser film on the surface of the polyester fabrics leading to better abrasion resistance of polyester fabrics compared to P/C fabrics.

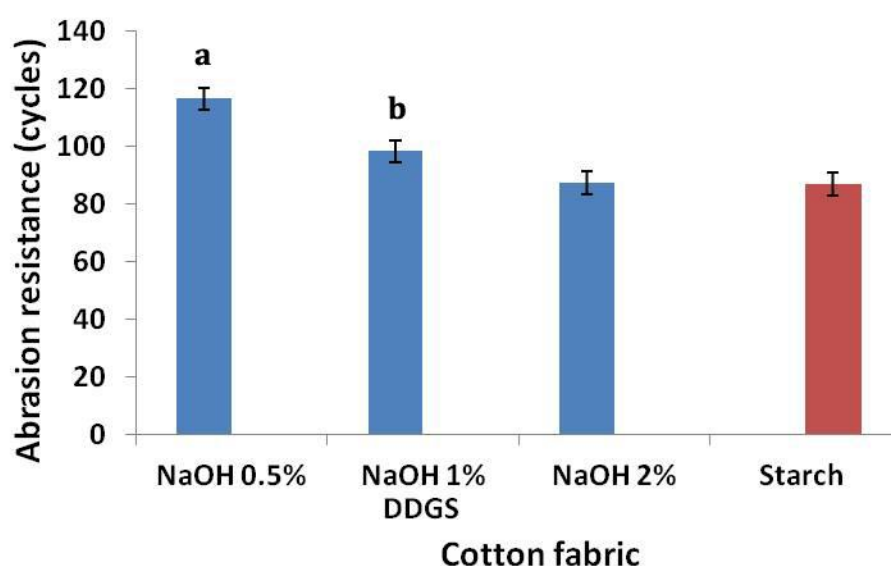


Figure 10.1 Abrasion resistance of cotton fabric treated with DDGS extracted with three different concentrations of alkali for 1 hour. The fabrics were sized at 90 °C for 5 minutes and had an add-on of 5%.

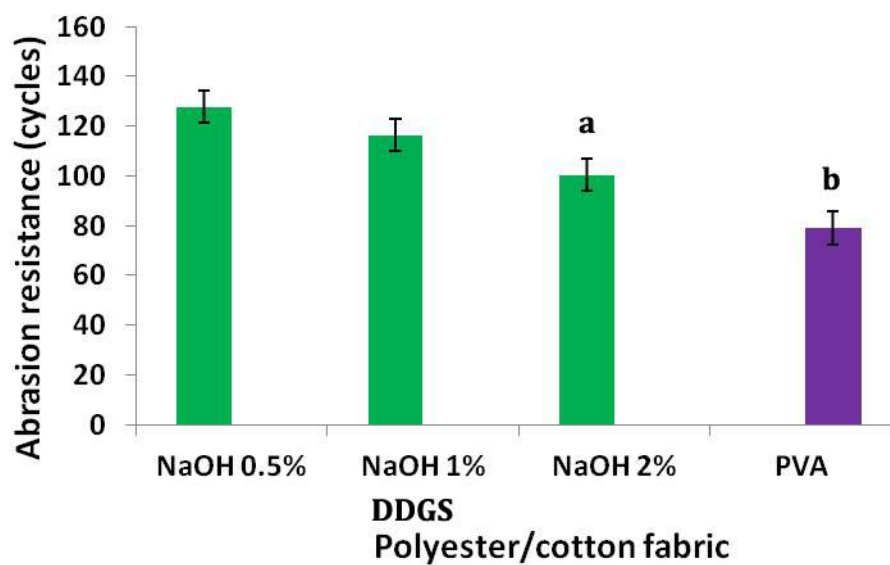
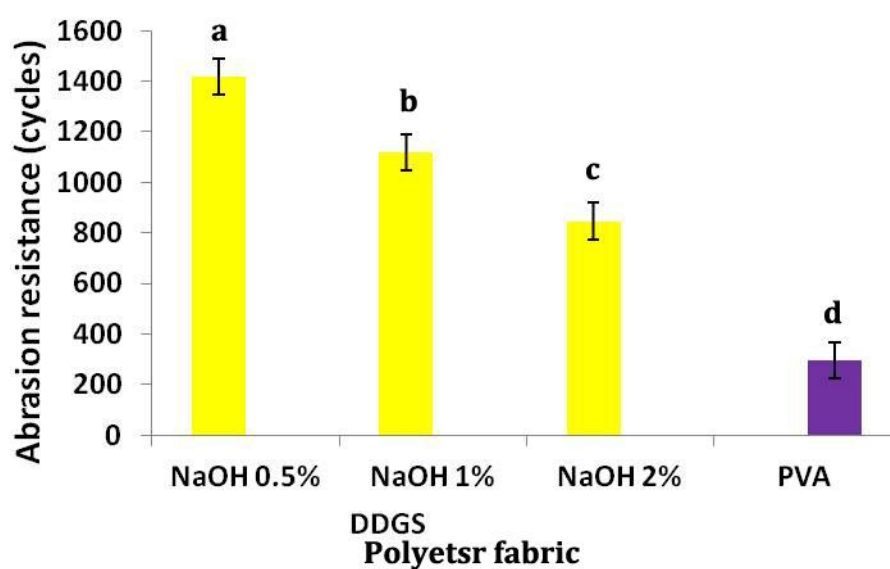


Figure 10.2 Abrasion resistance of poly/cotton fabric treated with DDGS extracted with three different concentrations of alkali for 1 hour. The fabrics were sized at 90 °C for 5 minutes and had an add-on of 5%.



(c)

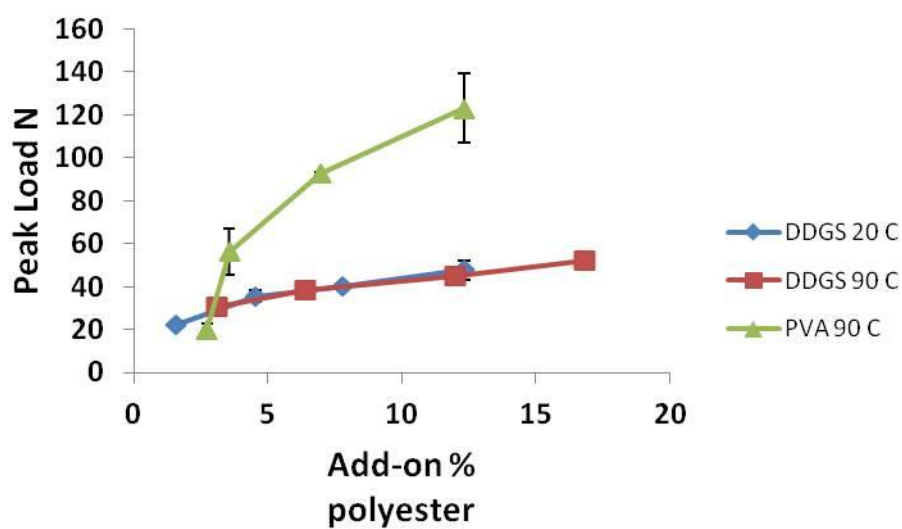
Figure 10.3 Abrasion resistance of polyester fabric treated with DDGS extracted with three different concentrations of alkali for 1 hour. The fabrics were sized at 90 °C for 5

minutes and had an add-on of 5%.

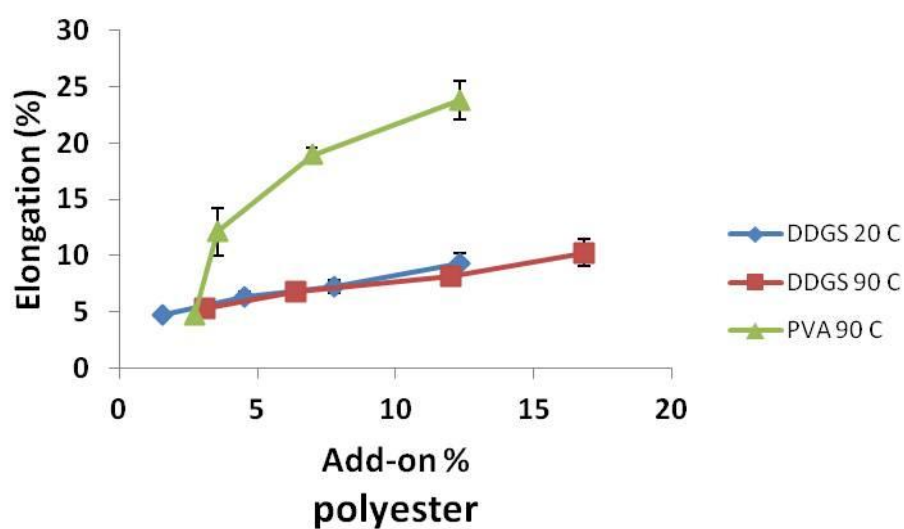
5.6 Effect of % add-on and temperature on sizing performance

A study of sizing with DDGS at room temperature (20 °C) and at 90 °C at different add-ons compared to PVA or starch size is shown in Figure 8. For polyester roving, peak load and elongation are almost the same at 90 °C and 20 °C. At low add-on (2-3%), DDGS size could have better adhesion on polyester fiber than PVA size. Increasing add-on, peak load and elongation of DDGS sized roving are slowly increased at the same time, while PVA sized roving tensile properties are enhanced sharply. Strength and elongation of DDGS sized polyester/cotton roving were much higher when sized at 90 °C compared to sizing at 20 °C, and PVA and DDGS have almost the same adhesion performance at 90 °C. No change was observed in the elongation of the cotton roving when the temperature and add-on increased, but the peak load of cotton roving was much higher at 90 °C than at 20 °C.

Higher temperature enables the DDGS size to penetrate easily and bind the cotton fibers, so the higher strength and elongation were provided. But temperature does not change the attraction between polyester and DDGS and therefore did not affect the adhesion with polyester fiber. While polyester/cotton and cotton yarn sizing need to be operating at high temperature, in order to provide the protection by DDGS size, polyester yarn sizing can be done at low temperature save the energy.

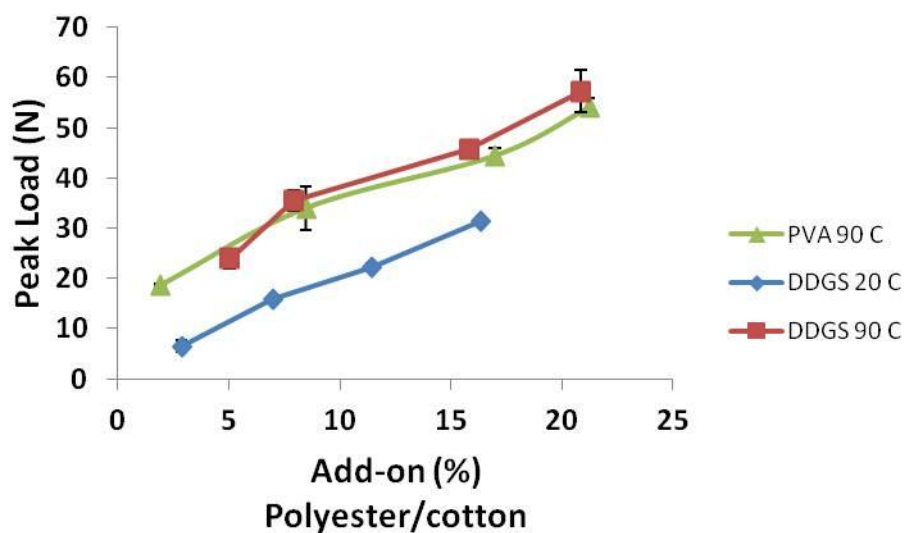


(a)

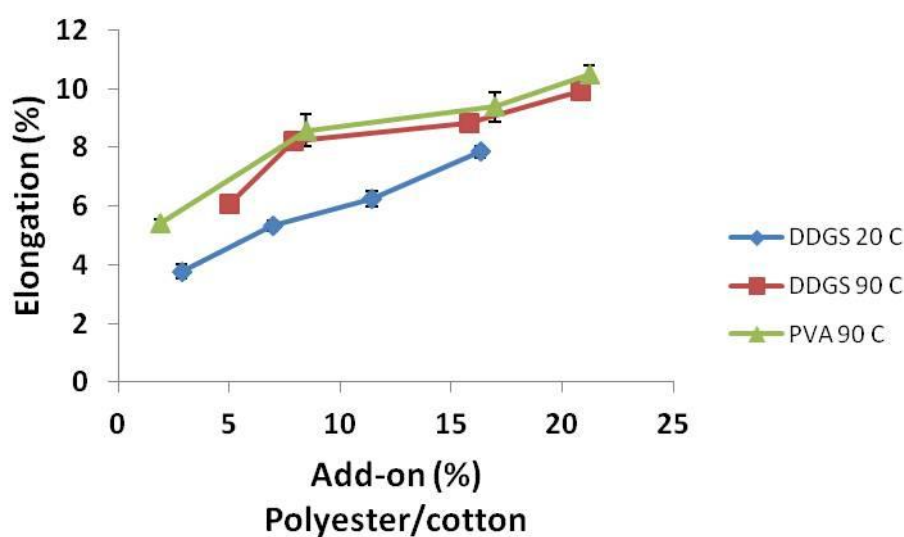


(b)

Figure 11.1 Influence of % size add-on on the peak load (a) and elongation (b) of polyester roving treated with DDGS that was pre-treated with 0.5% sodium hydroxide for 1 hour. PVA and DDGS sizing was done at 90 °C for 5 minutes.

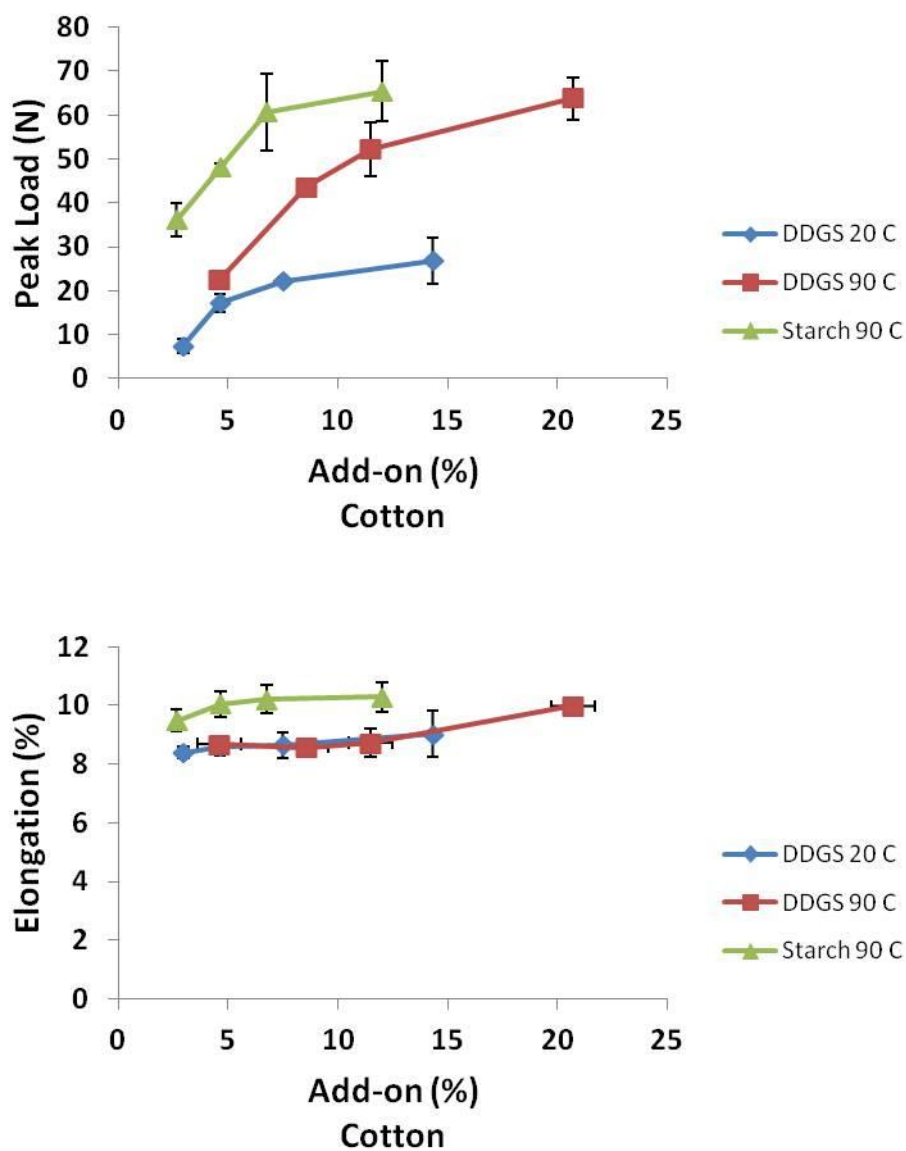


(a)



(b)

Figure 11.2 Influence of % size add-on on the peak load (a) and elongation (b) of poly/cotton roving treated with DDGS that was pre-treated with 0.5% sodium hydroxide for 1 hour. PVA and DDGS sizing was done at 90 °C for 5 minutes.



(c)

Figure 11.3 Influence of % size add-on on the peak load (a) and elongation (b) of poly/cotton roving treated with DDGS that was pre-treated with 0.5% sodium hydroxide for 1 hour. PVA and DDGS sizing was done at 90 °C for 5 minutes.

As seen from Figure 11, increasing the add-on of DDGS, PVA and starch size continually increased the strength of the polyester and poly/cotton and cotton rovings.

The strength and elongation of polyester roving sized with PVA increased more rapidly than sized with DDGS size. Poly/cotton roving sized with PVA and DDGS changed the performance almost at same rate. Cotton rovings sized with starch showed a continual increase in strength with increasing add-on but the change was considerably lower when compared to DDGS. The elongations of cotton roving remain about 8.6% and 10% with DDGS and PVA sizing agent at 90 °C, respectively.

In industrial production, the add-on of textile size on yarns is in the range from 7% to 15%. Polyester roving sized by PVA sizing agent provides excellent adhesion performance: with the add-on of 7%, the elongation and peak load are 19% and 93 N, respectively. With the add-on of 17%, polyester roving sized with DDGS cannot reach the performance of PVA with add-on of 7%. But polyester staple yarn has intensity strength itself; the high strength provided by sizing agent is the most crucial index. Higher add-on of DDGS, about 15%, could sized on cotton roving to provide strength comparable to starch at add-on of 6-7%. DDGS could replace PVA sizing agent, sized on poly-cotton roving, because they have similar strength.

5.7 Desizing

Comparison of the desizeability (% size removed) of DDGS, PVA and starch treated polyester, Poly/Cotton and cotton fabrics at various desizing conditions was shown in table 3. PVA and starch are usually recommended desized from the fabrics at high temperature. Washing liquid ratio and sizing agent have interaction effect (p value=0.007) on polyester fabric, so we proceed to look at the simple effects of

washing liquid ratio and sizing agent and the main effect of rinsing ratio. On cotton and poly/cotton fabric, main effect of washing ratio, rinse ratio and sizing agent were estimated. For PVA, three washing liquid ratios were found to be significant to each other.

For Poly/cotton and cotton fabric, higher liquid ratio had significant higher size removal. Rinsing with fabric to water ratio at 1:5 removed less size from poly/cotton and cotton fabrics compared to rinsing with a 1:20 liquid ratio, but was not significantly different with 1:10 ratio. Washing ratios had considerably larger influence on PVA sized polyester fabric, but less apparent on DDGS sized fabric. DDGS is easier to remove than control size on all three types of fabrics. Up to 90% DDGS could be removed even under the mildest condition studied compared to control size removal of 34%, 26% and 22% on P/C, polyester and cotton fabrics, respectively. DDGS size has higher affinity on cotton fiber, leads to the harder desize condition comparing to polyester and poly/cotton fabric. The ability to remove the DDGS sizes using low amounts of water even at low temperatures and without any chemicals would mean considerable savings in energy consumption and less water as effluent in textile mills.

Table 3. Comparison of the desizeability (% size removed) of DDGS, PVA and starch treated polyester, Poly/Cotton and cotton fabrics at various desizing conditions.

Type of fabrics	Desizing conditions		% Size Removed		
	Washing ratio	Rinsing ratio	DDGS	PVA	Starch
polyester	1:5	1:5	91.1 \pm 2.1	26 \pm 2.9	
		1:10	90.4 \pm 2.8	27.7 \pm 2.4	
		1:20	91.7 \pm 4.9	31.4 \pm 3.8	
	1:10	1:5	90.4 \pm 2.3	32.4 \pm 6.5	
		1:10	93.4 \pm 0.5	39.1 \pm 8.5	
		1:20	96.5 \pm 3.8	44.9 \pm 4.7	
	1:20	1:5	95.0 \pm 4.3	42.6 \pm 8.0	
		1:10	95.3 \pm 2.4	46.9 \pm 5.3	
		1:20	98.6 \pm 2.4	49.2 \pm 4.7	
Poly/cotton	1:5	1:5	91.5 \pm 1.7	34.1 \pm 4.7	
		1:10	93.6 \pm 2.9	35.5 \pm 4.8	
		1:20	93.3 \pm 1.6	36.7 \pm 2.4	
	1:10	1:5	98.4 \pm 0.9	38.1 \pm 4.3	
		1:10	99.2 \pm 2.9	40.3 \pm 2.3	
		1:20	98.8 \pm 2.0	43.9 \pm 8.3	
	1:20	1:5	98.4 \pm 0.8	42.1 \pm 7.1	
		1:10	99.2 \pm 1.5	44.9 \pm 7.9	
		1:20	99.0 \pm 1.7	46.5 \pm 4.2	
Cotton	1:5	1:5	68.7 \pm 3.4		7.3 \pm 3.7
		1:10	71.0 \pm 7.5		6.7 \pm 2.3
		1:20	79 \pm 7.5		6.7 \pm 1.8
	1:10	1:5	77.8 \pm 2.3		10.1 \pm 0.9
		1:10	81.4 \pm 5.0		13.4 \pm 1.2
		1:20	85.4 \pm 5.8		15.8 \pm 2.7
	1:20	1:5	86.3 \pm 2.3		18.6 \pm 2.2
		1:10	90.4 \pm 3.8		22.2 \pm 5.5
		1:20	91.7 \pm 2.2		22.0 \pm 2.3

5.7 Biodegradability

5.7.1 COD and BOD₅

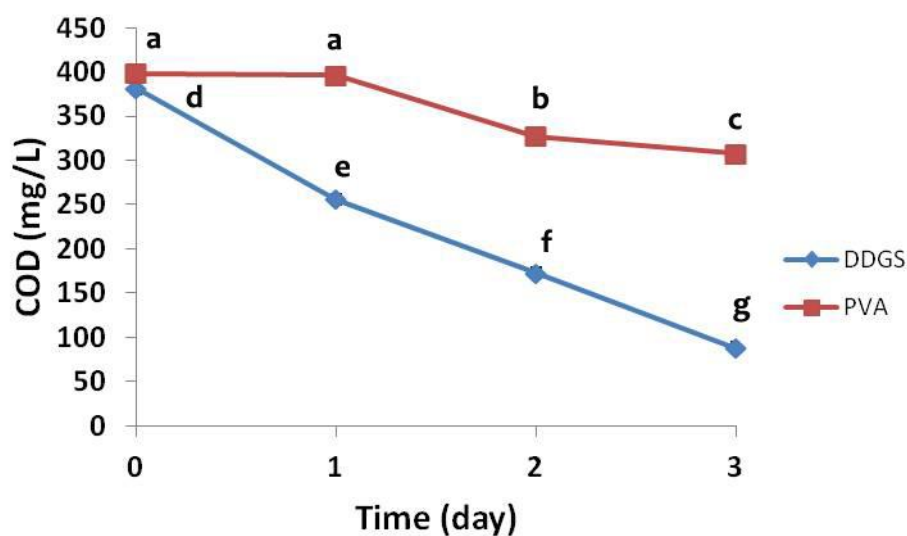


Figure 12 COD of DDGS and PVA (300 mg/L) treated in activated sludge

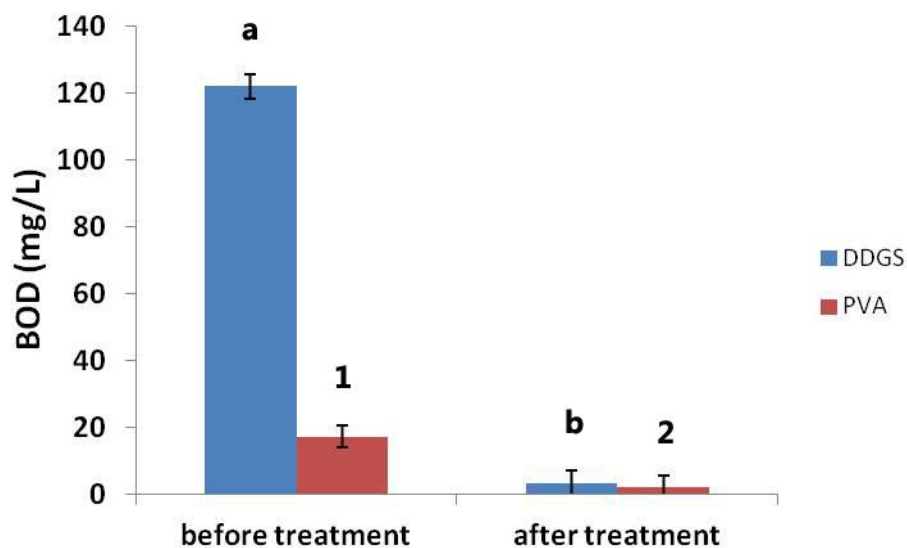


Figure 13 BOD₅ of DDGS and PVA (300 mg/L) before and after treatment in activated sludge

PVA has quadratic time effect on COD, but no material liner or quadratic effect;

while DDGS has quadratic time effect by material effect. The regression equation of DDGS (16) and PVA (17) were shown below.

$$\begin{aligned} \text{COD DDGS} = & 409.95 - 32.9529 * \text{DDGS} - 25.2471 * \text{day} - 99.9203 * \text{day} * \\ & \text{DDGS} - 4.1667 * \text{day} * \text{day} + 14.2667 * \text{day} * \text{day} * \text{DDGS} \end{aligned} \quad (16)$$

$$\text{COD PVA} = 409.95 - 25.2471 * \text{day} - 4.1667 * \text{day} * \text{day} \quad (17)$$

For the first three days, organic substance in DDGS extracted was largely deduced by micro organism in the sludge. Digestible proteins, amino acids hydrolyzed by sodium hydroxide, oil in DDGS are nutrients for the micro-organisms in the sludge. However, after three days' digestion, most of the nutrition was consumed, so for the first three days, COD decreased 75% from the original value.

COD of PVA commercial size decreased 30% from the original value, after 3 days and did not decrease further. Based on BOD₅ value of 1.25 on the third day it was determined that PVA not degradable Commercial PVA size contains other materials, like wax, which can be degraded during the initial three days, but most part of the commercial PVA size is non-degradable.

5.7.2 Total Nitrogen and ammonia

The total nitrogen curve trend of DDGS most is similar to the COD curve trend, which is decreases sharply in the first two days, and remains about 6 mg/L for the following days. All the proteins in DDGS and amino acids need nitrogen to form their structures. Amino acids and digestible proteins are fed by bio-organisms easily, but

small parts of the proteins are hard for the micro-organisms to utilize, which was reflected by the non-degradable nitrogen.

The regression equation of DDGS (18) and PVA (19) were shown below.

$$\begin{aligned} \text{Total nitrogen DDGS} = & 27.4041 - 4.9154 * \text{DDGS} + 0.01881 * \text{day} - \\ & 13.3232 * \text{DDGS} - 0.1924 * \text{day} * \text{day} + 2.7967 * \text{day} * \text{day} * \text{DDGS} \end{aligned} \quad (18)$$

$$\text{Total nitrogen PVA} = 27.4041 + 0.01881 * \text{day} - 0.1924 * \text{day} * \text{day} \quad (19)$$

PVA has quadratic time effect on total nitrogen, but no material liner effect; while DDGS has quadratic time effect by material effect.

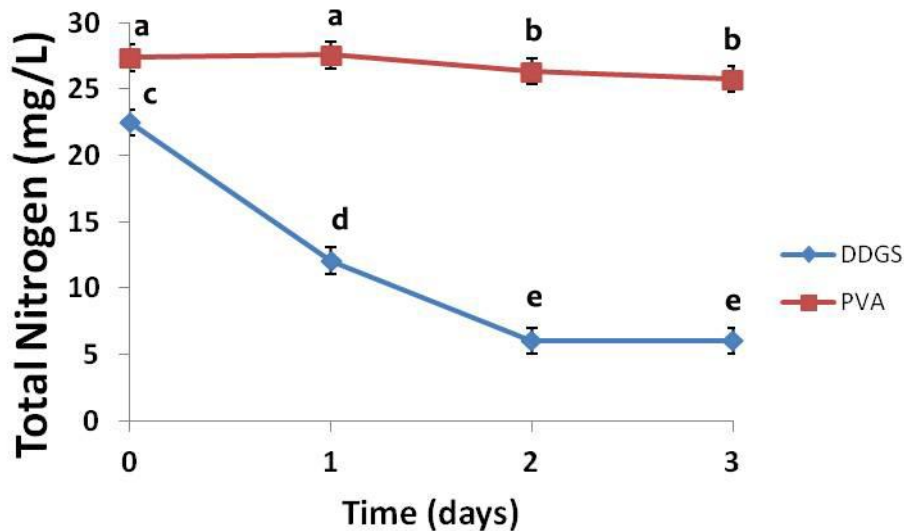


Figure 14 Total Nitrogen released from DDGS and PVA (300 mg/L) when treated in activated sludge.

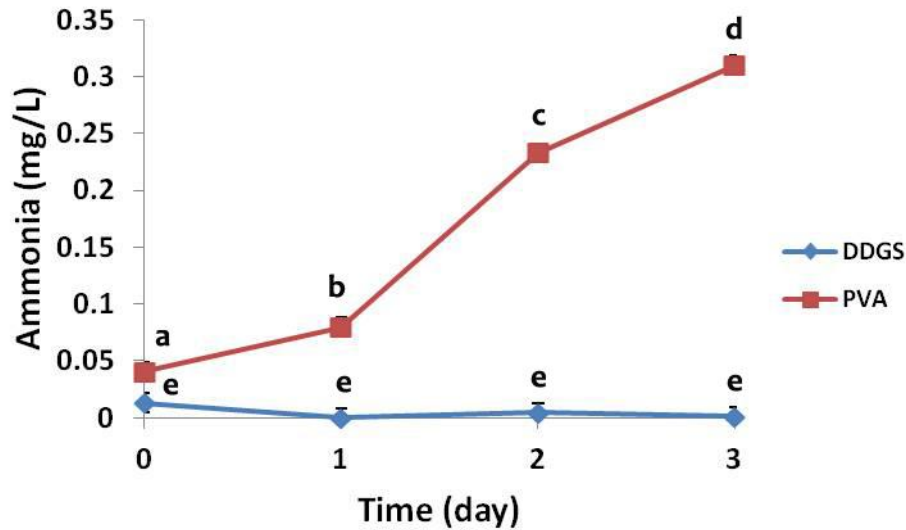


Figure 15 Ammonia released from DDGS and PVA (300 mg/L) when treated in activated sludge

The regression equation of DDGS (20) and PVA (21) were shown below.

$$\text{Ammonia DDGS} = 0.02291 - 0.01334 * \text{DDGS} + 0.07327 * \text{day} - 0.07953 * \text{day} * \text{DDGS} + 0.009442 * \text{day} * \text{day} - 0.00830 * \text{day} * \text{day} * \text{DDGS} \quad (20)$$

$$\text{Ammonia PVA} = 0.02291 + 0.07327 * \text{day} + 0.009442 * \text{day} * \text{day} \quad (21)$$

PVA has quadratic time effect on ammonia, but no material linear effect; while DDGS has quadratic time effect by material effect. The result shows the same as COD and total nitrogen.

For the ammonia figure, both PVA and DDGS have low ammonia value. Anaerobic organism might turn nitrogenous compounds into ammonia in oxygen-deficient environment. But in our experiments, sludge contained aerobic

bacteria and aerated, so they would use proteins or amino acids as their nutrition or could turn the protein into nitrates.

The low levels of total and ammonia nitrogen released from DDGS after 3 days of treatment in activated sludge indicate that DDGS will not adversely impact the operation of the effluent treatment plants.

CHAPTER 6: CONCLUSIONS

The potential of using DDGS as a textile warp sizing agent has been studied. Various extraction conditions were used to extract the proteins and carbohydrates from DDGS as sizing agents. The effects of DDGS extraction conditions on the adhesion, fabric abrasion resistance, film properties, viscosity and biodegradability were studied in comparison to commercially used PVA size and to starch. DDGS had better cohesion on poly/cotton fibers, and provided superior strength on poly/cotton roving. However, the abrasion resistance on polyester is higher than P/C and cotton fabrics sized by DDGS size. DDGS size was easily removed on fabrics (>90% removal) even with low amounts of water at room temperature. Unlike PVA, DDGS were easily biodegradable in activated sludge and the nitrogen in the proteins in DDGS did not adversely impact the biodegradability. Performance of sized materials, relatively easy biodegradability and simplicity in preparing the DDGS size are some of the advantages that promote the replacement of PVA with DDGS for textile warp sizing.

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	BOD5/COD
DDGS	0.29
PVA	0.04