THESIS

USE OF NOVEL POLYSACCHARIDES IN TEXTILE PRINTING

Submitted by

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ABSTRACT

USE OF NOVEL POLYSACCHARIDES IN TEXTILE PRINTING

Polysaccharides such as starches are utilized in textile applications for sizing, textile printing as a thickener, finishing agent and textile coating. Good sources of starch are corn, potato, maize and cereals such as millet and sorghum. In the United States, proso millet (*Panicum miliaceum*) and sorghum (*Sorghum bicolor L. Moench*) are two economically important crops, yet the current utilization of proso millet and sorghum are in low-end uses such as bird seed and livestock feed. This research is directed at utilizing starch extracted from proso millet and sorghum for value-added application in textile industry such as thickeners in textile printing.

The current work described in this thesis discusses an optimum method of extracting starch from both proso millet and sorghum cereal grains followed by characterization of starch using different physicochemical techniques like XRD, DSC, amylose content, spectrophotometric analysis of starch color, paste clarity analysis, rheological analysis, shear stability, stability to storage and starch swelling capacity. The starches were then incorporated as a thickener in a textile print formulation and print quality was evaluated on the basis of crocking fastness, bending length and washing fastness. The color depth of the textile print was determined according to the Kubelka- Munk equation.

The results of the detailed analysis of the starches show that both proso millet and sorghum could be utilized effectively as thickeners in textile printing. Both starches had desirable properties of a good thickener such as excellent paste clarity, adequate viscosity and high solubility and crystallinity. The properties of the printed textiles using millet and sorghum

starches were comparable to that of sodium alginate thickener further demonstrating the potential of these grains in value-added applications.

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CHAPTER 1

INTRODUCTION

1.1. Polysaccharides and textile printing

Polysaccharides are long repeated carbohydrate molecules joined together by glycosidic bonds. They are quite heterogeneous, containing slight modifications of the repeating unit. Polysaccharides range in structure from linear to highly branched. Depending on the structure, these macromolecules can have distinct properties from their monosaccharide building blocks.

An excellent example of a polysaccharide is starch. Starch is a storage polysaccharide in which the glocopyranose units are bonded by alpha linkages. Starch is an abundant carbohydrate distributed in green plants, where it accumulates as microscopic granules. It is a food reserve that sustains initial plant growth. Starch is and has been an important ingredient of human diet mainly as a high calorie food source (Zobel, 1992). It is also an essential component in food products such as a thickener, stabilizing and gelling agent and is also used in manufacturing of paper and textile products (Slattery, Kavakli, & Okita, 2000; Wurzburg, 1999). In addition to its use in human consumption, it has become a very important biopolymer and is used in many industries as a feedstock material. Cereal grains such as millets and sorghum are a good source of starch.

Textile printing is the process of applying color to textile substrate in defined patterns or designs. It is similar to dyeing in the dye-fiber bonding aspect but printing is a form of "localized dyeing" where colors are restricted to the design areas on the printed textile. A thick paste of dye is used in printing to prevent the color from spreading to unwanted areas by capillary effect and therefore the role of a thickener in printing is critical to its success. A textile thickener is defined as "a colorless, viscous paste made with one or a combination of thickening agents" (Miles,

2003). There are several different thickeners used in the textile printing industry such as polysaccharide- based thickeners (starch, British gum, cellulose ethers), emulsions of oil and water and synthetic polymer thickeners. Textile processing generates huge quantities of waste and pollution and this is true also in textile printing. Pollution in textile printing is caused by emissions of hydrocarbons, ammonia and other volatile organic matter (Pravathi, Maruthavanan, & Prakash, 2009). Synthetic polymer thickeners induce pollution in the environment in the form of these harmful emissions and toxic waste materials which cannot be degraded and assimilated into the environmental cycle (Qu, 2005). Starch thickeners by contrast are not only eco-friendly and sustainable but also an effective printing additive. The purpose of this investigation is to explore novel sources of polysaccharide thickeners for textile surface printing with minimal environmental waste and pollution.

1.2. Proso Millet

"*Millet*" is the term used for several small seeded annual grasses (Lorenz & Dilsaver, 1980a). Millets originated in eastern or central Asia and were important in Europe during the Middle Ages before the cultivation of corn and potatoes. Millets can adapt to various different climatic conditions and a wide range of soil types and require low moisture to grow. They are thus important crops in semiarid regions, due to their short growing season (Schery, 1963). There are five different species in the millet family that are of economic importance. Table 1 illustrates the different members of the millet family. Of all the millet species, proso grain millet is the primary millet in the world import and export market and is the only millet that is globally traded (Wietgrefe, 1989). Proso millet is also the only species of economic importance in the United States (Lorenz & Dilsaver, 1980a).

Table 1: Different species of Millet family (Lorenz & Dilsaver, 1980a)

Species	**Common names**
Setaria italic	Foxtail millet, Italian millet, German millet, Hay millet
Panicum miliaceum	Proso millet, Common millet, Hershey millet, Hog millet, White millet, Broomcorn millet
Frumentaceae	Japanese millet, Barnyard millet
Pennisetum americanum	Pearl millet
Eleusine coracana	Finger millet

Proso millet (*Panicum miliaceum*), which is also called hog millet, yellow hog, hershey or broom corn, belongs to the Gramineae family. There is evidence that it was cultivated in China from as long ago as 5000 B.C., making it one of mankind's most ancient cultivated crops (Lagler et al, 2005). It can grow well under arid, semi-arid conditions and requires low soil fertility. Most of the U.S. proso millet crop is produced in Colorado, Nebraska and South Dakota, with Colorado typically producing over 50% of the crop. Farmers use proso millet in three year and five year rotation systems in combination with wheat, to control infestation of annual weeds (Nelson & Daigger, 1975). In 2010, total U.S. production of proso millet was 11.5 million bushels from a harvested area of 363,000 acres. The average yield in 2010 was 31.8 bushels per acre. The total value of proso millet production was $48.6 million. The price was

$4.21 per bushel, an increase from $2.87 per bushel the previous year (Boland, 2011). Currently, proso millet produced in the United States is used primarily for birdseed and livestock feed; uses that are arguably at the lower end of commercial value. Compared to other cereal grains, limited research has been conducted on millets as a value added product for other end uses (Lorenz & Dilsaver, 1980b). It is for this reason that this research focuses on proso starch as one novel thickener with potential use in textile printing.

1.3. Sorghum

Sorghum (*Sorghum bicolor L. Moench*) is the fifth largest produced cereal in terms of acreage (Taylor, Schober, & Bean, 2006; Udanchan, Sahoo, & Hend, 2012). It is a staple food crop for millions of people in semi-arid tropical countries of the world. It is mostly grown as a subsistence dry land crop by resource limited farmers under traditional management conditions in regions of Africa, Asia and Latin America, which are frequently drought-prone and characterized by fragile environments.

Sorghum is used mostly for animal feed with only a small part used for food and industrial purposes (Rooney & Waniska, 2000). Production of sorghum in 2007-2008 in the world was 64 Million Metric Tons (USDA, 2012). Leading sorghum producing countries were United States (19.9%), Nigeria (15.5%), India (11.3%), Mexico (9.8%), Sudan (7%), and Argentina (5.4%) (USDA, 2012). India grows the largest acreage of sorghum in the world followed by Nigeria and Sudan (Udanchan et al, 2012). In the United States, major producers of sorghum are Texas, Kansas, Colorado and Nebraska (USDA, 2012). Inspite of being a major cereal grain and having the same general composition of corn, sorghum is currently used mainly as animal feed due to some of the shortcomings of the grain such as high fiber content, pronounced flavor and grittiness in flour. But due to its high starch content and economical

availability, significant opportunities exist for increased utilization of sorghum in other applications such as a thickener in textile printing.

CHAPTER 2

LITERATURE REVIEW

The literature review discusses the general properties of starch including proso millet and sorghum starches followed by descriptions of extraction and characterization techniques of starch from proso millet and sorghum. The review continues with a discussion on textile printing methods including requirements of a printing paste and properties of good thickeners. Gaps in literature are identified and a case for the research is presented.

2.1. Starch

In plants, starch is found in a semi-crystalline granular form that has a complex organization and structure. At an elementary structural level, it is organized in alternating amorphous and crystalline shells which are 100-400 nm thick as seen in Figure 1 (Gallant, Bouchet, & Baldwin, 1997; French, 1984; Yamaguchi, Kainuma, & French, 1979). Starch is a mixture of two types of polymers which are structurally different α-D-glucose molecules: amylose and amylopectin. In amylose, the glucose units are arranged in a linear chain arrangement and it contributes to thirty percent of the storage starches, whereas in amylopectin, the glucose units are branched and contributes to seventy percent of the storage starches.

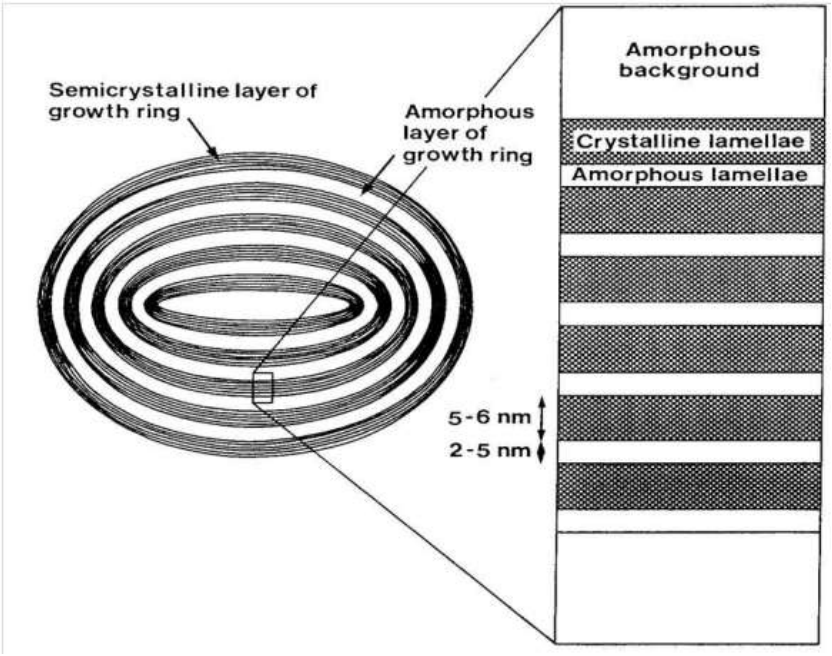

Figure 1. X-ray diffraction pattern of the starch molecule showing alternated amorphous and semi- crystalline lamellae (Asare, 2011).

2.1.1. Amylose

Amylose is the name given to linear sections of the starch molecule consisting of α-1, 4 linked glucose units (Figure 2). It can form an extended shape of hydrodynamic radius ranging from 7-22 nm (Parker & Ring, 2001). But as seen in Figure 3, it generally tends to wind up into a rather stiff left-handed single helix or form even stiffer parallel left-handed double helical junction zones (Imberty, Chanzy, & Perez, 1988). Amylose can be identified by its characteristic binding to chains of charged iodine molecules where each turn of the helix holds about two iodine atoms and a characteristic blue color is produced due to donor-acceptor interaction between water and the electron deficient polyiodides (Parker & Ring, 2001).

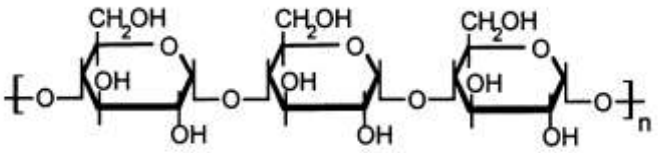

Figure 2. Chemical structure of Amylose (Rojas & Neuman, 1999).

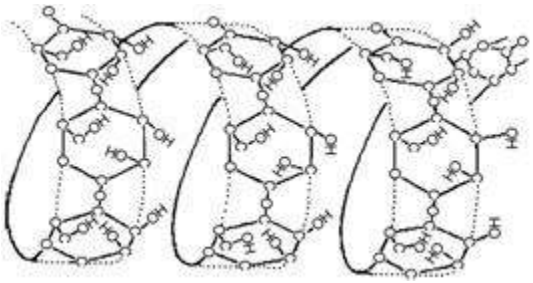

Figure 3. Helical structure of amylose (Wang, Li, Che, & Li, 2010).

Amylose content of starch granules contributes towards many properties of the starch. Higher the amylose content, the lower is the swelling power and more is the amorphous nature of starch granules. For the same starch concentration, highly amorphous starch granules have lesser paste clarity and smaller gel strength as compared to less amorphous starch. To a certain extent, however, a smaller swelling power due to high amylose content can be counteracted by a larger granule size (Li & Yeh, 2001). Amylose has the most useful function as a hydrocolloid because its extended conformation causes the high viscosity of water-soluble starch and varies very little with temperature. The extended helical chains possess a relatively hydrophobic inner surface that is unable to hold water and can be easily replaced by more hydrophobic molecules such as fats, lipids and aromatic compounds. Amylose is useful in the form of gels and films. Its association and crystallization on cooling and storage decreases the storage stability which causes shrinkage and release of water (synersis).

2.1.2. Amylopectin

Amylopectin is formed by non-random α-1--->6 branching of the amylose-type α-(1->4)-D-glucose structure (Figure 4). Each amylopectin molecule contains up to two million glucose residues in a compact structure with hydrodynamic radius 21-75 nm (Parker & Ring, 2001). The molecules are oriented radially in the starch granule and as the radius increases so does the number of branches required, filling up the space, with the consequent formation of concentric regions of alternating amorphous and crystalline structure (Figure 5). Amylopectin is responsible for retrogradation. Retrogradation is the thermochemical process of reorganization of starch molecules and formation of additional bonds after heat treatment of starch (Fechner, Wartewig, Kleinebudde, & Neubert, 2005). It is a characteristic behavior of starch– water systems which increases the rigidity of a starch paste. Storage and cooling of starch pastes increases the retrogradation and water is pushed out of the cells causing watery areas in the starch paste. Amylopectin also interferes with the interaction between amylose chains and thus a high-amylopectin starch solution can have an initial loss in viscosity followed by a more slimy consistency. Amylopectin is responsible for a characteristic red-brown color in the presence of free iodine molecules and for the increase in paste clarity, high crystallinity and more solubility.

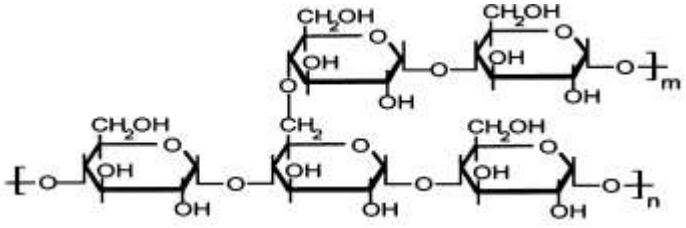

Figure 4. Amylopectin (Branched chain compound) (Rojas & Neuman, 1999)

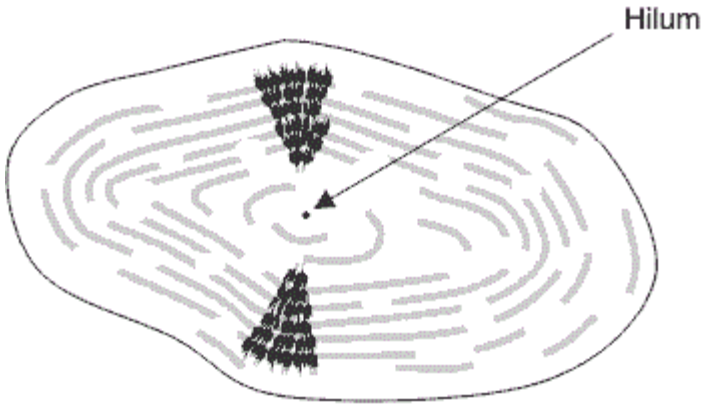

Figure 5. Starch molecules radially oriented with growing branches and central hilum (Wang et al., 2010).

2.2. Starch and cereal grains

The proso millet seed contains approximately 15% protein, 72% starch, 0.5% sugar, 3.9% fat, 0.5% cellulose and 1.2% minerals. Due to the high starch content, it is used as a raw material in processing industries (Hulse, Laing, & Pearson, 1980). Sorghum grain contains starch ranging from 68-75% depending upon cultivar, region and climatic conditions (Subramanian, Hoseney, & Bramel-Cox, 1994; Shinde, 2005; Singh, Singh, Sodhi, & Singh, 2009). The sorghum starch is unique among carbohydrate classes because it occurs naturally as discrete particle/granules (Watson, 1984).

2.3. Extraction and Characterization

There are different extraction techniques employed for isolation and processing of proso starch and sorghum starch. They differ from each other in terms of the pH at which the grains are steeped. The acidic wet milling technique illustrated by Nerying and Reilly (1984) was originally formulated for corn, but has been also tested for proso millet starch extraction. This method of isolation is carried out using sulfur dioxide solution in the steeping stage, which is the first stage of isolation of starch. In the raw grain, the starch granules are embedded in a protein network

which swells during the steeping stage and tends to form tiny globules of protein (Radley, 1951 and 1952). Sulphur dioxide is utilized to accelerate the separation of starch from the proteins in the proso grains. The separation effect of sulphur dioxide, in the steep water, is due to its reducing property and not due to its acidic property (Cox, MacMasters, & Hilbert, 1944). Sulfur dioxide is also used to prevent the growth of microbes in the steep, thus bringing about a sterilizing effect. Alternatively, the alkaline isolation method by Juliano (1984) was originally used for rice starch preparations, in which an alkali was used for steeping and steeping times were shorter. Due to the similarity between the microscopic size and shape between the proso starch and rice starch, this method was chosen for the current research. The yield of starch depends on the steep temperature and the concentration of alkali. With a few modifications, these extraction techniques can also be utilized to extract sorghum starch (Bartling, 1939; Starr, 1949; Kerr, 1950; Singh et al., 2009).

Characterization is a process of evaluation of substances, processes or environment and is performed to determine their nature and reactivity. This process is an essential part of describing characteristics of any chemical substance involving numerous physicochemical experiments to which the substance is subjected to in order to gain information regarding its reactivity and physical state. The amylose and amylopectin content of starch is characterized because they influence the behavior of starch under stress, its viscosity gradient, swelling power, gelatinization temperature, the extent of crystallinity and gel firmness (Tester & Morrison, 1990; Choi & Shin 2004; Thongngam & Chanapamokkhot, 2007).

2.4. Textile Printing

The process of addition of color in a restricted area to form a colored pattern is called printing. The term ‘printing’ was coined in the 18th century and is derived from a Latin word

meaning pressing (Storey, 1992). The production of such colored designs on textile substrate is called textile printing and is one of the cheapest methods of ornamentation of fabrics. It is a branch of dyeing and can be generally defined as 'localized dyeing' where confined portions of fabric are dyed. In textile printing, color is applied in the form of thick paste and dye is present in the concentrated form. There are 5 basic steps of printing that are as follows (Rupin, 1976):

1. The preparation of the fabric
2. The preparation of the printing paste
3. Making an impression (printing)
4. Fixation of the dried prints
5. After-treatment

Printing can be classified either by methods of printing or styles of printing. Method of printing is a means of transferring a design to a textile substrate. The various methods of printing are block printing, stencil printing, hand screen printing, automatic flat-bed screen printing, rotary screen printing, roller printing and transfer printing. Style of printing describes the means of application of the dye to the material. Direct style, resist style and discharge style are the main styles of printing. For this research, screen printing with five vertical stripes was used and therefore this method of printing is reviewed in detail.

2.4.1. Screen Printing

Screen Printing is fundamentally a form of stencil printing. The screen consists of a synthetic fiber or metal gauze stretched taut over a frame. Parts of the gauze have the holes blocked off (no-printing area) and the printing paste is forced through the open printing areas by a rubber or metal blade, called a squeegee, and on to the fabric beneath. In hand

screen printing the fabric is pinned to the printing table, which is covered with a resilient felt, wax cloth or rubber material (Clark, 1977). Each screen is placed on the fabric in turn, the paste applied to one end of the screen and the squeegee drawn by hand through the paste and across the screen, forcing it through the open mesh areas on to the fabric beneath. Guide rails along the edges of the table ensure each screen is applied in register. Although the highly skilled printer can produce good quality prints by a hand screen technique, the production rates are extremely slow, therefore automatic screen printing machines have been developed (Dawson, 1992). There are two main types of automatic screen printing processes; flat-bed screen printing and rotary screen printing.

2.4.1.1. Flat -bed screen printing

The fabric is now in a continuous length, the immobile hand printing table being replaced by an endless conveyor belt as shown in Figure 6. All the screens making up the pattern are arranged side by side above this belt and the belt is automatically set to move forward by one or several patterns repeats at a time (Jacobs, 1952). When the belt is stationary the screens are lowered, the colors are applied to the fabric and the screens are lifted for the belt to move the fabric on to the next repeat. Color is pumped or hand-fed on to each screen and the squeegee movement is mechanized.

Figure 6. Automatic Flat-bed Screen printing machine (Hawkyard, 1994)

Two main types of squeegee system are used in the flat-bed machine. Either a conventional squeegee blade is driven forwards or backwards across the screen by a motor, or the squeegee is a small-diameter roller bar which is attracted to and rolled over the screen by a powerful electromagnet moving beneath the printing blanket (Hardalov, Velev, & Gluharov, 1992).

2.4.1.2. Rotary Screen Printing

Flat-bed screen printing is an intermittent printing method and so cannot compete with roller printing in terms of its productivity. Rotary screen printing has been developed as a fully continuous screen-printing technique to rival engraved roller printing. Rotary screen printing uses seamless cylindrical screens which are composed of a nickel mesh with end-rings soldered or stuck on to tension the cylinder and prevent collapse (Knecht & Fothergill, 1952) .Each rotary screen is positioned across the fabric and is independently driven at one end (Figure 7). As the screen rotates, it is fed internally with print paste which is forced through the open mesh areas by a stationary squeegee at the base of the screen and on to the fabric being carried beneath by the continuously moving metal or polymeric

blade, or against a metal bar held against the base of the screen by a stationary electromagnet beneath the printing blanket.

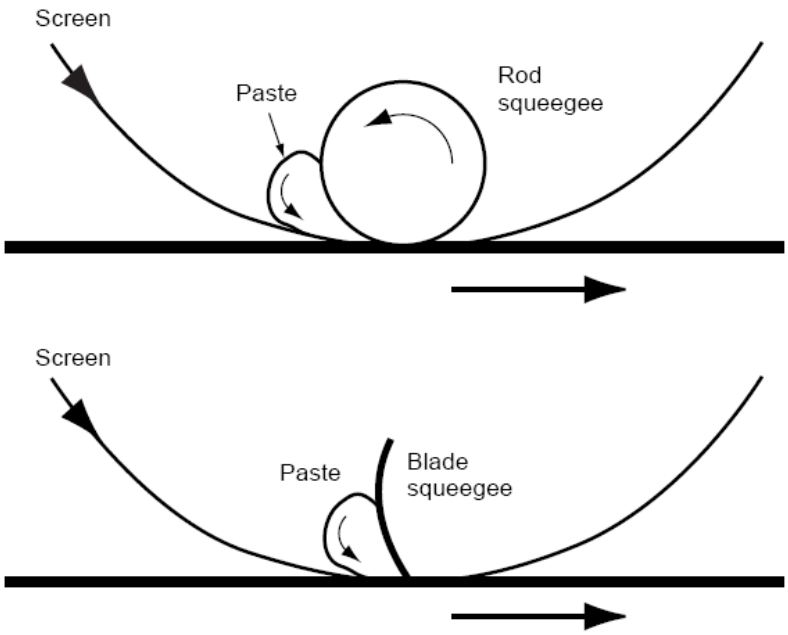

Figure 7. Rotary Screen printing (Hawkyard, 1994)

On most modern screen-printing machines, fabric is dried by a conveyor passage through a hot-air dryer. On both the flat-bed and rotary screen machines, the positioning of each screen can be very precisely controlled to ensure correct registration of the pattern.

2.4.2. Properties of printing paste

The mechanism of dye fixation on fabric is the same in both dyeing and printing. But the dyes that are used in a print paste should have a high solubility because the amount of water in the print paste is severely limited and at the fixation stage, the dye must be re-dissolved in a

small volume of condensed steam. The specifics of print paste formulation depend on the fiber content of the fabric, the colorant system used, the fixation method used and to some extent, the type of printing machine employed (Trotmann, 1984). However, the typical ingredients found in most paste formulations include the following: dyes or pigments, thickeners, sequestering agents, dispersing or suspending agents (surfactants), water-retaining agents (humectants), defoamers, catalysts, and hand modifiers. In addition to the ingredients, pigments require a binder or resin system to fix the pigment and may include adhesion promoters.

2.4.2.1. Dyes and Pigments

The most important ingredients of any print paste formulation are the colorants and the thickener system. Different dyes have affinity to different fibers. The fabric substrate to be used for this research is 100% cotton print cloth. Dyes that are usually used for printing on cellulose fabrics are reactive, vats, naphthols, and direct. Reactive dyes dominate the dyes used for printing these fibers, because of their wide shade range, bright colors, good wash fastness, and good availability. Vat dyes are also quite popular for textile printing. They usually have very good overall colorfastness properties, but have a limited shade range and are available in mainly deep colors such as violets, blues, and greens. Naphthols or azoic coupling components are unique in that the dye is actually made through a reaction of two separate chemicals inside the fiber. The typical method uses a stabilized naphthol and coupling component print paste mixture printed onto the fabric then exposed to an acid steaming to develop the color. These are known as the rapid fast or rapidogen colors. The use of naphthols is limited due mostly to application complexity. For all of these dye systems for cotton, thorough after-washing is essential for good crock fastness and wash fastness (Storey, 1992).

Pigments are not dyes, but are colored particles that are bound to the surface of the fabric

using a chemical. Thus, a main difference between dyes and pigments is that dyes chemically bond with the fibers by penetrating the fabric surface while pigments bond only with the surface of the fabric without penetrating it. Once applied, fixation of a pigment color requires dry heat for a defined amount of time. The colorfastness of pigments directly depends on the binder system employed. Binders are chemicals, which have the ability of forming a three-dimensional film used to hold the pigment particles in place on the surface of a textile substrate (Dawson, 1992). Binders can be water-based or solvent-based and vary widely in their stiffness. The major drawbacks of pigment prints include poor crock fastness and stiffening of the fabric.

2.4.2.2. Thickeners in textile printing

The thickener system is the crucial component of the print paste. The purpose of the thickener system is two-fold. First, the thickener gives the print paste the proper viscosity or flow characteristics, so the color can be applied uniformly and evenly. Second, it holds the color in place so that one color paste can be applied adjacent to another without the color bleeding onto the other. With dyes, the thickener also holds the color in place after drying until the printed fabric goes through the fixation process where the dye is released from the thickener and is diffused into the fiber. There is a wide range of thickener materials available including alginates, natural vegetable gums, synthetic polymers, or even foams (Miles, 2003). A criterion of choosing the appropriate thickener for a printing system is that it should not react with the dye/pigment in the system. For example, starch thickeners are generally not used in a reactive dye printing paste because much of the dye will react chemically with the thickener rather than the textile substrate. Therefore, sodium alginate is used in place of starch with reactive dyes (Rupin, 1976). Sodium alginate (Figure 8) is a commercial textile printing thickening agent that is derived from brown *Phaeophycae* seaweeds. This thickener primarily has alginic acid that is

extracted from the seaweed using sodium carbonate (Miles, 2003). Sodium alginate is an important thickener for reactive dye printing systems because it has minimum reactivity towards the dyes due to the absence of primary hydroxyl groups. Also under alkaline conditions, the ionized carboxyl groups of sodium alginate repel the dye anions, further decreasing the dye-thickener reactivity.

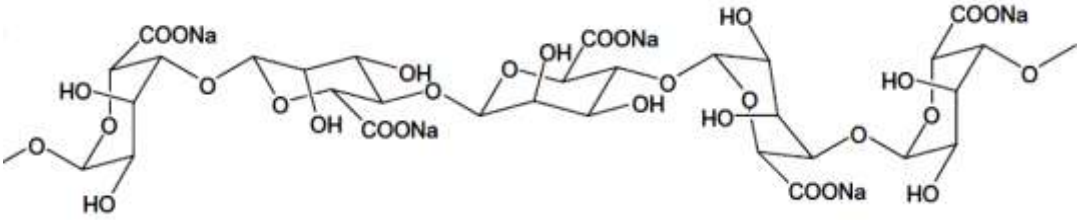

Figure 8. Structure of sodium alginate (Huang, Tan, Zhou, Wang, & Che, 2008)

Thickeners used with dyes are washed off the fabric before any chemical or mechanical finishing is performed. However, the thickener applied with a pigment system remains with the print as no after washing is required.

2.4.2.3. Evaluation of printed textiles

A fabric's ability to retain its original color is one of the most important properties of a textile product. Thus after printing, it is essential that the quality of the print be evaluated by performing various standard textile tests. The tests are chosen to simulate conditions to which the fabrics would be subjected while in an environment of standard use. These tests are the standard means to determine the stability of a dye to washing and abrasion. The thickener in the printing paste should be washable and should not stay or react with the fabric because it will change the hand and feel of the fabric. To evaluate the hand of the fabric a bending length test is performed that tests the stiffness of the fabric.

2.4. Gaps in literature

Most of the studies in recent years have focused on analyzing different varieties of starch extracted from popular cereals like corn, potato, maize, wheat and rice. The starch from the aforementioned cereals are mostly studies in context of application in food sciences and only a small body of literature dealing with textile-related end uses is available. Proso millet and sorghum are fairly new recognized sources of starch and are still being characterized for use in various applications. Consequently, the methods of extraction of starch from these sources are not customized to the cereal's unique properties. These cereals have never been studied in the context of application as a textile print paste thickener which makes this study unique in its approach.

The goal of the investigation was to optimize an extraction technique for extraction of starch from proso millet and sorghum grains followed by characterization of the extracted starch using a variety of physicochemical techniques. The characterization of starch will further knowledge on the degree of compatibility of the starch with other print paste auxiliaries and aid the choice of modification of the starch molecule to increase the compatibility. Upon the completion of characterization of extracted starch granules, the next step was to use the extracted starch as a thickener in a conventional print paste recipe. The resultant print quality was analyzed for its performance on the basis of crock fastness, bending length, washing fastness and depth of the color using the Kubelka- Munk equation. This study will enable the new sources of starch (proso millet and sorghum) to be used in a commercial high value end use and will help make production of these grains more profitable thus benefitting farmers in Colorado and other states.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Proso millet (*Panicum miliaceum*) grains of the "plateau" variety and Sorghum (*Sorghum bicolor L. Moench*) grains were used for this study. A 100% cotton print cloth was used as the textile printing substrate (TestFabrics Inc., USA). The equipments used for textile screen printing were pre-designed screens, squeegees and other materials (Silk Screen Supplies). Standard reagent grade chemicals and dyes were used for printing and testing.

3.2. Methods

3.2.1. Extraction

The starch samples from both proso millet and sorghum grains were extracted using the alkaline steeping method as described by Juliano (1984). The cereal grains were milled in a Warring blender and steeped in 2.5% (w/w) solution of NaOH for 24 hours. The supernatant was drained and the rest of the residue filtered through a 40 mesh screen. This process was repeated two additional times and the resultant slurry washed, filtered through a 200 mesh screen, washed with distilled water and centrifuged at 4000-5000 rpm for 10 minutes. The upper dark gluten-rich layer was then scraped out and discarded and the remaining solids washed, filtered and dried to obtain pure starch granules. The weight of each sample was measured and recorded.

3.2.2. Characterization

The characteristics of the extracted starch samples were determined by employing the following methods.

3.2.2.1. Determination of Crystallinity using X-Ray Diffraction

X-Ray Diffraction analysis is a method done to determine the changes in crystallinity throughout a sample. About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (phase), a diffraction pattern is obtained. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance (Wei et al., 2011). The diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The main use of diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. In an X-ray diffraction measurement, a crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup. The X-ray diffraction analysis was carried out using a Scintag X2 Theta-Theta X-Ray Powder Diffractometer (Scintag Inc), at an angular (θ -2θ) range of 4˚ - 50˚, with a 1 second wait time between angles.

3.2.2.2. Estimation of color of starch powder using Spectrophotometer

The natural color of the starch is an important feature that can affect the decision of selection of the starch sample for a particular end use. For use in textile printing, color of starch is an important physical attribute. Starch that has a bright white color appearance is useful because it ensures that the color characteristic of the print on the fabric is influenced only by the color of the dye used in the print paste and not the starch thickener. In this study, the color of the extracted starch samples was analyzed using a HunterLab ColorQuest XE spectrophotometer and the characteristic color of each variety of cereal type was obtained on the basis of the CIE Whiteness index.

3.2.2.3. Determination of swelling power of starch granules

The swelling power of starch granules is determined as the ratio in weight of the wet sediment to the initial weight of the dry starch and is reported in terms of g/g (Subramanian et al., 1994). A gram of starch was heated with 30 ml of water to 95°C for one hour using a mechanical shaker. Lump formation was prevented by using a magnetic stirrer. The mixture was then centrifuged at 1600 X g (rcf) for 10 minutes. The supernatant solution was carefully removed and the swollen starch sediment was weighed (Leach, McCowen, & Schoch, 1959).

3.2.2.4. Iodine binding capacity of starch

The amylose content of starch samples is determined colorimetrically by assessing the iodine binding capacity. This process was initially conducted to analyze milled rice starch and was modified to examine the two types of starch samples in this study. One hundred grams of sample was measured accurately into a 50 ml conical flask and a

solution of 1 ml of 95% ethanol and 9 ml of 1N NaOH was added to the flask. The sample was then heated for 10 minutes in a boiling water bath to gelatinize the starch. Mechanical shaking action prevented lump formation. This sample was cooled and transferred with several water washings into a 100 ml volumetric flask which was then brought up to volume with water and mixed well. Five milliliters of this starch solution was pipetted into a 100 ml volumetric flask in which a solution of 1 ml 1N acetic acid and 2 ml of iodine solution (0.2 gm. iodine and 2 gm potassium iodide in 100 ml aqueous solution) was later added. The solution was made up to volume with distilled water, shaken and left to stand for 20 minutes (Juliano, 1971). Absorbance of this solution was measured at 620 nm with the help of the HunterLab ColorQuest XE spectrophotometer. Distilled water acted as the reference standard and the amylose content was reported as a percent of light absorbed with reference to water. Amylose (starch) can bind molecular iodine due to the fact that sugar can form a helix, into which iodine fits to form a complex that produces a deep blue color. This chemical characteristic allows starch to be used as an indicator for titrations involving the reduction of iodine (Reddy, Subramanian, Ali, & Bhattacharya, 1994).

3.2.2.5. Thermal stability of starch paste

Thermal stability of starch paste is a physical property of the extracted starch which highlights the behavior of starch granules under the influence of heat and high temperature (Tatongjai & Lumdubwong, 2010). Gelatinization is one of the most important properties of starch when it is heated in excess of water. It is a phenomenon associated with starch which is practically a phase transition associated with transformation of granule crystalline phase in amorphous one, which causes irreversible

changes of different functional properties such as granule swelling power, solubility and loss of optical birefringence. Gelatinization occurs initially in the amorphous regions, as opposed to the crystalline regions of the granule because hydrogen bonding is weakened in these areas (Singh et al., 2003). Thus, the differences which can appear in transition temperatures for different kinds of starches may be attributed to the differences in the degree of crystallization. High transition temperatures have been reported to result from a high degree of crystallinity which provides structural stability and makes the granule more resistant towards gelatinization (Barichello, Yada, Coffin, & Stanley, 1990). Both gelatinization and swelling are properties partially controlled by the molecular structure of amylopectin (unit chain length, extent of branching, molecular weight, and polydispersity), amylose to amylopectin ratio and granule architecture (crystalline to amorphous ratio) (Tester & Morrison, 1990).

The enthalpy of gelatinization (Δ H) indicates the amount of thermal energy required in the process of gelatinization and also gives a determination of the temperature range where gelatinization occurs. This involves breaking of H-bonds between starch molecules and formation of new bonds involving water in an overall endothermic process. It was determined that the Δ H value increases with the amylopectin content of the cereal (Stevens & Elton, 1971). Differential scanning calorimetry (DSC) is known as an extremely valuable tool to characterize and control the gelatinization phenomenon of starch because it provides a quantitative measurement of the enthalpy, ΔH. In this study, the thermal properties of the extracted starch was analyzed by recording the Onset temperature (T_0), Peak temperature (T_p), Glass Transition Temperature (T_g), Conclusion

Temperature (Tc) and Heat-gelatinization (ΔH). The information that was obtained by this method is explained as follows:

Onset temperature (T_0): Determines the onset of any thermal transition that changes the baseline slope.

Peak temperature (T_p): determines the height of a peak relative to a linear baseline.

Conclusion temperature (T_c): Determines the end of the gelatinization process.

Glass Transition Temperature (T_g): Determines the transition temperature by calculating the onset, end and inflection of a step transition.

Heat-gelatinization (ΔH): This is the area under the peak in a plot of heat flow versus temperature. It is a phase transition of granules from an ordered state to a disordered one during heating in excess water. It involves melting of ordered regions, both on the crystallite and on the level of double-helical order (Herceg, Batur, Jambrak, Badanjak et al., 2010)

A differential scanning calorimeter was used to determine the thermal stability. Starch samples each of 3 mg (dry weight basis) was weighed in aluminum pan and 7.5 µl distilled water was added. The pan was sealed and left overnight at room temperature to attain equilibrium. The pan was then heated from 35 to 130°C at a rate of 10 °C/min (Fan & Marks, 1998). The thermal properties of the starch samples were analyzed by comparison of the peak temperatures (T_p) and gelatinization enthalpy (ΔH) with other commercial starch sources.

3.2.2.6. Rheological properties of starch paste

The viscosity of starch samples and the internal structural bonding can be determined by rheological analysis of starch solutions (El-Molla, 2000). Starch solutions

of 3% concentration were prepared by adding distilled water and the solutions were then cooked in a water bath for 15-20 min at 95°C with constant stirring to avoid lump formation. The gelatinized starch samples were then allowed to cool down and a Brookfield viscometer (Model DV-E) was used to determine the apparent viscosity in centipoise at a uniformly increasing shear rate of 5-50 rpm at a temperature of 25 °C (Ragheb, Haggag, & Abd El-Thalouth, 1989).

3.2.2.7. Paste clarity by spectrophotometer

The clarity of a starch paste in an important attribute of starch and can be altered by chemical modification of the granules. Light reflectance of pastes is closely related to optical homogeneity within swollen granules and therefore is an important factor to investigate (Craig, Maningat, Seib, & Hoseney, 1989). Paste clarity was determined by measuring the paste's transmittance rather than reflectance. High transmittance is desired in textile printing so that the paste used does not significantly alter dye color on a fabric. Starch pastes were produced by suspending 50 mg of starch (dry weight basis) in 5 ml water. The paste was placed in boiling water bath for 30 minutes. The solutions were then shaken thoroughly every 5 min and after cooling them to room temperature, the percent transmittance (%T) at 650 nm were determined using a HunterLab ColorQuest XE spectrophotometer with water as the standard solution.

3.2.2.8.Shear stability

In the presence of a shear force, starch pastes tend to lose their viscous stability and break down. The resistance against reduction in viscosity at high shear rates is termed as shear stability. Shear stability of millet starch and sorghum starch was determined for 5%

(w/w) aqueous starch suspensions which were equilibrated in a water-bath within 30 min at 95 °C at constant stirring (Praznik, Mundigler, Kogler, Pelzl, & Huber, 1999). Viscosity profiles were determined using a Brookefield Viscometer LVDE for increasing shear rates of 10 rpm, 20 rpm and again 10 rpm for 5 min at each speed. Shear stability is computed as the ratio of viscosity at the end of first period (end of 5 min at 10 rpm) (ηbefore) and viscosity after second period (ηafter) (end of 5 min at 10 rpm after 5 min at 20 rpm) of shear stress in terms of shear stability percentage: % Shear stability = (ηafter / ηbefore) x 100 .Closer the ratio is to 1, better the shear stability of the particular starch paste.

3.2.2.9.Storage stability

A useful characteristic of starch pastes is maintenance of viscosity upon storage. Storage stability of both the proso millet and sorghum starches was tested using Sanseethong, et al's (2006) method with a few modifications. A suspension of starch (15%, w/w) in distilled water was heated in a water bath at 95°C for 15 minutes with continuous stirring in the first 5 minutes. The starch paste was then maintained at 50°C in a temperature-controlled water bath. When the temperature of starch paste reached 50°C, the initial viscosity profile of the sample was determined with a Brookefield Viscometer at an increasing shear rate of 5-20 rpm. The temperature was regulated using a shaking water bath with an accuracy of $\pm$ 1°C. The viscosity stability of starch paste was determined by measuring the viscosity of the sample after being maintained at 50°C for 1, 2, 4 and 8 hours.

3.2.3. Formulation of print paste

The starch thickener was utilized in a vat dye paste along with other additives followed by printing on bleached 100% cotton print cloth using the pre-reduction method. A paste of dye was first made with the aid of a very small quantity of water. A 10% concentration of thickener was prepared by using 1:9 ratio of proso millet starch/sorghum starch to water on weight basis. The thickener system gained viscosity on cooking, therefore it was first mixed with a small amount of water and the resultant paste was boiled for 30 minutes in a water bath. The print paste formulation on weight basis is as follows (Teli, Shanbag, Dhande, & Singhal, 2006).

Vat dye ----------2 percent

Urea+ Glycerin (1:1) (humectants) ----------1 percent

Potassium carbonate (alkali) ----------16 percent

Sodium formaldehyde sulfoxylate (reducing agent) ----------16 percent

Thickener paste (10 percent conc.)----------X percent (to adjust viscosity)

All the printing ingredients including the dye (except the thickener and reducing agent) were mixed and kept at 60°C for 30 minutes. Then, the mixture was cooled to room temperature and the reducing agent was added and stirred well. Depending on the viscosity required, the appropriate amount of thickener paste was then stirred into the mixture. The paste was made uniform by stirring. The urea and glycerin act as humectants which prevents the dye from drying out before the fixing stage. Potassium

carbonate acts as the alkali and reducing agent required to reduce the vat dye chromophore into a soluble leuco vat form. Sodium formaldehyde sulfoxylate is a reducing agent. The printing paste was cooled to room temperature and then used in screen printing on the fabric.

3.2.4. Screen printing method

The print paste was applied through a pre-designed screen onto the fabric using a squeegee. The paste was applied on one end of the screen and pushed through the mesh of the screen using the squeegee. As the number of strokes with the squeegee increases, the quantity of the color transferred on the fabric increases. Thus for uniformity, the print paste was transferred using two strokes of the squeegee. The printed fabric was then dried at 80 °C for 10 min prior to the fixation step. The printed fabric was fixed by steaming at 102 °C for 4 min in a standard steamer. The sample was then oxidized in a solution containing 2% soap solution and 2 g/L sodium carbonate (Na_2 CO_3 or soda ash) to develop the color. In the final step, the fabric samples were boiled for 30 minutes in non-ionic soap solution and hot water to remove excess dye and printing auxiliaries followed by rinsing with cold water and air-drying the printed fabrics.

3.2.5. Evaluation of printed textiles

The evaluation of the printed fabric samples was performed and the results were compiled for analysis. Each sample was analyzed on the basis of color value, wash fastness, crock fastness and bending length. Standard methods for each test are as follows:

3.2.5.1. Color Value

The color depth and richness of the print was evaluated using a HunterLab ColorQuest XE spectrophotometer by the reflectance method. The Kulbelka Munk function (K/S) defines the depth of color in a diffused spectrum and is given by:

$K/S = (1-R)^2/2R$

Where:

K is the absorption coefficient

S is the scattering coefficient and

R is the reflectance at complete opacity

Higher the K/S value better is the depth of color of the printed sample. The color values of the starch thickener printed fabrics were compared with a sodium alginate thickener printed fabric.

3.2.5.2. Crock fastness

The crocking fastness of the printed samples was evaluated using a crock-meter on the basis of AATCC Test Method 8. Both dry and wet crocking fastness tests were performed.

3.2.5.3. Wash Fastness

For testing the wash fastness of the starch thickener printed fabrics and the sodium alginate thickener printed fabric, AATCC Test Method 61 was used. The evaluation of the test samples was done using the Gray Scale where the changes in color before and after laundering were evaluated.

3.2.5.4. Bending length

This test was used to evaluate the stiffness or the flexural rigidity imparted to the fabric by the thickener in the printing paste. Printed fabrics are usually rinsed thoroughly after fixation step to remove any traces of thickener, printing auxiliaries and excess amount of dye that is not fixed to the fabric. The bending length test also gave information about the wash ability of the thickener. ASTM DB88 - 64 method was used to determine the bending length of the fabrics and a fabric stiffness tester aided the analysis. The bending lengths of the starch thickener printed fabrics were compared to the sodium alginate thickener printed fabric as the standard.

3.2.5.5. Comparison of proso millet and sorghum starch printed fabric with sodium alginate printed fabric

Print properties of the fabrics printed with pros millet and starch thickener were compared against fabrics printed with sodium alginate using the same print formulation.

3.2.6. Statistical analysis and research design

The investigation was a study that was done to understand the applicability of millet starch and sorghum starch in textile printing. The small size of the sample group enabled the analysis of data to be done using simple statistical methods. The data was analyzed by obtaining the mean or average value for any characteristic of starch or characteristic of printed fabric. The mean values for the characteristics of starches were measured and were then benchmarked against the values of the characteristics of other starches reported in the literature.

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CHAPTER 4

CONCLUSIONS

4.1. Conclusions

The study showed that proso millet and sorghum grains are excellent sources of polysachharides and starches extracted from these two grains can be successfully utilized as thickening agents in textile printing applications. The properties of the extracted starches were studied via physiochemical characterization using methods such as swelling capacity, paste clarity analysis, amylose content, spectrophotometric analysis of starch color, XRD analysis, thermal stability analysis and rheological examination. Results showed that starches had desirable properties of a good thickener such as excellent paste clarity, adequate viscosity and high solubility and crystallinity. Characterized starch was then incorporated as a thickener in a vat dye print formulation and printed on a 100% cotton fabric. Print quality was evaluated in terms of color depth, bending length, crocking fastness and washing fastness. The properties of the printed textiles using millet and sorghum starches were comparable to that of sodium alginate thickener thereby highlighting the potential of these grains in value-added applications. Though comparison between the two starches was not a focus of the current research, an evaluation of the data suggests that millet starch performed better than sorghum starch in terms of better paste clarity, color depth and bending properties of the printed textiles. The superior performance of millet starch is probably due to its high levels of amylopectin which contributes positively to the crystallinity and paste clarity of the printing formulation.

4.2. Limitations of current study and suggestions for future studies

The current study involved the investigation of one variety each of proso millet and sorghum grains. Further studies involving additional varieties of proso millet and sorghum grains can provide an opportunity to compare between varieties; thus presenting comprehensive insights into the properties and characteristics of the cereals. Research can also be done to investigate chemical modification of millet and sorghum starches using polymer grafting techniques with the objective of improving the properties of the extracted starches. For example, the insertion of suitable end groups may enhance the desirable characteristics of the starch granules by making them more stable to heat, shear, acid and storage. Starch from these grains can also potentially be used in other textile processing applications such as sizing. Sizing is a pre-treatment process where the warp yarn is coated with a starch based paste to protect against effects of excessive abrasion during the weaving process. Proso millet and sorghum starches in their native or modified form could be studied for use as warp sizing agents. Finally, a cost and economic feasibility study with the help of agricultural economists will be needed to realize the promise of industrial-scale utilization of the grains in higher value-added applications.

APPENDICES

APPENDIX I

Manuscript 1: Extraction, Characterization and Evaluation of Proso Millet *(Panicum miliaceum)* Starch for Textile Printing Applications

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Abstract: Proso millet *(Panicum miliaceum)* is an excellent source of polysaccharides with potential for various applications in textile processing. Presently, proso millet is an economically important crop in the United States albeit for low-end uses such as bird seed and livestock feed. The current research is directed at utilizing starch extracted from proso millet for higher value-added applications such as a thickener in textile printing. The paper describes an optimum method of extracting starch from proso millet followed by physiochemical characterization of the extracted starch using methods such as swelling capacity, paste clarity analysis, amylose content, spectrophotometric analysis of starch color, XRD analysis, thermal stability analysis via DSC, and rheological examination. Characterized starch was then incorporated as a thickener in a vat dye print formulation and printed on a 100% cotton fabric. Printed quality was evaluated in terms of color depth, bending length, crocking fastness and washing fastness. Additionally, print quality was benchmarked against samples printed with sodium alginate as the thickener in the print formulation. Results showed starch from proso millet had desirable properties of a good thickener such as excellent paste clarity, adequate viscosity and high solubility and crystallinity. Proso starch printed samples demonstrated comparable color value, flexibility, crocking fastness

and washing fastness when compared with sodium alginate printed samples. The results suggest that proso millet starch is an effective thickener in textile printing applications.

Keywords: Proso Millet, polysaccharide, extraction, characterization, thickener, textile printing

Introduction

Polysaccharides are long repeated carbohydrate molecules joined together by glycosidic bonds. They are quite heterogeneous, containing slight modifications of the repeating unit. Polysaccharides range in structure from linear to highly branched. Depending on the structure, these macromolecules can have distinct properties from their monosaccharide building blocks.

An excellent example of a polysaccharide is starch. Starch is a storage polysaccharide in which the glocopyranose units are bonded by alpha linkages. Starch is an abundant carbohydrate distributed in green plants, where it accumulates as microscopic granules. It is a food reserve that sustains initial plant growth. Starch is and has been an important ingredient of human diet mainly as a high calorie food source (Zobel, 1992). It is also an essential component in food products such as a thickener, stabilizing and gelling agent and is also used in manufacturing of paper and textile products (Slattery, Kavakli, & Okita, 2000; Wurzburg, 1999). In addition to its use in human consumption, it has become a very important biopolymer and is used in many industries as a feedstock material. Cereal grains such as millets are a good source of starch.

Proso millet (*Panicum miliaceum*), which is also called hog millet, yellow hog, hershey or broom corn, belongs to the Gramineae family and is a small seeded annual grass. There are five different species in the millet family that are of economic importance. Of all the millet species, proso grain millet is the primary millet in the world import and export market and is the only millet that is globally traded (Wietgrefe, 1989). Proso millet is also the only species of economic importance in the United States (Lorenz & Dilsaver, 1980a). There is evidence that it was cultivated in China from as long ago as 5000 B.C., making it one of mankind's most ancient cultivated crops (Lagler et al, 2005). It can grow well under arid, semi-arid conditions and requires low soil fertility. Most of the U.S. proso millet crop is produced in Colorado, Nebraska

and South Dakota, with Colorado typically producing over 50 percent of the crop. Farmers use proso millet in three year and five year rotation systems in combination with wheat, to control infestation of annual weeds (Nelson & Daigger, 1975). In 2010, total U.S. production of proso millet was 11.5 million bushels from a harvested area of 363,000 acres. The price was $4.21 per bushel, an increase from $2.87 per bushel the previous year of 2009 (Boland, 2011). Currently, proso millet produced in the United States is used primarily for birdseed and livestock feed; uses that are arguably at the lower end of commercial value. Compared to other cereal grains, limited research has been conducted on millets as a value added product for other end uses (Lorenz & Dilsaver, 1980b). It is for this reason that this research focuses on proso starch as a novel thickener with potential use in textile printing. The purpose of this research was to explore proso millet starch as a novel source of starch for textile printing purposes. The goal of the investigation was to optimize an extraction technique for extraction of starch from proso millet grains followed by characterization of the extracted starch using various physicochemical techniques. Finally, the performance of extracted starch as a textile printing thickener against sodium alginate thickener was studied.

Materials and Methods

Materials

Proso millet (*Panicum miliaceum*) grains of the "plateau" variety were used for this study. A 100% cotton print cloth was used as the textile printing substrate (TestFabrics Inc., USA). The equipments used for textile screen printing were pre-designed screens, squeegees and other materials (Silk Screen Supplies). Standard reagent grade chemicals and dyes were used for printing and testing.

Methods

Extraction

Starch samples from proso millet grains were extracted using the alkaline steeping method as described by Juliano (1984). The cereal grains were milled in a Warring blender and steeped in 2.5% (w/w) solution of NaOH for 24 hours. The supernatant was drained and the rest of the residue filtered through a 40 mesh screen. This process was repeated two additional times and the resultant slurry washed, filtered through a 200 mesh screen, washed with distilled water and centrifuged at 4000-5000 rpm for 10 minutes. The upper dark gluten-rich layer was then scraped out and discarded and the remaining solids washed, filtered and dried to obtain pure starch granules. The weight of each sample was measured and recorded.

Characterization

The characteristics of the extracted starch samples were determined by employing the following methods.

Determination of Crystallinity using X-Ray Diffraction

X-Ray Diffraction analysis is a method done to determine the changes in crystallinity throughout the sample. When X-rays interact with a crystalline substance (phase), a diffraction pattern is obtained. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance (Wei et al., 2011). The diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The X-ray diffraction analysis was carried out using a Scintag X2 Theta-Theta X-Ray Powder Diffractometer (Scintag Inc), at an angular (θ -2θ) range of 4˚ - 50˚, with a 1 second wait time between angles.

Estimation of color of starch powder

The natural color of the starch is an important feature that can affect the decision of selection of the starch sample for a particular end use. For use in textile printing, color of starch is an important physical attribute. Starch that has a bright white color appearance is useful because it ensures that the color characteristic of the print on the fabric is influenced only by the color of the dye used in the print paste and not the starch thickener. The color of the extracted starch samples was analyzed using a Hunterlab ColorQuest XE spectrophotometer and the characteristic color of the extracted proso starch was obtained on the basis of the CIE Whiteness index.

Determination of swelling power of starch granules

The swelling power of starch granules is determined as the ratio in weight of the wet sediment to the initial weight of the dry starch and is reported in terms of g/g (Subramanian et al., 1994). A gram of starch was heated with 30 ml. of water to 95°C for one hour using a mechanical shaker. Lump formation was prevented by using a magnetic stirrer. The mixture was

then centrifuged at 1600 X g (rcf) for 10 minutes. The supernatant solution was carefully removed and the swollen starch sediment was weighed (Leach, McCowen, & Schoch, 1959).

Iodine binding capacity of starch

One hundred grams of sample was measured accurately into a 50 ml conical flask and a solution of 1 ml of 95% ethanol and 9 ml of 1N NaOH was added to the flask (Juliano, 1971). The sample was then heated for 10 min in a boiling water bath to gelatinize the starch. Mechanical shaking action prevented lump formation. This sample was cooled and transferred with several water washings, into a 100 ml volumetric flask which was then brought up to volume with water and mixed well. Five ml of this starch solution was pipetted into a 100 ml volumetric flask in which a solution of 1 ml 1N acetic acid and 2ml of iodine solution (0.2 gm iodine and 2 gm potassium iodide in 100 ml aqueous solution) was later added. The solution was made up to volume with distilled water, shaken and let to stand for 20 min. Absorbance of this solution was measured at 620 nm with the help of a Hunterlab ColorQuest XE spectrophotometer. Distilled water acted as the reference standard and the amylose content was reported as a percent of light absorbed with reference to water.

Thermal stability of starch paste

Thermal stability of starch paste is a physical property of the extracted starch which highlights the behavior of starch granules under the influence of heat and high temperature (Tatongjai & Lumdubwong, 2010). Gelatinization is one of the most important properties of starch when it is heated in excess of water. It is a phenomenon associated with starch which is practically a phase transition associated with transformation of granule crystalline phase in amorphous one, which causes irreversible changes of different functional properties such as

granule swelling power, solubility, loss of optical birefringence. Gelatinization occurs initially in the amorphous regions, as opposed to the crystalline regions of the granule because hydrogen bonding is weakened in these areas (Singh, Singh, Kaur, Sodhi, & Gill, 2003). Thus, the differences which can appear in transition temperatures for different kinds of starches may be attributed to the differences in the degree of crystallization. The enthalpy of gelatinization (Δ H) indicates the amount of thermal energy required in the process of gelatinization and also gives a determination of the temperature range where gelatinization occurs. This involves breaking of H-bonds between starch molecules and formation of new bonds involving water in an overall endothermic process. It was reported that the Δ H value increases with the amylopectin content of the cereal (Stevens & Elton, 1971). A differential scanning calorimeter was used to determine the thermal stability because it provides a quantitative measurement of the enthalpy, Δ*H.* Starch samples each of 3 mg (dry weight basis) was weighed in an aluminum pan and 7.5µl distilled water was added. The pan was sealed and left overnight at room temperature to attain equilibrium. The pan was then heated from 35 to 130 °C at a rate of 10 °C/min (Fan & Marks, 1998). The thermal properties of the extracted starch was analyzed by recording the Onset temperature (T_0), Peak temperature (T_p), Glass Transition Temperature (T_g), Conclusion Temperature (Tc) and Heat-gelatinization (ΔH). The peak temperature (T_p) and gelatinization enthalpy (ΔH) was also compared with other commercial starch sources.

Rheological properties of starch paste

Starch solutions of 3% concentration were prepared by adding distilled water and the solutions were then cooked in a water bath for 15-20 mins at 95°C with constant stirring to avoid lump formation. The gelatinized starch samples were then allowed to cool down and a Brookfield viscometer (Model DV-E) was used to determine the apparent viscosity in centipoise

at a uniformly increasing shear rate of 5-50 rpm at temperature of 25°C (Ragheb, Haggag, & Abd El-Thalouth, 1989).

Paste clarity by spectrophotometer

Paste clarity was determined by measuring the paste's transmittance. Starch pastes were produced by suspending 50 mg of starch (dry weight basis) in 5 ml water. The paste was placed in boiling water bath for 30 minutes. The solutions were then shaken thoroughly every 5 min and after cooling them to room temperature, the percent transmittance (%T) at 650 nm were determined using a Hunterlab ColorQuest XE spectrophotometer with water as the standard solution.

Shear stability

In the presence of a shear force, starch pastes tend to lose their viscous stability and break down. The resistance against reduction in viscosity at high shear rates is termed as shear stability. Shear stability of millet starch was determined for 5% (w/w) aqueous starch suspensions which were equilibrated in a water-bath within 30 min at 95 °C at constant stirring (Praznik, Mundigler, Kogler, Pelzl, & Huber, 1999). Viscosity profiles were determined using a Brookefield Viscometer LVDE for increasing shear rates of 10 rpm, 20 rpm and again 10 rpm for 5 min at each speed. Shear stability is computed as the ratio of viscosity at the end of first period (end of 5 min at 10 rpm) (ηbefore) and viscosity after second period (ηafter) (end of 5 min at 10 rpm after 5 min at 20 rpm) of shear stress in terms of shear stability percentage: % Shear stability = (ηafter / ηbefore) x 100. Closer the ratio is to 1, better the shear stability of the particular starch paste.

Storage stability

A useful characteristic of starch pastes is maintenance of viscosity upon storage. Storage stability of proso millet starch was tested using Sanseethong, et al's (2006) method with a few modifications. A suspension of starch (15%, w/w) in distilled water was heated in a water bath at 95°C for 15 minutes with continuous stirring in the first 5 minutes. The starch paste was then maintained at 50°C in a temperature-controlled water bath. When the temperature of starch paste reached 50°C, the initial viscosity profile of the sample was determined with a Brookefield Viscometer at an increasing shear rate of 5-20 rpm. The temperature was regulated using a shaking water bath with an accuracy of $\pm$ 1°C. The viscosity stability of starch paste was determined by measuring the viscosity of the sample after being maintained at 50°C for 1, 2, 4 and 8 hours.

Formulation of print paste

The starch thickener was utilized in a vat dye paste along with other additives followed by printing on bleached 100% cotton print cloth using the pre-reduction method. A paste of dye was first made with the aid of a very small quantity of water. A 10% concentration of thickener was prepared by using 1:9 ratio of proso millet starch to water on weight basis. The thickener system gained viscosity on cooking, therefore it was first mixed with a small amount of water and the resultant paste was boiled for 30 minutes in a water bath. The print paste formulation on weight basis is as follows (Teli, Shanbag, Dhande, & Singhal, 2006).

Vat dye ----------2 percent

Urea+ Glycerin (1:1) (humectants) ----------1 percent

Potassium carbonate (alkali) ----------16 percent

Sodium formaldehyde sulfoxylate (reducing agent) ----------16 percent

Thickener paste (10 percent conc.)----------X percent (to adjust viscosity)

All the printing ingredients including the dye (except the thickener and reducing agent) were mixed and kept at 60°C for 30 minutes. Then, the mixture was cooled to room temperature and the reducing agent was added and stirred well. Depending on the viscosity required, the appropriate amount of thickener paste was then stirred into the mixture. The paste was made uniform by stirring. The urea and glycerin act as humectants which prevents the dye from drying out before the fixing stage. Potassium carbonate acts as the alkali and reducing agent required to reduce the vat dye chromophore into a soluble leuco vat form. Sodium formaldehyde sulfoxylate is a reducing agent. The printing paste was cooled to room temperature and then used in screen printing on the fabric.

Screen printing method

The print paste was applied through a pre-designed screen onto the fabric using a squeegee. The paste was applied on one end of the screen and pushed through the mesh of the screen using the squeegee. As the number of strokes with the squeegee increases, the quantity of the color transferred on the fabric increases. Thus for uniformity, the print paste was transferred using two strokes of the squeegee. The printed fabric was then dried at 80 °C for 10 min prior to the fixation step. The printed fabric was fixed by steaming at 102 °C for 4 min in a standard steamer. The sample was then oxidized in a solution containing 2% soap solution and 2 g/L

sodium carbonate to develop the color. In the final step, the fabric samples were boiled for 30 minutes in non-ionic soap solution and hot water to remove excess dye and printing auxiliaries followed by rinsing with cold water and air-drying the printed fabrics.

Evaluation of printed fabrics

The evaluation of the printed fabric samples was performed and the results were compiled for analysis. Each sample was analyzed on the basis of color value, wash fastness, crock fastness and bending length. Standard methods for each test are as follows:

Color Value

The color depth and richness of the print was evaluated using a Hunterlab ColorQuest XE spectrophotometer by the reflectance method. The Kubelka-Munk function (K/S) defines the depth of color in a diffused spectrum and is given by:

$$K/S = (1-R)^2/2R$$

Where:

K is the absorption coefficient

S is the scattering coefficient and

R is the reflectance at complete opacity

Higher the K/S value better is the depth of color of the printed sample. The color values of the starch thickener printed fabrics were compared with a sodium alginate thickener printed fabric.

Bending length

This test was used to evaluate the stiffness or the flexural rigidity imparted to the fabric by the thickener in the printing paste. Printed fabrics are usually rinsed thoroughly after fixation step to remove any traces of thickener, printing auxiliaries and excess amount of dye that is not fixed to the fabric. The bending length test also gave information about the wash ability of the

thickener. ASTM D1388 method was used to determine the bending length of the fabrics and a fabric stiffness tester aided the analysis. The bending lengths of the starch thickener printed fabrics were compared to the sodium alginate thickener printed fabric as the standard.

Wash Fastness

For testing the wash fastness of the starch thickener printed fabrics and the sodium alginate thickener printed fabric, AATCC Test Method 61 was used. The evaluation of the test samples was done using the Gray Scale where the changes in color before and after laundering were evaluated.

Crock fastness

The color crocking fastness of the printed samples was evaluated using a crock-meter on the basis of AATCC Test Method 8. Both dry and wet crocking fastness tests were performed.

Comparison of proso millet starch printed fabric with sodium alginate printed fabric

Print properties of the fabrics printed with proso millet starch thickener were compared against fabrics printed with sodium alginate using the same print formulation.

RESULTS AND DISCUSSION

Physiochemical characteristics of the extracted proso millet starch are reported in Table II. The diffraction pattern of the extracted starch showed several narrow high intensity peaks at different θ-2θ angles (Figure 9). Since amorphous component of the polymer contributes to broad peaks and crystalline component results in sharp narrow peaks, millet starch is more crystalline in nature (Wei et al., 2011). High crystallinity of starch granules is a result of high amylopectin content of the starch and positively influences the melting point, paste clarity and the starch's reactivity with iodine.

Table II.
Characteristics of Proso Millet Starch

% Crystallinity		48.19
Color of starch (CIE Whiteness index)		68.27
Swelling power (g/g)		21.47
Amylose (%)		10.44
Thermal properties	**T_P (°C)**	78.00
	T_C (°C)	86.75
	Δ H (J/g)	11.29
	T_g (°C)	76.16
Paste clarity (% transmittance)		50.62
% Shear stability		104

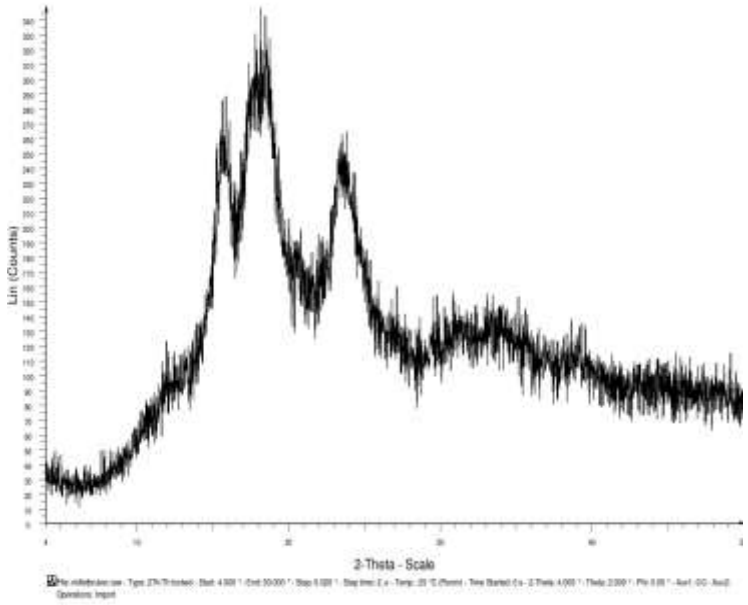

Figure 9. X-Ray diffraction pattern of the extracted Proso Millet starch sample

The natural color of the starch is an important feature that can affect the decision of selection of the starch sample for a particular end use. For use in textile printing, color of starch is an important physical attribute. Starch that has a bright white color appearance is useful because it ensures that the color characteristic of the print on the fabric is influenced only by the color of the dye used in the print paste and not the starch thickener. The color of the extracted millet starch was inherently white with CIE Whiteness index of 68.27. The color of millet starch in terms of whiteness is superior to corn starch (Anton, Fulcher, & Arntfield, 2009), sorghum starch (Taylor, Schober, & Bean, 2006), amaranthus starch and wheat starch (Teli et al., 2006). This positively contributed to the good attributes of proso millet starch and bolstered the case for its use as a textile printing thickener.

The swelling power of a starch sample determines its ability to hydrate and solubilize in the presence of water and higher the swelling power; greater is the paste clarity (Singh & Sandhu, 2007). As shown in the table, the swelling power of millet starch was 21.47% which is comparable to that of wheat starch and potato starch previously reported by other researchers (Nemtanu & Brasoveanu, 2010). Therefore, millet starch has adequate swelling power for textile printing applications.

Amylose in starch can bind molecular iodine due to the fact that sugar can form a helix, into which iodine fits to form a complex that produces a deep blue color. This chemical characteristic allows starch to be used as an indicator for titrations involving the reduction of iodine (Reddy, Subramanian, Ali, & Bhattacharya, 1994). As seen in Figure 10, in the presence of millet starch the iodine molecules exhibited a reddish yellow color. This indicates the presence of low levels of amylose in the starch as illustrated by the value in Table II (10.44%). In other words, millet starch contains a high level of amylopectin, which explains the high crystallinity of the starch sample (Wei et al., 2011).

Figure 10. Reddish-yellow proso millet starch-iodine complex solution

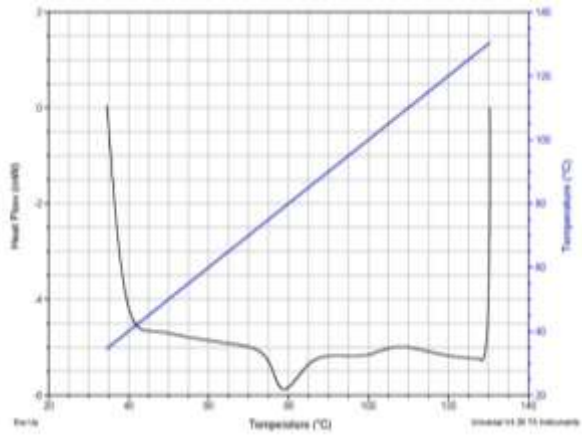

Figure 11. Differential Scanning Calorimeter profile of proso millet starch

Figure 11 illustrates the thermal profile of the extracted millet starch granules. The thermal profile indicates that millet starch is characterized by a high peak temperature (T_p) that is comparable to those of rice, tapioca, maize and arrowroot starches (Fujita, Morita, & Fujiyama, 1993). High glass transition temperatures (T_g) have been reported to result from a high degree of crystallinity which is possessed by millet starch. Greater crystallinity of starch granules provides structural stability and makes the granule more resistant towards gelatinization and melting (T_M or T_p) (Barichello, Yada, Coffin, & Stanley, 1990). Both gelatinization and swelling are properties partially controlled by the molecular structure of amylopectin such as unit chain length, extent of branching, molecular weight, and polydispersity. Other factors include amylose to amylopectin ratio and granule architecture (crystalline to amorphous ratio) (Tester & Morrison, 1990). The heat required to gelatinize the starch molecules (Δ H) increases with the amount of amylopectin present in the granules (Stevens & Elton, 1971), and since millet starch has high amylopectin content, the energy required to gelatinize is also high.

Light reflectance of pastes is closely related to optical homogeneity within swollen granules and therefore is an important factor to investigate (Craig, Maningat, Seib, & Hoseney, 1989). The clarity of a starch paste in an important attribute of starch and can be altered by chemical modification of the granules. High transmittance is desired in textile printing so that the paste used does not significantly alter dye color on a fabric. Millet starch suspensions transmitted 50.62% as seen in Table II and this clarity is comparable to wheat starch and waxy corn starch (Craig et al., 1989). Thus millet starch is capable of forming stable, clear solutions that do not adversely influence the color or quality of the textile print.

The viscosity of starch samples and the internal structural bonding can be determined by rheological analysis of starch solutions (El-Molla, 2000). The data from the viscosity analysis of millet starch is given by the viscosity as a function of shear rate profile in Figure 12. From the profile it can be deduced that the viscosity of the millet starch paste decreased with increasing shear rate. Thus proso millet starch exhibits Non-Newtonian fluid properties with shear thinning behavior (thixotropic). Additionally, shear stability measurements showed the final viscosity was

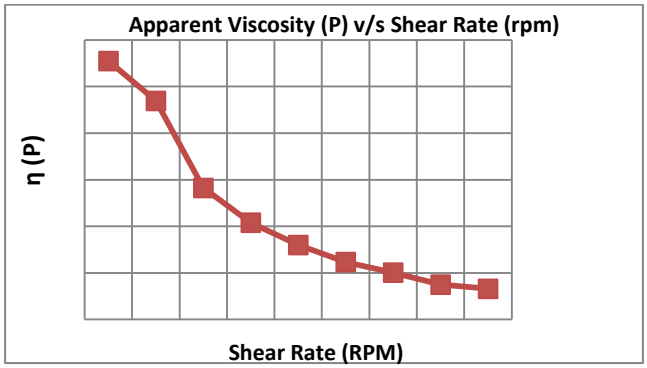

Figure12. Viscosity profile of proso millet starch

higher than the initial viscosity at the same shear rate. Thus the shear ratio of millet starch was greater than 1 and the percentage shear stability was calculated to be 104. The increase in final

viscosity could be the result of the shear-induced response of the millet starch suspensions. The shear stability of millet starch is comparable to wheat and amaranthus starches (Praznik et al., 1999).

Storage stability of millet starch was determined by recording the viscosity at different shear rates at 0, 1, 2, 4 and 8 hours. Figure 13 shows the trend in viscosity at different shear rates for different time periods. A slight increase in viscosity before the gradual decrease was observed at the end of the 1st, 2nd and 4th hour. This anomaly could be attributed to the change in molecular and supermolecular conformations of the millet starch granules at high temperatures (Praznik et al., 1999). Thus the millet starch molecules exhibit desirable and uniform stability when stored for extended periods of time in a controlled environment.

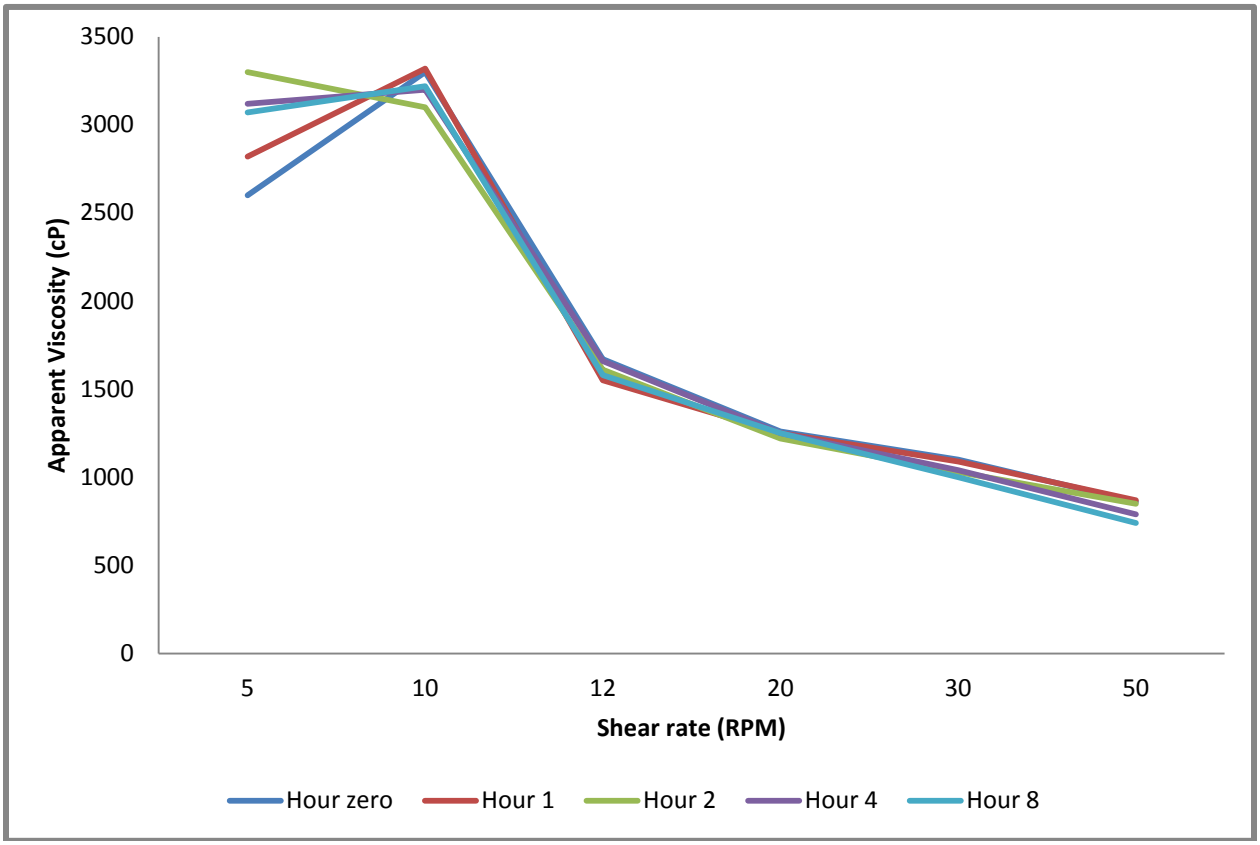

Figure 13. Storage stability profile of millet starch suspension at 50°C.

Evaluation of printed fabrics

The performance of proso millet printed fabrics was compared to sodium alginate printed fabrics and data reported in Table III. When the color value of the printed fabrics was compared, millet starch thickener when used with red dye had superior K/S value as compared to the red sodium alginate printed fabric (Figure 14). Conversely, the green vat dye had better color value when used with sodium alginate thickener. This loss in color richness in case of green dye could be attributed to the high solubility and swelling power of millet starch. High solubility of starch molecules increase the chances of dye removal during the washing off process (Teli et al., 2006) leading to loss in richness of the color. By increasing the temperature and time of fixation of the printed fabric, the problem of loss of dye during washing could be minimized. The blue vat dye K/S values are comparable for millet starch and sodium alginate printed samples.

Table III.
Evaluation of Samples Printed with Proso Millet Starch and Sodium Alginate

Thickener	Dye	% shade	K/S	Bending length (cm)	Washing fastness	Crocking fastness	
					Color Change	dry	Wet
Proso millet starch	Vat Red 13	2	3.17	2.57	3-4	4-5	3
	Green Vat dye	2	2.92	2.73	3-4	4-5	3
	Vat Blue 6	2	2.87	2.76	3-4	4-5	3
Sodium alginate	Vat Red 13	2	2.39	2.64	2-3	4	2-3
	Green Vat dye	2	4.45	2.85	3	4-5	3
	Vat Blue 6	2	2.91	2.78	3-4	4-5	3

Figure 14. Fabrics printed with Vat Red 13 using Proso millet starch (left) and sodium alginate (right)

The bending length of the printed fabrics ascertains the stiffness of the print. Lower bending length indicates higher efficiency of thickener and negligible residue on the fabric. Table III shows the results of the bending length of fabrics printed with millet starch and sodium alginate thickeners. The results indicate that bending length of millet starch printed fabrics is lower than that of sodium alginate. Thus samples printed with millet starch were more flexible than sodium alginate printed fabrics. This flexibility could be attributed to the good wash ability and solubility of millet starch.

The fabric samples printed with proso millet starch and sodium alginate thickener showed comparable washing fastness ratings (Table III). Since vat dyes are inherently wash resistant, the use of millet starch did not adversely affect the dye qualities. Indeed, in case of the red vat dye, the wash fastness characteristics of millet starch printed fabrics were superior to that of sodium alginate printed fabrics (Figure 15).

Figure 15. Washing fastness of fabrics printed with Vat Red 13 using proso millet starch (left) and sodium alginate (right)

The colorfastness to crocking of the printed fabrics was measured by a crockmeter. The results of the crocking fastness in Table III indicate that the choice of thickener (proso millet or sodium alginate) does not affect the crocking fastness rating and both thickeners produced comparable results (Figure 16).

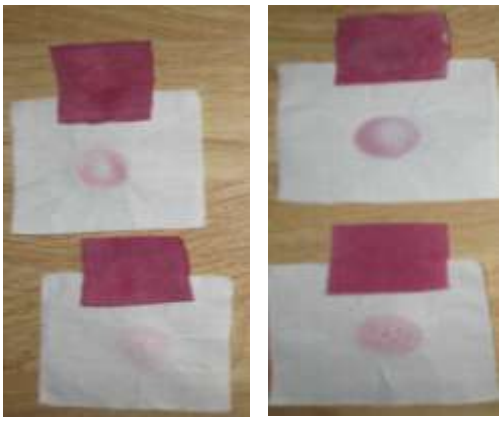

Figure 16. Dry (bottom) and wet (top) crocking fastness of fabrics dry printed with Vat Red 13 using proso millet starch (left) and sodium alginate (right)

Conclusions

The use of proso millet starch as a thickener in vat dye printing on cotton textiles is a viable option as demonstrated by the results of this study. Physiochemical studies of proso millet starch indicated its excellent potential as a thickener which was confirmed by evaluation of printed fabrics and benchmarking against a commercially available thickener. Proso millet starch printed fabrics had comparable or better color depth, flexibility, crocking fastness and washing fastness when compared to sodium alginate printed fabrics. Proso millet is an underutilized crop and this research shows that the crop has commercial potential for value-added uses thus providing supplemental revenue for growers and farmers of proso millet.

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APPENDIX II

Manuscript 2: Extraction, Characterization and Evaluation of Sorghum (*Sorghum bicolor L. Moench*) Starch for Textile Printing Applications

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Abstract: Sorghum (*Sorghum bicolor L. Moench*) is an annual drought tolerant crop grown in dry and arid regions of the world. It is the fifth largest produced cereal in the world and is a rich source of fiber and starch. In spite of high rates of production in the United States, it is currently used as animal feed due to its unpalatable flavor. The current research is aimed at utilizing starch extracted from sorghum for higher economically valuable applications such as a thickener in textile printing. Starch was extracted from sorghum, characterized using various physicochemical techniques and then incorporated in a vat printing formulation. Printing was done on 100% cotton fabrics. The results showed starch from sorghum had appropriate qualities such as good paste viscosity, suitable starch color and desirable paste clarity. The sorghum starch printed fabrics had comparable color value, flexibility, crocking fastness and washing fastness. The results are promising and demonstrate sorghum starch to be a viable thickener in textile printing applications.

Keywords: Sorghum, polysaccharide, extraction, characterization, thickener, textile printing.

Introduction

Polysaccharides are long repeated carbohydrate molecules joined together by glycosidic bonds. They are quite heterogeneous, containing slight modifications of the repeating unit. Polysaccharides range in structure from linear to highly branched. Depending on the structure, these macromolecules can have distinct properties from their monosaccharide building blocks.

An excellent example of a polysaccharide is starch. Starch is a storage polysaccharide in which the glocopyranose units are bonded by alpha linkages. Starch is an abundant carbohydrate distributed in green plants, where it accumulates as microscopic granules. It is a food reserve that sustains initial plant growth. Starch is and has been an important ingredient of human diet mainly as a high calorie food source (Zobel, 1992). It is also an essential component in food products such as a thickener, stabilizing and gelling agent and is also used in manufacturing of paper and textile products (Slattery, Kavakli, & Okita, 2000; Wurzburg, 1999). In addition to its use in human consumption, it has become a very important biopolymer and is used in many industries as a feedstock material. Cereal grains such as sorghum are a good source of starch.

Sorghum (*Sorghum bicolor L. Moench*) is the fifth largest produced cereal in terms of acreage (Taylor, Schober, & Bean, 2006; Udanchan, Sahoo, & Hend, 2012).It is an annual grass that is extremely drought tolerant crop that is mostly grown in dry and arid regions of the world. It is a staple food crop for millions of people in semi-arid tropical countries of the world. It is mostly grown as a subsistence dry land crop by resource limited farmers under traditional management conditions in regions of Africa, Asia and Latin America, which are frequently drought-prone and characterized by fragile environments.

Sorghum is used mostly for animal feed with only a small part used for food and industrial purposes (Rooney & Waniska, 2000). Production of sorghum in 2007-2008 in the world was 64 Million Metric Tons (USDA, 2012). Leading sorghum producing countries were

United States (19.9%), Nigeria (15.5%), India (11.3%), Mexico (9.8%), Sudan (7%), and Argentina (5.4%) (USDA, 2012). India grows the largest acreage of sorghum in the world followed by Nigeria and Sudan (Udanchan et al, 2012). In the United States, major producers of sorghum are Texas, Kansas, Colorado and Nebraska (USDA, 2012). In spite of being a major cereal grain and having the same general composition of corn, sorghum is currently used mainly as animal feed due to some of the shortcomings of the grain such as high fiber content, pronounced flavor and grittiness in flour. But due to its high starch content and economical availability, significant opportunities exist for increased utilization of sorghum starch in other applications such as a thickener in textile printing.

The purpose of this research was to study sorghum starch as a novel source of starch for textile printing purposes. The goal of the investigation was to optimize an extraction technique for removal of starch from sorghum grains followed by characterization of the extracted starch using various physicochemical techniques. The performance of extracted starch as a textile printing thickener against sodium alginate thickener was also investigated.

Materials and Methods

Materials

Sorghum (*Sorghum bicolor L. Moench*) grains were used for this study. A 100% cotton print cloth was used as the textile printing substrate (TestFabrics Inc., USA). The equipments used for textile screen printing were pre-designed screens, squeegees and other materials (Silk Screen Supplies). Standard reagent grade chemicals and dyes were used for printing and testing.

Methods

Extraction

Starch samples from sorghum grains were extracted using the alkaline steeping method as described by Juliano (1984). The cereal grains were milled in a Warring blender and steeped in 2.5% (w/w) solution of NaOH for 24 hours. The supernatant was drained and the rest of the residue filtered through a 40 mesh screen. This process was repeated two additional times and the resultant slurry washed, filtered through a 200 mesh screen, washed with distilled water and centrifuged at 4000-5000 rpm for 10 minutes. The upper dark gluten-rich layer was then scraped out and discarded and the remaining solids washed, filtered and dried to obtain pure starch granules. The weight of each sample was measured and recorded.

Characterization

The characteristics of the extracted starch samples were determined by employing the following methods.

Determination of Crystallinity using X-Ray Diffraction

X-Ray Diffraction analysis is a method done to determine the changes in crystallinity throughout the sample. When X-rays interact with a crystalline substance (phase), a diffraction pattern is obtained. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance (Wei et al., 2011). The diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The X-ray diffraction analysis was carried out using a Scintag X2 Theta-Theta X-Ray Powder Diffractometer (Scintag Inc), at an angular (θ -2θ) range of 4˚ - 50˚, with a 1 second wait time between angles.

Estimation of color of starch powder

The natural color of the starch is an important feature that can affect the decision of selection of the starch sample for a particular end use. For use in textile printing, color of starch is an important physical attribute. Starch that is free of unwanted color is useful because it ensures that the color characteristic of the print on the fabric is influenced only by the color of the dye used in the print paste and not the starch thickener. The color of the extracted starch samples was analyzed using a Hunterlab ColorQuest XE spectrophotometer and the characteristic color of the extracted millet starch was obtained on the basis of the CIE Whiteness index.

Determination of swelling power of starch granules

The swelling power of starch granules is determined as the ratio in weight of the wet sediment to the initial weight of the dry starch and is reported in terms of g/g (Subramanian et al., 1994). A gram of starch was heated with 30 ml. of water to 95°C for one hour using a mechanical shaker. Lump formation was prevented by using a magnetic stirrer. The mixture was

then centrifuged at 1600 X g (rcf) for 10 minutes. The supernatant solution was carefully removed and the swollen starch sediment was weighed (Leach, McCowen, & Schoch, 1959).

Iodine binding capacity of starch

One hundred grams of sample was measured accurately into a 50 ml conical flask and a solution of 1 ml of 95% ethanol and 9 ml of 1N NaOH was added to the flask (Juliano, 1971). The sample was then heated for 10 min in a boiling water bath to gelatinize the starch. Mechanical shaking action prevented lump formation. This sample was cooled and transferred with several water washings, into a 100 ml volumetric flask which was then brought up to volume with water and mixed well. Five ml of this starch solution was pipetted into a 100 ml volumetric flask in which a solution of 1 ml 1N acetic acid and 2ml of iodine solution (0.2 gm iodine and 2 gm potassium iodide in 100 ml aqueous solution) was later added. The solution was made up to volume with distilled water, shaken and let to stand for 20 min. Absorbance of this solution was measured at 620 nm with the help of a Hunterlab ColorQuest XE spectrophotometer. Distilled water acted as the reference standard and the amylose content was reported as a percent of light absorbed with reference to water.

Thermal stability of starch paste

Thermal stability of starch paste is a physical property of the extracted starch which highlights the behavior of starch granules under the influence of heat and high temperature (Tatongjai & Lumdubwong, 2010). Gelatinization is one of the most important properties of starch when it is heated in excess of water. It is a phenomenon associated with starch which is practically a phase transition associated with transformation of granule crystalline phase in amorphous one, which causes irreversible changes of different functional properties such as

granule swelling power, solubility, loss of optical birefringence. Gelatinization occurs initially in the amorphous regions, as opposed to the crystalline regions of the granule because hydrogen bonding is weakened in these areas (Singh, Singh, Kaur, Sodhi, & Gill, 2003). Thus, the differences which can appear in transition temperatures for different kinds of starches may be attributed to the differences in the degree of crystallization. The enthalpy of gelatinization (Δ H) indicates the amount of thermal energy required in the process of gelatinization and also gives a determination of the temperature range where gelatinization occurs. This involves breaking of H-bonds between starch molecules and formation of new bonds involving water in an overall endothermic process. It was reported that the Δ H value increases with the amylopectin content of the cereal (Stevens & Elton, 1971). A differential scanning calorimeter was used to determine the thermal stability because it provides a quantitative measurement of the enthalpy, Δ*H.* Starch samples each of 3 mg (dry weight basis) was weighed in an aluminum pan and 7.5µl distilled water was added. The pan was sealed and left overnight at room temperature to attain equilibrium. The pan was then heated from 35 to 130 °C at a rate of 10 °C/min (Fan & Marks, 1998). The thermal properties of the extracted starch was analyzed by recording the Onset temperature (T_0), Peak temperature (T_p), Glass Transition Temperature (T_g), Conclusion Temperature (Tc) and Heat-gelatinization (ΔH). The peak temperature (T_p) and gelatinization enthalpy (ΔH) was also compared with other commercial starch sources.

Rheological properties of starch paste

Starch solutions of 3% concentration were prepared by adding distilled water and the solutions were then cooked in a water bath for 15-20 mins at 95°C with constant stirring to avoid lump formation. The gelatinized starch samples were then allowed to cool down and a Brookfield viscometer (Model DV-E) was used to determine the apparent viscosity in centipoise

at a uniformly increasing shear rate of 5-50 rpm at temperature of 25°C (Ragheb, Haggag, & Abd El-Thalouth, 1989).

Paste clarity by spectrophotometer

Paste clarity was determined by measuring the paste's transmittance. Starch pastes were produced by suspending 50 mg of starch (dry weight basis) in 5 ml water. The paste was placed in boiling water bath for 30 minutes. The solutions were then shaken thoroughly every 5 min and after cooling them to room temperature, the percent transmittance (%T) at 650 nm were determined using a Hunterlab ColorQuest XE spectrophotometer with water as the standard solution.

Shear stability

In the presence of a shear force, starch pastes tend to lose their viscous stability and break down. The resistance against reduction in viscosity at high shear rates is termed as shear stability. Shear stability of sorghum starch was determined for 5% (w/w) aqueous starch suspensions which were equilibrated in a water-bath within 30 min at 95 °C at constant stirring (Praznik, Mundigler, Kogler, Pelzl, & Huber, 1999). Viscosity profiles were determined using a Brookefield Viscometer LVDE for increasing shear rates of 10 rpm, 20 rpm and again 10 rpm for 5 min at each speed. Shear stability is computed as the ratio of viscosity at the end of first period (end of 5 min at 10 rpm) (ηbefore) and viscosity after second period (ηafter) (end of 5 min at 10 rpm after 5 min at 20 rpm) of shear stress in terms of shear stability percentage: % Shear stability = (ηafter / ηbefore) x 100 .Closer the ratio is to 1, better the shear stability of the particular starch paste.

Storage stability

A useful characteristic of starch pastes is maintenance of viscosity upon storage. Storage stability of sorghum starch was tested using Sanseethong, et al's (2006) method with a few modifications. A suspension of starch (15%, w/w) in distilled water was heated in a water bath at 95°C for 15 minutes with continuous stirring in the first 5 minutes. The starch paste was then maintained at 50°C in a temperature-controlled water bath. When the temperature of starch paste reached 50°C, the initial viscosity profile of the sample was determined with a Brookefield Viscometer at an increasing shear rate of 5-20 rpm. The temperature was regulated using a shaking water bath with an accuracy of $\pm$ 1°C. The viscosity stability of starch paste was determined by measuring the viscosity of the sample after being maintained at 50°C for 1, 2, 4 and 8 hours.

Formulation of print paste

The starch thickener was utilized in a vat dye paste along with other additives followed by printing on bleached 100% cotton print cloth using the pre-reduction method. A paste of dye was first made with the aid of a very small quantity of water. A 10% concentration of thickener was prepared by using 1:9 ratio of sorghum starch to water on weight basis. The thickener system gained viscosity on cooking, therefore it was first mixed with a small amount of water and the resultant paste was boiled for 30 minutes in a water bath. The print paste formulation on weight basis is as follows (Teli, Shanbag, Dhande, & Singhal, 2006).

Vat dye ----------2 percent

Urea+ Glycerin (1:1) (humectants) ----------1 percent

Potassium carbonate (alkali) ----------16 percent

Sodium formaldehyde sulfoxylate (reducing agent) ----------16 percent

Thickener paste (10 percent conc.)----------X percent (to adjust viscosity)

All the printing ingredients including the dye (except the thickener and reducing agent) were mixed and kept at 60°C for 30 minutes. Then, the mixture was cooled to room temperature and the reducing agent was added and stirred well. Depending on the viscosity required, the appropriate amount of thickener paste was then stirred into the mixture. The paste was made uniform by stirring. The urea and glycerin act as humectants which prevents the dye from drying out before the fixing stage. Potassium carbonate acts as the alkali and reducing agent required to reduce the vat dye chromophore into a soluble leuco vat form. Sodium formaldehyde sulfoxylate is a reducing agent. The printing paste was cooled to room temperature and then used in screen printing on the fabric.

Screen printing method

The print paste was applied through a pre-designed screen onto the fabric using a squeegee. The paste was applied on one end of the screen and pushed through the mesh of the screen using the squeegee. As the number of strokes with the squeegee increases, the quantity of the color transferred on the fabric increases. Thus for uniformity, the print paste was transferred using two strokes of the squeegee. The printed fabric was then dried at 80 °C for 10 min prior to the fixation step. The printed fabric was fixed by steaming at 102 °C for 4 min in a standard steamer. The sample was then oxidized in a solution containing 2% soap solution and 2 g/L sodium carbonate to develop the color. In the final step, the fabric samples were boiled for 30 minutes in non-ionic soap solution and hot water to remove excess dye and printing auxiliaries followed by rinsing with cold water and air-drying the printed fabrics.

Evaluation of printed fabrics

The evaluation of the printed fabric samples was performed and the results were compiled for analysis. Each sample was analyzed on the basis of color value, wash fastness, crock fastness and bending length. Standard methods for each test are as follows:

Color Value

The color depth and richness of the print was evaluated using a Hunterlab ColorQuest XE spectrophotometer by the reflectance method. The Kubelka-Munk function (K/S) defines the depth of color in a diffused spectrum and is given by:

$K/S = (1-R)^2/2R$

Where:

K is the absorption coefficient

S is the scattering coefficient and

R is the reflectance at complete opacity

Higher the K/S value better is the depth of color of the printed sample. The color values of the starch thickener printed fabrics were compared with a sodium alginate thickener printed fabric.

Bending length

This test was used to evaluate the stiffness or the flexural rigidity imparted to the fabric by the thickener in the printing paste. Printed fabrics are usually rinsed thoroughly after fixation step to remove any traces of thickener, printing auxiliaries and excess amount of dye that is not fixed to the fabric. The bending length test also gave information about the wash ability of the thickener. ASTM D1388 method was used to determine the bending length of the fabrics and a fabric stiffness tester aided the analysis. The bending lengths of the starch thickener printed fabrics were compared to the sodium alginate thickener printed fabric as the standard.

Wash Fastness

For testing the wash fastness of the starch thickener printed fabrics and the sodium alginate thickener printed fabric, AATCC Test Method 61 was used. The evaluation of the test samples was done using the Gray Scale where the changes in color before and after laundering were evaluated.

Crock fastness

The color crocking fastness of the printed samples was evaluated using a crock-meter on the basis of AATCC Test Method 8. Both dry and wet crocking fastness tests were performed.

Comparison of sorghum starch printed fabric with sodium alginate printed fabric

Print properties of the fabrics printed with sorghum starch thickener were compared against fabrics printed with sodium alginate using the same print formulation.

Results and Discussion

The physicochemical characteristics of the extracted sorghum starch are listed in Table IV. The X-ray diffractogram of sorghum starch (Figure 17) revealed the starch to be amorphous in nature because of the presence low intensity broad peaks at different θ-2θ angles in the diffraction pattern (Wei et al., 2011). Sorghum starch is 23.78% crystalline, which is comparable to germinated wheat starch (Teli, Rohera, Sheikh, & Singhal, 2009).

Table IV.
Characteristics of Sorghum Starch

% Crystallinity		23.78
Color of starch (CIE Whiteness index)		59.99
Swelling power (g/g)		16.97
Amylose (%)		48.04
Thermal properties	**T_P (°C)**	72.54
	T_C (°C)	81.28
	Δ H (J/g)	4.93
	T_g (°C)	70.42
Paste clarity (% transmittance)		26.47
%Shear stability		111

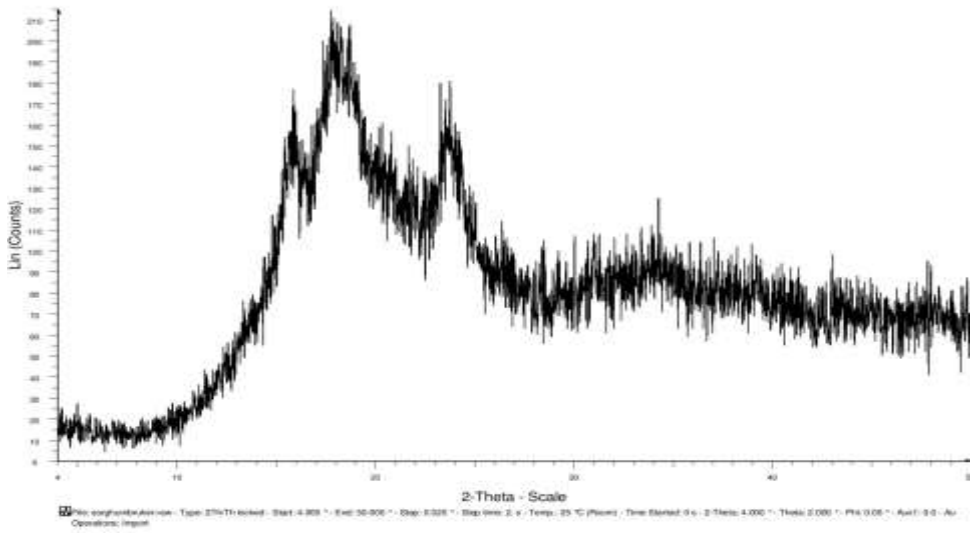

Figure 17. X-Ray diffraction pattern of the extracted Sorghum starch sample

The natural color of the starch is an important feature that can affect the decision of selection of the starch sample for a particular end use. For use in textile printing, color of starch is an important physical attribute. Starch that has a bright white color appearance is useful because it ensures that the color characteristic of the print on the fabric is influenced only by the color of the dye used in the print paste and not the starch thickener. The color of the extracted sorghum starch was sufficiently white for textile printing with a CIE Whiteness index of 59.99.

The swelling power of a starch sample determines its ability to hydrate and solubilize in the presence of water and higher the swelling power; greater is the paste clarity of starch (Singh & Sandhu, 2007). The swelling power of the extracted sorghum starch is 16.97% which is comparable to the average swelling power of wheat and potato starches (Nemtanu & Brasoveanu, 2010). Thus sorghum starch has adequate swelling power for use as a textile printing thickener.

Amylose in starch can bind molecular iodine due to the fact that sugar can form a helix, into which iodine fits to form a complex that produces a deep blue color. This chemical

characteristic allows starch to be used as an indicator for titrations involving the reduction of iodine (Reddy, Subramanian, Ali, & Bhattacharya, 1994). As seen in Figure 18, in the presence of sorghum starch the iodine molecules exhibited a deep bluish black color. This indicates the presence of high levels of amylose (48.04%) in the starch. High levels of amylose corresponds to the amorphous nature of sorghum starch (Wei et al., 2011), thus corroborating with the crystallinity results. The amylose content of sorghum was higher than wheat and amaranthus starches (Teli et al., 2006).

Figure 18. Deep bluish black sorghum starch-iodine complex solution

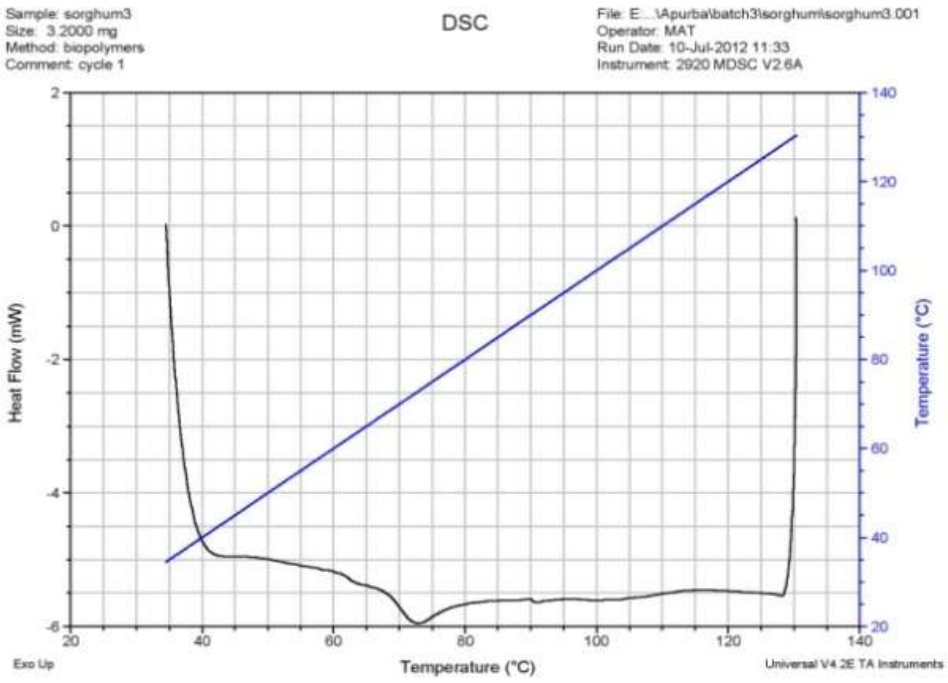

Figure 19. The Differential Scanning Calorimeter profile of sorghum starch

Figure 19 illustrates the thermal profile of the extracted sorghum starch granules. The peak temperature of sorghum starch falls in the range of temperature previously reported in literature (Jackson, Waniska, & Rooney, 1989). The peak temperature of sorghum starch is also comparable to those of corn (Nemtanu & Brasoveanu, 2010; Jackson, Waniska, & Rooney, 1989), barley, foxtail millet (Fujita, Morita, & Fujiyama, 1993), maize (Stevens & Elton, 1971) but is higher than that of wheat and potato starches (Nemtanu & Brasoveanu, 2010; Fujita et al., 1993; Stevens & Elton, 1971). The heat required to gelatinize the starch molecules (Δ H) increases with the amount of amylopectin present in the granules (Stevens & Elton, 1971), and since sorghum starch has low amylopectin content, the energy required to gelatinize low (Δ H=4.93 J/g)

Light reflectance of pastes is closely related to optical homogeneity within swollen granules and is therefore important (Craig, Maningat, Seib, & Hoseney, 1989). High transmittance is desired in textile printing so that the paste used does not significantly alter dye color on a fabric. Sorghum starch suspensions had a transmittance of 26.47% and though this value in on the lower side it is still adequate for forming stable, clear solutions that will not adversely influence the color or quality of the textile print.

The viscosity of starch samples and the internal structural bonding can be determined by rheological analysis of starch solutions (El-Molla, 2000). Viscosity analysis profile of sorghum starch is shown in Figure 20. From the profile it can be inferred that the viscosity of the sorghum starch paste decreased with increasing shear rate. Thus sorghum starch exhibits Non-Newtonian fluid properties with shear thinning behavior (thixotropic).

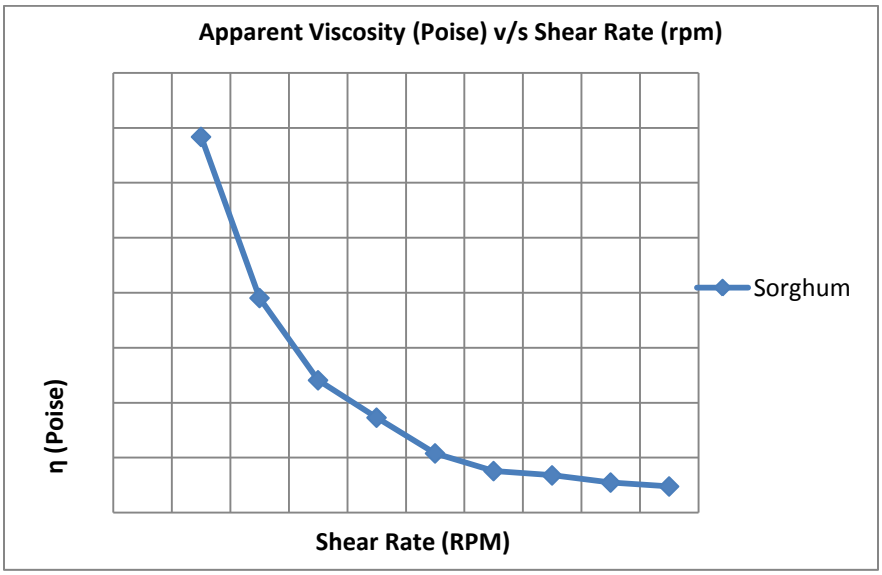

Figure 20. Viscosity profile of sorghum starch

The shear stability measurements of sorghum starch confirmed its thixotropic behavior. Additionally, shear stability measurements showed the final viscosity was higher than the initial viscosity at the same shear rate. Therefore, the shear ratio of sorghum starch was greater than 1 and the % shear stability was calculated to be 111. The increase in final viscosity could be the result of the shear-induced response of the sorghum starch suspensions. The shear stability of sorghum starch is comparable to that of wheat and amaranthus starches (Praznik et al., 1999).

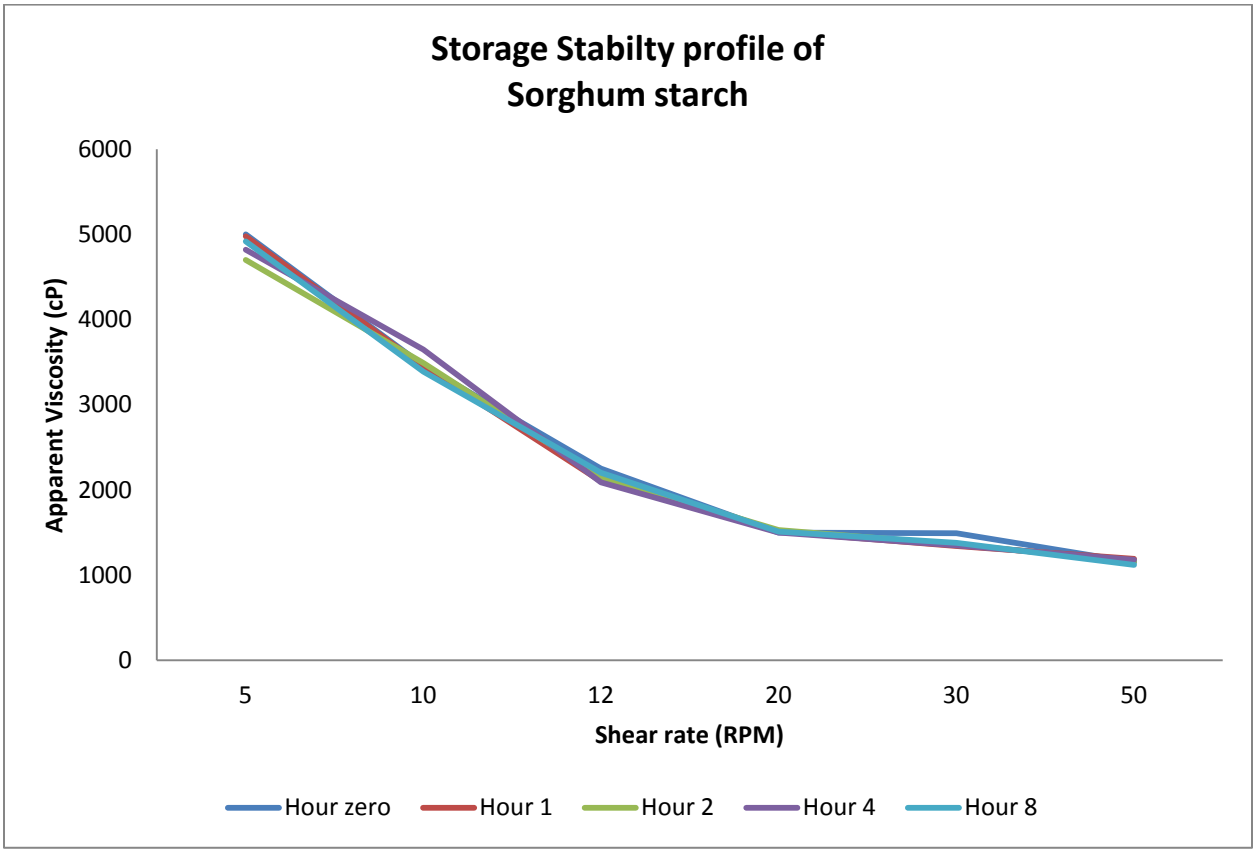

Figure 21. Storage stability profile of sorghum starch suspension at 50°C.

Storage stability of sorghum starch was determined by recording the viscosity at different shear rates at 0, 1, 2, 4 and 8 hours. Figure 21 shows the trend in viscosity at different shear rates for different time periods. The stability profile shows smoothly decreasing viscosity with increasing shear rates. The profiles in the initial hour and at the end of the 1st, 2nd and 4th hour are

observed to coincide with each other, indicating good storage stability of sorghum starch granules for extended periods of time in a controlled environment.

Evaluation of printed fabrics

The performance of sorghum printed fabrics was compared to sodium alginate printed fabrics and the data is reported in Table V.

Table V.
Evaluation of Samples Printed with Sorghum Starch and Sodium Alginate

Thickener	Dye	% shade	K/S	Bending length (cm)	Washing fastness	Crocking fastness	
					Color Change	Dry	wet
Sorghum starch	Vat Red 13	2	2.59	2.59	3	4-5	3
	Green Vat dye	2	2.71	2.74	3-4	4-5	3
	Vat Blue 6	2	2.43	2.77	3-4	4-5	3
Sodium alginate	Vat Red 13	2	2.39	2.64	2-3	4-5	3
	Green Vat dye	2	4.45	2.85	3	4-5	3
	Vat Blue 6	2	2.91	2.78	3-4	4-5	3

The color depth of the Vat Red 13 sorghum starch printed fabric (K/S=2.59) was higher than the sodium alginate printed fabric (K/S=2.39), a fact also clearly visualized in Figure 22. However, the blue and green vat dyes had better color values with sodium alginate thickener than sorghum starch. This loss in color richness in case of green dye could be attributed to the good solubility and swelling power of sorghum starch. High solubility of starch molecules increase the

Figure 22. Fabrics printed with Vat Red 13 using Sorghum starch (left) and sodium alginate (right)

chances of dye removal during the washing off process (Teli et al., 2006). By increasing the temperature and time of fixation of the printed fabric, the problem of loss of dye during washing can be minimized.

The bending length of the printed fabrics ascertains the stiffness of the print. Lower bending length indicates higher efficiency of thickener and negligible residue on the fabric. Table V shows the results of the bending length of fabrics printed with sorghum starch and sodium alginate thickeners. The results indicate that bending lengths of sorghum starch printed fabrics are lower than that of sodium alginate. Thus samples printed with sorghum starch were more flexible than sodium alginate printed fabrics. This flexibility is attributed to the good wash ability and solubility of sorghum starch.

The fabric samples printed with sorghum starch and sodium alginate thickener show comparable washing fastness ratings (Table V). Since vat dyes are inherently wash resistant, the use of sorghum starch did not adversely affect the dye qualities. Particularly, in the case of red vat dye, the wash fastness characteristics of sorghum starch printed fabrics were superior to that of sodium alginate printed fabrics (Figure 23).

Figure 23. Washing fastness of fabrics printed with Vat Red 13 using Sorghum starch (left) and sodium alginate (right)

The crocking fastness of the printed fabrics was measured by a crock meter. The results of the crocking fastness in Table V indicate that the choice of thickener (sorghum starch or sodium alginate) does not affect the crocking fastness rating and both thickeners produced comparable results.

Conclusions

Sorghum starch was found to be an effective print paste thickening agent for printing with vat dyes on cotton fabric. The characteristics of sorghum starch ascertained by the physicochemical methods of this study were found to be appropriate and desirable for use as a thickener. Results of subsequent evaluation of sorghum thickener vat dye prints validate the efficiency and potential use of sorghum starch in textile printing. Sorghum starch had good color value, flexibility, wash and crocking fastness properties. The research presents a commercially important end use of sorghum starch with potential to supplement the income of cultivators and farmers of sorghum crop.

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