ADVANCES IN SPUN-DYEING OF REGENERATED CELLULOSE FIBERS

BENJAMIN TAWIAH¹ & BENJAMIN K. ASINYO²

¹Key Laboratory of Eco-Textile, Jiangnan University, Ministry of Education, Wuxi, Jiangsu, China
²Department of Industrial Art, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

ABSTRACT

Spun-dyeing has proven to be very efficient for the coloration of textiles for several decades now. This method of colored fiber production has unparalleled advantages in terms of environmental safety and color fastness. This review seeks to highlight the developments in spun-dyeing of regenerated cellulose fibers over the years with emphasis on choice of colorants and their effect on the fibers produced. Excerpts of results obtained from our research work on the compatibility of spun-dyed alginate fibers and their thermal/crystalline properties with fluorescent pigments have been included in this review. It was observed from literature that dissolved dyes have not been appreciably used in spun-dyeing dyeing due to the high temperature and alkaline nature of the spinning dope usually used in the production of regenerated cellulose. These perceived challenges however sets the pace for further research into the use of dissolved dyes for fiber spinning. The possibility of adding other functional finishes such as antimicrobial, antistatic and flame retardant properties to the spinning dope during the spun-dying process has made it more attractive than ever. However, there is the need for further research into the compatibility of some these finishes with the spinning dope and their possible effect on the microstructure and the tensile properties of the dyed fibers.

KEYWORDS: Regenerated Cellulose, Spun-dyeing, Mass Coloration, Spinning Dope, Colorants

INTRODUCTION

Cellulose, one of the world’s most abundant, natural and renewable biopolymer is extensively present in various forms of biomasses, such as trees, plants, tunicate and bacteria (Wilkes, 2001; Zhou et al., 2003; Fras Zemljic et al., 2012). Besides naturally grown cellulose fibers like cotton, hemp or flax, interest in textile fibers made up from regenerated cellulose has grown over the past few years (Fras Zemljic et al., 2012. A recent study by Transparency Market Research (TMR) forecasts that the global cellulose fibers market will grow at a CAGR of 9.8% between 2012 - 2018. Out of this figure the market for rayon fiber alone will grow at a CAGR of 10% over the period 2014-2019. This global cellulose fibers market has been propelled by the rising demand for skin friendly, eco-friendly, and biodegradable fabrics from the textiles market. Some of the extensively used man-made cellulose fibers include rayon and its various types like viscose fibers, triacetate, and acetate.

The production of man-made cellulose fibers involves the application of cheaper and renewable feedstock as against their synthetic alternatives. Moreover, these renewable biopolymer materials are readily available in nature in huge quantities, which favors their use as more sustainable material compared to oil-based products. While polyester fibers can be understood as cost-effective high-performance material, the unique moisture and water-related properties of cotton can only be substituted by use of cellulose-based fibers, so-called man-made cellulosics (Wilkes, 2001; Manian et al., 2008; Fras Zemljic et al., 2012).
Regenerated cellulosic obtained from biopolymer materials are colored by dissolution and incorporation of colorants followed by reshaping of the cellulose via various physico-chemical processes to obtain colored fibers. (A glossary of AATCC, 2000; Avinash et al., 2005)

The Case for Spun-dyeing

As substitute to conventional wet-dyeing processing for most technical textiles, spun-dyeing overcomes the disadvantages of conventional methods and provides its final products with excellent characteristics, such as uniform coloration, level shade, and is considered as environmentally friendly production process. Its use is not limited to regenerated cellulose but has become the most prominent and preferred choice of method for coloring most synthetic fabrics (Wilkes, 2001; Kamide et al., 2001; Kurahashi et al, 2003; Sui et al., 2012). Another characteristic feature of spun-dyed fibers is their vibrant color and luster, good water-resistance, and excellent color-fastness and light fastness. Spun-dyed fibers do not only possess outstanding quality of the ordinary fiber, but also reduce the color differences between batches, and cuts down on environmental pollution (Manian et al., 2008; Fu et al., 2013). Besides, spun-dyeing is cost efficient, and is therefore mostly preferred choice for coloring synthetic polymers that are otherwise difficult to dye, e.g. polypropylene (Manian et al., 2007; Kurahashi, 2003). The cost and environmental benefits of spun-dyeing as reported by Sardana in (table1) (The Rupp Report, 2013) are amazing; and with the recent clamor for eco-friendly productions in some of the world’s leading producers of textiles such as China, India, Italy, and USA, it has become necessary for further research to be conducted into spun-dyeing as the next viable alternative to the current environmental mess created by the conventional dyeing techniques.

Table 1: Process Savings from Using Spun Shades Viscose [The Rupp Report 2013]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Piece-dyed</th>
<th>Spun-dyed</th>
<th>Savings (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical costs [US$/KG]</td>
<td>0.91</td>
<td>0.24</td>
<td>74</td>
</tr>
<tr>
<td>Power costs [US$/KG]</td>
<td>0.04</td>
<td>0.02</td>
<td>50</td>
</tr>
<tr>
<td>Water costs [US$/KG]</td>
<td>0.02</td>
<td>0.01</td>
<td>50</td>
</tr>
<tr>
<td>ETP Costs [US$/KG]*</td>
<td>0.03</td>
<td>0.01</td>
<td>66</td>
</tr>
<tr>
<td>Coal and furnace oil costs [US$/KG]</td>
<td>0.14</td>
<td>0.08</td>
<td>39</td>
</tr>
<tr>
<td>Total costs [US$/KG]</td>
<td>1.13</td>
<td>0.36</td>
<td>68</td>
</tr>
<tr>
<td>Total water used (liters/100kg)</td>
<td>9,100</td>
<td>3,100</td>
<td>66</td>
</tr>
<tr>
<td>Total Time [min]</td>
<td>575</td>
<td>190</td>
<td>67%</td>
</tr>
</tbody>
</table>

In a world where water resources are becoming increasingly sparse and disposal of industrial wastewater is been subjected to stricter environmental controls, spun-dyeing present a unique opportunity of coloring fibers with very little water use (Manian et al., 2007). In the coloration of both synthetic and regenerated fibers, spun-dyeing ensure less environmental damage compared to the conventional bath dyeing.

Challenges of Spun-dyeing

The disadvantage spun-dyeing is speed of reaction to market demands by the fiber producers who have to either stockpile many different colors of yarns or be prepared to extrude fibers on demand of quixotic fashion and home furnishing markets (Wilkes, 2001; Kurahashi, 2003; Manian et al., 2008). Depending upon the positioning of the fiber producer in the supply chain, this can be a major problem and create minor inconvenience. Another disadvantage of mass coloration is the clean-out required between colors. Extruders, transfer lines, screen packs, and spinneret channels must be purged from one color prior to starting a run of another color. If the fiber producer is large and diversified, there may be an
outlet for off-color fiber (recycle or using a low-value application). The fiber producer may also reduce waste through intelligent scheduling of color on spin lines (light colors followed by dark colors). Practically, the clean-out necessities makes short runs difficult with higher efficiency resulting from longer runs of color (Holme, 2004; Avinash et al., 2005; Bredereck, 2005).

One of the primary considerations in the spun-dyeing process is to ensure the physico-chemical compatibility of the polymer-colorant in the dope mixture (Kurahashi et al., 2003; Fras Zemljic et al., 2012; Wang et al., 2015). Regenerated cellulose’s present unique challenges in this regard because their manufacturing processes often involve treatment of the cellulose with strong reducing and/or oxidizing agents, which may militate against the stability of colorants or affect the tensile strength of the ensuing fiber. Despite these perceived challenges, spun-dyeing of regenerated cellulose’s have been made possible and various methods for its achievement have been reported in literature (Zhou et al., 2003; Fras Zemljic et al., 2012). This script therefore seeks to offer a review of the state of the art systems available for mass coloration of regenerated cellulose fibers.

Applications of Spun-dyed Regenerated Fibers

Previously, most regenerated fiber production capacity serve the technical textiles market especially in the area of medical textiles for specialized applications and for military uniforms, sportswear and automotive textiles (Zhou et al., 2003; Fras Zemljic et al., 2012; Avinash et al., 2005). Currently, production of general-purpose textiles have increased over the past 15 years. For instance, viscose fiber capacity has increased lately to serve the production of general-purpose textiles. These fibers are increasingly been used as household furnishing and for industrial purposes.

Choice of Colorant for Spun-dyeing Regenerated Fibers

The selection of colorants for a particular regenerated fiber is dependent on many factors with the most critical one being the compatibility of polymer-color mixture and its possible effect on the mechanical properties of the fiber (Wang et al., 2015; Fu et al., 2013). Another important aspect worth mentioning is the color performance of the fiber and its intended end use. As a result, several important factors which can significantly influence the fabric properties ought to be made in selecting colorants for spun-dyeing. Some of the most defining properties of colors which can significantly affect regenerated fibers are:

- **The Limiting Concentration:** The limiting concentration of a colorant determines its thermal stability profile in the chosen polymer. Values for the heat stability of a colorant for instance are usually derived from a pre-determined concentration i.e. Standard depth $\frac{1}{3}$ (Modlich, 1999; Clariant Data sheet 2007). The limiting concentration determines the lowest dilution at which a colorant is thermally stable at a given temperature. For instance, in a study conducted by Wang et al., 2015 on thermal behavior of spun-dyed alginate fiber using fluorescent pigment (Figure 1) they observed that the thermal stability of the fiber was compromised as the content of fluorescent pigment in the polymer matrix increased from 2 to 4%.
Similar phenomenon is observed in most regenerated polymers during spun-dyeing. The limiting concentration also determines the tensile strength of the fibers to some extent because the ratio of colorant to dissolved polymer can affect the microstructure and the crystalline alignment of the fiber during extrusion (Fu et al. 2013; Wang et al., 2015). More so, the acidity or alkalinity of the spinning dope can also have a significant effect on the limiting concentration of the regenerated cellulose because this phenomenon plays a decisive role in determining whether the pigment in the polymer matrix behaves as a proton acceptor or donor otherwise and its direct effect on the stability of pigment particles in the polymer-color mixture hence the need for a carefully computation of the dope stoichiometry (Fu et al., 2013). It is worth mentioning that, values obtained for a specific polymer cannot be generalized for all polymers because each polymer has its unique limit concentration (Modlich, 1999, Shenoy & Aroon 1999).

**Particle Size and Its Distribution:** In paste and liquid dispersions such as those used for regenerated fibers, particle size and specific surface area of pigment can significantly influence the rheology of the system (Shenoy & Aroon 1999, Lambourne et al., 1999). The larger the particle size, the lower the specific surface area of a pigment and the consequential lower viscosity. In spun-dyeing of regenerated cellulose, a pigment with high specific surface area will require additional “wetting out” in order to obtain an optimum dispersion. A larger particles size in spinning solutions leads to higher opacity and lower color strength in comparison with a finer milled product (Kunkle et al., 1988; Bilgili et al., 2004) besides its consequential effect on tensile strength. Particle size distribution is also important factor in obtaining optimum dispersion in spun-dyeing applications (Maile et al., 2005; Herbst & Klaus, 2006). A narrow band distribution with a minimum over and undersized particles will more readily disperse in a thermoplastic system particularly when physical dispersion forces and pigment wetting reach their premium (Günthert, 1989; Fu et al., 2013), but this will not work for regenerated fibers hence the need for proper dispersion and distribution of the particles before addition to the spinning dope. The particle size distribution in spinning solution determines the greater extent the crystalline structure and tensile strength of spun-dyed fibers hence the need to even particle size distribution within the spinning dope in order to avoid having weak points with the fiber strand.

**Color Dispersibility:** Optimum colorant dispersion is very essential to the provision of fiber functionality in everyday use (Parfitt, 1969; Herbst & Klaus, 2006; Fu et al., 2013). A careful selection ought to be made in this regard especially in the case of spun-dyeing since this can eventually affect the crystalline properties of the fiber.

**The Light Fastness:** A colorant is primarily determined by its chemistry even though particle size and particle size
distribution can also be influencing factors. Optimal dispersion of mill base, thus pigment and other water insoluble colorants is critical to the achievement of light fastness properties of particular colorant (Giles et al, 1977; Herbst & Klaus, 2006; El-sayed et al., 2012). It has been suggested that processing parameters can also affect the light fastness properties of spun-dyed regenerated fibers but this can be minimized to some extent when monitored properly in dope dyeing process.

Pigments and polymer soluble dyes selected for mass coloration of fibers must meet the above-mentioned requirements and in order to survive the multi-step processing and its end-applications.

Classification of Colorants for Spun-Dyeing of Regenerated Fibers

Vat dyes/leuco Compounds

Spun-dyed fibers are generated by evenly and continually adding the innocuous dye grain of nano-grade colorants into the spinning solution by a special blending technique by which the dye grains are evenly dispersed into the fiber (Boerstoel, 2001; Fu et al., 2007)

Several blending techniques have been proposed for spun-dyeing of viscose or cuprammonium rayon, some of which comprises the addition of vat dyes to spinning dopes, wherein the vat dye is reduced to its leuco form and oxidized back to its parent form in the course of manufacturing the substrate. Some techniques involve addition of reduced vat dye to the spinning dope (Ruesch & Schmidt, 1936; I. G. Farbenindustrie 1936; Manian et al., 2008). Others have proposed that the vat dye should be reduced in the spinning dope either by utilizing the chemical reagents already present in the system (Kline, 1939) or by the addition of reducing agents such as sodium hydrosulphite (Lockhart, 1932). Similar techniques such as dispersion of the vat dye in the spinning dope as a pigment to form the regenerated substrate, and treating the formed substrate with reagents to reduce the vat dye within the fiber (Ruesch & Schmidt, 1936; Batt, 1961; I. G. Farben industrie 1936. In all these techniques, the oxidation of the vat dye back to its parent form is achieved in general by treating the formed substrate with oxidizing agents.

There are however, some limitations to these techniques. For instance, adding the reduced vat dyes to the spinning dope may result in the destabilization (Ruesch & Schmidt, 1936) and therefore proper ageing and coagulation of the spinning dope is hindered, which eventually affects the development of suitable viscosities for fiber/filament spinning. More so, reduced vat dyes are also predisposed to premature oxidation, which normally results in non-uniform distribution of dye in the spinning dope thereby creating ‘weak links’ along the length of the spun fiber. (Maloney, 1967). The ‘weak links’ ultimately create fibers with weak tensile strength with color patches which defeat the purpose for spun dyed fibers. It is well known that many vat dyes are not reduced under conditions that exist in spinning dopes hence the addition of reducing agents to the system which in most cases make the dope susceptible to gel formation (Lockhart, 1932; Dosne, 1936). This makes using vat dyes for spun-dyeing a big challenge. As a result, a technique of dispersing vat dyes in the spinning dope and reducing them in the dyed fiber has been suggested (Lutgerhorst, 1956) but this system has also not been very successful because other problems like uniform distribution of the dyestuff in the substrate is difficult to achieve, and besides, not all the dyestuff in the substrate is reduced, causing visible specks of dyestuff particles to remain in and on the substrate (Boerstoel, 2001; Avinash et al., 2005).

Subsequently, vat acids and their ester derivatives of leuco compounds of vat dyes has been proposed as alternative technique for successful spun-dyeing regenerated cellulose where these compounds are added to the spinning dope.
dope (Maloney, 1967; Dosne, 1936). Nonetheless, these leuco compounds and their derivatives are highly susceptible to oxidation and results in formation of coarse dyestuff particles in the dope thereby affecting the subsequent regeneration steps (Dosne, 1936; Batt, 1961; Maloney, 1967). This can result in poor tensile strength and color levelness across the length of the resultant fiber. Despite the perceived challenges to effective use of vat dyes and their derivatives in spun-dyeing of regenerated cellulose, some success have been achieved lately (Zhou et al., 2003; Fras Zemljic et al., 2012) but for the environmentally effect of these dyes lately in the wake of cleaner productions.

Dissolved Colorants

Dissolved colorants for mass dyeing must be able to withstand the high temperature of polymer melt (typically in the region of 150 melt) to give level dyeing. Yet still the dye must not only have a good affinity to the polymer, but also must not migrate out of the substrate after dyeing (i.e. must not bleed or bloom) (Maloney, 1967; Jones, 1959). Despite the stringent conditions of spun-dyeing, dissolved colorants in polar water-miscible solvents or in the spinning dope have been used extensively to spun-dye various regenerated cellulosics (Keil, 1961; Ciba Ltd, 1965, Ciba Ltd, 1966; Ciba Ltd, 191963; Riehen et al., 1971; Wegmann & Booker, 1966). The colorants used in these methods are selected dyes and their derivatives. The choice of dyestuffs available for this technique is limited by the fact that not all dyestuffs can withstand the strong alkaline conditions present in the spinning dope or the strong acid treatments imparted to substrates during regeneration (Maloney, 1967; Steiert et al., 2007). Besides, different polymers behave differently in strongly acidic or basic medium. Also, it has been established that certain water soluble dyes such as reactive dyes undergo strong hydrolysis reaction in strong alkaline solution and therefore may not be suitable in polymer solutions that requires strong basic medium to remain stable for spun dyeing. Moreover, the use of water-soluble dyestuffs in mass coloration of regenerated cellulosics has been observed to result in poor wet fastness of the resultant fiber (Marcincin, 2002). Despite the perceived challenges, a method which may be categorized as quasi-mass coloration has been proposed where naphthol dye grounders are dissolved or mixed in alkaline spinning dope (Manian et al., 2007; Manian et al., 2008) after which the fibers are treated with coupling components to develop the color. Colored fibers with good tensile strength were achieved using this approach but color patches easily develop along the fiber strand which results in unlevelled dyeing and poor light fastness. Due to these limitations, the use of dissolved colorants in spun-dyeing is not very popular even though a significant success have been achieved. Further research is also need in this area to take advantage of large number of dissolved colorants available on the market.

Dispersed Colorants (Pigments)

The dispersion of superbly pulverized organic or inorganic pigments in spinning dopes has been intimat ed as a possible route for mass coloration (Broda et al., 2007; Nypelo et al., 2012; Hao et al., 2012), with additives being recommended in some cases to improve pigment dispersibility (Fu et al., 2011, Fu et al., 2013). The process of milling pigments to obtain a suitable particle size is time intensive and accompanied by risks of recrystallization and/or agglomeration (Fu et al., 2013). Several approaches for milling pigments have been developed lately. Milling pigments with the aid of polymeric dispersants has been suggested to produce stable pigment dispersions, which builds voluminous shells to intensify the charges on pigment surface, thus avoiding the flocculation and coagulation of pigment in aqueous media (Novacel, 1953; Fu et al., 2011).

However, the possibility of poor pigment dispersion in spinning dope is almost a predictable risk with this technique. This may lead to problems in the regeneration process and that could consequently result in non-uniformity in
color in the spinning dope due to flocculation or coagulation (Novacel, 1953; Marcincin, 2002; Hao et al., 2012). This can greatly impair the quality of spun-dyed regenerated cellulose fibers substrates (Manufactures de produitschimiques du Nord, 1956; Ciba Ltd, 1966; Fu et al., 2013). Apart from the problem of flocculation, foam forming in the spinning mass is believed to be caused by dispersants used in the pigment formulation process (Riehen et al., 1971, Fu et al., 2013). The colored substrates tend to be opaque (Wegmann et al., 1966), exhibit dull shades and dichroism (Maloney, 1967: Ciba, 1965). This technique of mass coloration can also have adverse effect on substrate strength and its microstructure (Wang et al., 2015).

Besides, the use of pigments has been reported in recent times to significantly affect the spinning process, the microstructure, surface morphology, color performance and the mechanical properties of the regenerated cellulose fibers due to the large particles sizes and uneven distribution in the spinning dope (Bale, 1941; Mamaza et al, 1996). However, pigment presents a unique opportunity because it is easily adaptable to several fiber types and problems such as large particle sizes and uneven distribution can be controlled by the use hyper branched and high molecular weight dispersants (Fu et al, 2007).

Also, pigment encapsulation technology seem quite appropriate solution to the challenges associated with the regular approach to pigment application in spun-dyeing of regenerated cellulose due to its perceived advantages as compared with other methods (Tiarks et al., 2001; Steiert et al., 2007) Unfortunately, this has not been the case due to its associated effect on tensile strength. Several techniques such as emulsion or miniemulsion polymerization (Lelu et al, 2003; Broda et al, 2007; Fu et al., 2011; Fu et al., 2013) microencapsulation (Schoenbach et al., 1967, Lelu, 2003; El-Sayed et al, 2012), phase separation (Gomm et al, 1964; Dong et al., 2012) in situ polymerization (Liu, 2007; Roy et al., 2012), layer-by-layer assembly (Yuan et al., 2008), sol–gel Gomm et al., 1964; Li et al., 2008), and free-radical precipitation polymerization (Fu et al., 2010) has been proposed.

Out of the several approaches researched above, miniemulsion polymerization has been suggested to be the most efficient technique due to its attractive advantages (Schoenbach et al., 1967; Fu et al., 2013). The problem of producing stable pigment/latex still resurfaced because of defect with the emulsifier used during the process of miniemulsion polymerization (Yuan 2008, Fu et al., 2013). The emulsifier is desorbed from the latex, especially in highly alkaline solutions at high temperatures thus making it quite unstable for spun-dyeing of regenerated cellulose fibers (Tiarks et al., 2001, Fu et al., 2013). To this end, the use of polymerizable dispersant as an emulsifier in miniemulsion polymerization has been suggested (Tiarks et al., 2001, El –Sayed et al., 2012). This polymerizable dispersant serve as monomer in copolymerization by forming covalent bond on the surface of the formed latex, thus overcoming the downsides of the common emulsifier (Steiert, 2007; Taniguchi et al., 2008; Fu et al., 2013-69).

In a recent study conducted by Wang and coworkers, a polymerizable dispersant was used as an emulsifier in miniemulsion polymerization for encapsulation of carbon black (CB) with latex. The CB/latex composite dispersion showed excellent stability with superior color yield when used for spun-dyeing of regenerated cellulose fibers. The spun-dyed regenerated cellulose fiber by CB/latex composite dispersion had enhanced tensile properties with excellent color strength and fastness (Wang et al., 2013).

The Use of Sulphur Dyes

Spun-dyeing of regenerated cellulose fibers using Sulphur dyes have been proposed as an alternative to pigment
dyes but this has not received much research attention since its postulation in 1938 by Whitehead and others. The use of this approach involved the suspension of Sulphur dyes intermediates in the spinning dopes (Whitehead, 1938; Cassella, 1961; Ino et al., 1979) before the addition of dye itself after which the spinning is carried out. Another approach suggested was to simply mix waste Sulphur dyed cotton textiles with fresh cellulose biopolymer where the mixture is subjected to the popular xanthation process and spinning to obtain the colored filaments (Hama et al., 1972; Von der Eltz, 1996). This process however did not receive much attention due to the toxic nature of the xanthation process and the many color and structural defects of colored fibers (Ino et al., 1979; Bechtold & Manian 2005). There is the need for further research into the potential of using Sulphur dyes for spun-dyeing of regenerated cellulose.

**Spun-dyeing of lyocell**

The lyocell fiber has received much research attention in recent times due to its high strength, rigid crystalline morphology. Lyocell fiber gives higher mechanical modulus which substantially makes it effective material for use in different biometerials, paper industry, nonwoven fabric for packaging purposes (Kunal Singha, 2012). Lyocell is the generic name for a biodegradable fabric that's made out of treated wood pulp and commonly sold under the brand name Tencel, made by Lenzing AG. Lyocell is known for its versatility, durability, and strength when both wet and dry, this material is used in everything from clothing to cars. Lyocell fibers compared with other regenerated cellulosics is relatively new being that the first commercial samples appeared in the mid-1980s with full-scale commercial production beginning in the early 1990s (Bartsch et al., 1999; Ruef, 2001).

Lyocell production is considered as being more environmentally friendly because the amine oxide used for dissolving the pulp is normally recycled and re-used during the production process making it a better alternative to viscose production (Bartsch et al., 1999; Bechtold & Manian, 2005) as illustrated in figure 3. Hence, there are only a few methods reported for the mass coloration of lyocell.

![Figure 3a: Lyocell Production Process (Bartsch & Ruef, 1999)](image-url)
Bartsch et al. 1999, suggested that selected inorganic pigments, which contain small amounts of heavy metals that does not significantly lead to a severe decomposition in temperature of the spinning mass be mixed with the cellulose solution prior to spinning of lyocell fiber. In a similar work done by (Ruef, 2001), he proposed that colorants or colorant precursors be mixed with the cellulose solution with the caution that the colorants remain insoluble or sparingly soluble in amine oxide. The most recent method reported by (Bechtold & Manian 2005), suggested that the cellulose pulp be dyed with a vat dye where the dyed pulp will be optionally mixed with undyed pulp that will eventually be used for spinning the lyocell fibers. The disadvantage of this method is that, the fibers produced have lighter shades because the undyed pulp is mixed with the dyed pulp as illustrated in figure 3b.

![Figure 3b: Flow Diagram of lyocell Coloration Process (Bechtold & Manian, 2005)](image)

In the case of spun-dyeing of lyocell using pigment colorants, research has shown that particle size and distribution in dispersion can significantly impact the color attributes of the resultants fiber (Fu et al., 2010; Mohmmad et al., 2011). It has been postulated that a small particle size and its even distribution in the polymer matrix results in bright shade with high tensile strength (Fang et al., 2005 Alexandra & Bermel, 1999; Antton et al., 2004). This assertion has been collaborated by (Taniguchi et al., 2008; Fu et al., 2010; Mohmmad et al., 2011; Jaturapiree et al., 2011; El-Sayed et al., 2012) that carbon black dispersion with small particles in lyocell spinning solution minimizes the effect of irregularities in microstructure, surface morphology and mechanical properties of lyocell fibers and as such ensures a continuous spinning process without problems.

In a study conducted by (Tiarks et al., 2001, Wang et al., 2013), nanoscale carbon black dispersion was prepared and used to spun-dye lyocell. In their study, a polymerized dispersant was used as the emulsifier in the miniemulsion polymerization process to enhance the compatibility of the carbon black/latex composite dispersion with the lyocell spinning solution. Also, they observed that the stability of the color/polymer matrix to pH plays a very important role for successful spun dyeing of lyocell fiber. They concluded that the stability of the CB/latex composite dispersion decreases slightly as pH increases from 8 to 14 (Wang et al. 2013). It is worth noting that this phenomenon may not apply to every pigment during the process of spun-dyeing of lyocell because different pigments behave differently under different processing conditions before their eventual incorporation into polymer matrixes and therefore, the chemical properties of the specific pigment.
ought to be carefully studied in order to successfully incorporate it into the specific polymer matrix.

**Spun-dyeing of Alginate Fibers**

Alginate fibers are derived from brown algae consisting of -(1-4)-linked-d-mannuronic acid (M) and -l-guluronic acid (G) segments to form a macromolecule polymer. These fibers have inherently bioactive properties and are highly biocompatible. Spun-dyeing of alginate fibers is very new because there is basically no literature on it until our research team (Wang et al., 2015) investigated the compatibility of spun-dyed sodium alginate fiber using fluorescent pigment dispersion. Below are excerpts of the results; fluorescent pigment dispersion was prepared with styrene maleic anhydride (SMA) and was then introduced into the sodium alginate fiber spinning solution as shown in the figure 4. (Full manuscript can be downloaded from dyes and pigment journal)

![Figure 4: Spun-dyeing Process for Sodium Alginate Fiber (Wang et al, 2015)](image)

The fluorescent pigment dispersions was highly compactible with alginate spinning dope with the resultant fiber having excellent rubbing and light fastness with interestingly high fluorescence intensity (Wang et al., 2015) but unfortunately, its bioactive properties were not investigated. This sets the pace for further research into the bioactive properties of spun-dyed alginate fibers and the possibility of using other colorants besides fluorescent pigments.

**Future Prospects**

With increasing oil and cotton prices coupled with the growing preference for bio-based products, especially those derived from non-food materials, markets for dissolving pulp are well placed to grow in the mere future. The growth in bio-based products will drive newer technologies and coloration chemistries for these fibers. And with the unparalleled advantages of spun-dyeing combined with the advancement in color chemistry in recent years; it is certain that spun-dyeing is the future of the regenerated textile materials. The buoyant environmental prospects of this coloration technique compared to the traditional method of fiber coloration will create an avenue for achieving fibers with special properties.
Advances in Spun-dyeing of Regenerated Cellulose Fibers

The incorporation of such functional elements such as flame retardant finish, antimicrobial properties, antistatic finishing, and deodorant into structure of the regenerated cellulose spinning dope besides the coloring finishes will even make it more attractive than ever. With these precursors, it is expected that fibers with specific functions will be produced through spun-dyeing. The market for spun-dyed regenerated cellulose will expand greatly because spun-dyed fabrics have superb color quality. The technology for spun-dyeing will in the near future reduce waste generated by 97% compared with other coloring techniques because “green” approaches for dissolution of cellulosics are being proposed as real alternatives to the viscose process (Grinshpan et al., 2013).

REFERENCES

15. Ciba Ltd. (1968) Process for the preparation of transparent colored shaped articles of regenerated cellulose with the aid of organic dyestuffs of low solubility in water. GB 1128158


Regenerated Cellulose Fiber Production


40. Heinrich E. (1966) Spin-dyed regenerated cellulose products and process for their manufacture. GB 1046299


45. [http://www.marketsandmarkets.com/Market-Reports/cellulose-fiber-market-189312904.html?

46. I. G. Farbenindustrie AG (1936) Process for the manufacture of dyed filaments and films. GB 448447

47. G. Farbenindustrie AG (1937) The manufacture of dyed artificial masses from regenerated cellulose. GB 465606


50. Jones, FB (1959) Glossy spun-dyed threads from aqueous cellulose solutions. DE 1067173


53. Kline, HB, & Helm, EB (1939) Manufacture of artificial silk. US 2143883

U.S. Patent No. 4,793,985.


61. Lockhart GR (1932) Manufacture of rayon. US 1865701,


63. Lutgerhorst, AG. (1956) Spun-dyed rayon. US 2738252


82. Ruef H. (2001) Colored cellulosic shaped bodies. WO 01/ 11121,


Impact Factor (JCC): 0.9458- This article can be downloaded from www.bestjournals.in


96. Wegmann J, & Booker, C (1966) Colored viscose dope. DE 1220964


