

A Review of Some Significant Insights on Nano Finishing of Protein Fibres

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Abstract

The article critically reviews the recent trends in nano finishing of protein fibres such as wool and silk. The finishing methods adopt an eco-friendly approach aimed at sustainability. Plasma treatment as an environmentally friendly process was used to prepare Wool/PET fabric for enhanced deposition of titanium dioxide nanoparticles. TiO₂ nanoparticles were stabilized on the fabric using citric acid as cross linking agent in the presence of sodium hypophosphite by a pad-dry-cure process. Wool fabrics are subjected to different surface modification methods in order to improve their hydrophilicity, dyeability, antimicrobial, shrink proofing properties. Especially environmental friendly methods and application of biopolymers are gaining importance instead of conventional processes and textile chemicals. Silver nano particles have been applied on silk using cross linking binders by pad dry cure method. Application parameters have been optimized and relevant physical, structural and antimicrobial properties are evaluated. Mechanism of the binder action is found to be impregnation or adhesion. A novel functionalization approach has been addressed by using sodium alginate (Na-Alg) assisted green silver nanoparticles (AgNPs) on traditional "Rajshahi silk" fabric via an exhaustive method. The synthesized nanoparticles and coated silk fabrics were characterized by different techniques, including ultraviolet-visible spectroscopy (UV-vis spectra), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FT-IR), which demonstrated that AgNPs with an average size of 6–10 nm were consistently deposited in the fabric surface under optimized conditions. Recent developments in different treatments that confer functional characteristics on wool have been reviewed. Wool fabrics are subjected to different surface modification methods in order to improve their hydrophilicity, dyeability, antimicrobial, shrink proofing properties. Especially environmental friendly methods and application of biopolymers are gaining importance instead of conventional processes and textile chemicals. In this study, nano chitosan particles were synthesized, applied on wool fabrics and compared

with bulk chitosan in terms of various properties. Ag-loaded chitosan nanoparticles was also synthesized and examined in terms of its antibacterial activity by different application methods.

Keywords: Nano finishes; Functional; Wool; Silk; Silver nano particles; Cross linking; Nano chitosan; Plasma

Introduction

The various kinds of textile materials include natural fibres like cotton, wool and silk, synthetic fibres like polyester-polyamide-acrylic, regenerated cellulosic fibres like viscose and their blend fibres. Due to the economic recession these commercial fibers have been negatively affected. The production of wool globally has declined. Approximately world wool production is 1.3 million tons per year. Whereas, the global production trend in synthetic fibres has shown upward trend during recent years, particularly polyester fibres. Hence, various types of treatment are required to improve them. In order to alter their properties, textile materials are sometimes finished by chemical processes. Earlier starching has been widely used to produce clothing more resistant to stains and wrinkles. Recently the fabrics have been rendered stronger and wrinkle free by emerging technologies like permanent press process and finishing agents. Very recently, new developments have emerged for permanent treatments based on metallic nano particles for making textiles more resistant to water, stains, wrinkles, and pathogens. Many types of treatments have been applied on textile materials before reaching the end user. There exist several possibilities ranging from formaldehyde finishes (to improve crease-resistance) to biocides finishes and from flame retardants to dyeing of many types of fabrics. But, a number of such finishes can also have adverse influences on the end user. As a result, presence of chemical treatment, quality control and testing techniques are considered crucial [1-4]. The scope for application of innovative chemical finishes has been prompted by the rapid growth in textile industry and in their end-uses. Thus, it is crucial to show the functional properties of wool and certain synthetic fibres like felting and shrinkage, pilling, microbial, surface characteristics, and so on. The above type of proofing can be affected by organically grown fibres treated with toxic

chemicals, and such chemicals can result in issues relating to health and environment [5].

For various applications such as water purification, indoor air purification/deodorization, antibacterial effect, antifogging and self-cleaning glasses, titanium dioxide nano particle coatings have been used widely. Recently, several studies have reported deposition of nanocrystalline TiO₂ layers on textiles to obtain self-cleaning properties [6]. When TiO₂ is exposed to photon radiations with energy higher than or equal to the band gap, electron hole pairs can induce the formation of reactive oxygen species, which oxidize and degrade pollutants and bacteria [7].

The use of wool fibers in the textile industry has gained prominence. It is composed of keratinous protein as a basic constituent and the minor component Cell Membrane Complex (CMC). CMC forms a continuous phase in the fiber, links cortical and cuticular cells. The cuticular cells are located on the outermost part of the fiber surrounding the cortical cells. The surface of these cells is hydrophobic nature due to the presence of a fatty acid monolayer covalently bounded to the epicuticle layer [8-10].

Owing to its superior properties silk has been considered as one of the popularly used textile materials and also as the queen of textiles [11]. Fabrics produced from silk are distinctly luxurious and possess a number of outstanding qualities such as lustre, wearing comfort, fine and smooth texture, fine and smooth texture, soft handle, and excellent draping quality. Over the years natural silk has been used conventionally in textiles because of its inherently elegant sheen, great flexibility, environmental friendliness and excellent mechanical strength. As a natural protein fibre, silk possesses a chemical structure very similar to human skin with smooth, breathable, soft, non-itching and antistatic characteristics, which endow it a suitable material for high grade clothing [12]. But, potential defects of silk fabrics include their tendency to crease easily during home laundering, tendering nature when wet and easy microbial attack due to its hygroscopic nature [13].

Recently, nano particles have attracted a good deal of attention in various areas, including chemistry, physics, materials science, life sciences, and engineering because of their superior characteristics, such as optical, magnetic, electronic and catalytic properties [14]. Among metallic nanoparticles (NPs), the size of AgNPs ranges between 1 nm and 100 nm, making them one of the best candidates for several applications including biosensing, antibacterial, antiviral, and antifungal activities, drug delivery, catalysis, electrochemical, conductivity, and so on, with exponential accretion production [15,16]. For the preparation of metal nano particles many physical and chemical techniques are available. But they are not eco-friendly [17,18].

Literature Review

Enhancement in functional properties of wool

The recent years have opened up new and prospective avenues for wool fibre owing to major research and development achievements in technical applications. Nanotechnology is the science of self-regulating materials and processes that are controlled at the molecular level. A number of techniques are available for coating of fabrics. These are spraying, transfer printing, washing, rinsing and padding. The most widely used is padding. A padder enables attachment of the nano-particles to the fabrics, which is adjusted to appropriate speed and pressure, and is then cured and dried [19,20]. During the past few years photo grafting technique has been adopted to prepare the wool fibre using silver loaded silicon dioxide nano-antibacterial agent, and on the wool fibre surface antibacterial layer has been formed [21]. The hydrophobic nature and scale structure of the wool fiber led to the fiber to move towards their root end under mechanical action in the wet state [22]. The shrinkage of wool fibres has been prevented through a number of techniques and chemical treatments. This has primarily been achieved by coating with resins like polyamide epichlorohydrin or grafting polymers onto wool fibres and secondarily by means of morphological modification of the cuticular cells through chemical or physical treatment [23].

Certain functional properties of wool and synthetic fibres (acrylic, polyamide and polyester) brought about by various techniques have been highlighted. Wool has been treated using glycerol polyglycidylether (GPE) in concentrated salt solutions. Also, the use of sodium methoxide or sodium hydroxide in a 2-propanol medium is required to overcome shrinkage of wool. The pilling and shrinkage get enhanced by DCCA (Dichlorodicyanuric acid) treatments. Particularly in industry chemical treatment followed by enzyme is better preferable [24]. Enzymes are biocatalysts and can be used to overcome demerits in properties like shrinkage, pilling, hydrophilic, etc. for wool and synthetic fibers. The felting properties can be imparted on wool by means of sericin which is a biopolymer. Also, casein, which is a natural polymer has been used for enhancement of the surface of acrylic fabrics. The decrease in shrinkage, felting and pilling in the case of wool, polyester, polyamide and polyester has been caused by application of cyclodextrins. On the other hand such application resulted in properties like antimicrobial, hydrophilic, soil-resistant, and so on. Owing to their non-toxicity and biodegradability their use will get enhanced thus providing "green" solutions for improvement of such important functional properties of textiles. Plasma technology, as a very active tool applied to wool to modify the surface substrate. In the long term the increasing importance of environmental issues will favour the use of this technology. Nanotechnology in the textile is mainly being tried into areas of fibre formation and processing of fabric. It enables enhancement of characteristics such as wrinkle-resistance, soil and water repellency, antistatic, antibacterial and UV protection with regard to chemical processing area. Use of

silver, titanium dioxide and zinc oxide nano particles in textile finishes result in antibacterial and UV blocking.

Enhancement of functional properties of textile materials is considered crucial to the textile industry. The developments in chemical treatments of textile materials for imparting functional properties will be determined by factors like economic forces, market demands, and environmental concerns. Textile chemicals are required at economical cost at global level, which is achieved by decrease in the quantity of water to be shipped. Generally undesirable side effects are caused by the use of textile chemicals. Products like plasma need less energy and water to perform such functional characteristics. Textile industries see a promising future for plasma technology, with the environmental and energy conservation benefits, in developing high-performance materials for the world market [24]. Cyclodextrins are non-toxic and biodegradable, there by offering "green" solutions to enhance the properties and providing new functionalities to textile products. Biopolymer like sericin, can be opted for use so as to enhance functional characteristics arising from their economic cost in comparison with other chemicals and also prove to be safe ecologically. It is expected that the constraints in application of conventional techniques in imparting specific characteristics to textile materials will be overcome by nano technology in the times to come. There will be an increase in the improvements on the application areas of nanotechnology in textile industry like anti-bacterial textiles, antistatic textile, flame-retardant textiles, and so on.

Eco friendly method of coating PET/Wool fabric

One of the widely used blend textile materials in the textile industry is Wool/PET fabric. Investigation has been carried out regarding the self-cleaning finishing of this fabric. The loading of titanium dioxide nano particles have been improved by pre-treatments using lipase enzyme and potassium permanganate as oxidizing agent [25,26]. The adsorption of titanium dioxide nano particles on fibres has been improved by oxygen plasma treatment which introduces oxygen containing functional groups to the surface of wool and polyester fibers and removes the hydrophobic scales of wool. This is affected without yellowing and affecting the physical properties of the fabric. In this study the wool/PET fabric was functionalized with oxygen plasma and coated with TiO₂ nanoparticle and the self-cleaning property of the finished fabric was evaluated.

Before coating with titanium dioxide nano particles, wool/PET fabric has been treated with oxygen plasma. There has been improvement in the amount of nano particle loading on the fabric by means of plasma treatment. In comparison with noncoated and raw coated samples the plasma treated and coated sample exhibit better self-cleaning property [27]. The physical properties of the fibres can be preserved by plasma treatment which can substitute processes like oxidizing and enzyme pretreatments that do not consume water and chemicals.

Discussion

Application of nano sized chitosan for wool finish

The outer surface of the fiber comprises of cell bundles that possess a scaly structure [28]. The presence of scales with relatively hard and sharp edges hinders the sorption characteristic of wool since which pose a barrier for the diffusion. The performance and quality of finished wool fabric with regard to handle, lustre, pilling dyeability felting, and shrinkage is influenced by its scaly structure. Different techniques of surface modification on surface of fiber are required so as to overcome the problems associated with shrinkage and hydrophilicity of wool. Chemical methods have been the major treatment for eliminating such problems earlier. But, owing to the increasing environmental pressure, textile industry has been encouraged to use ecological processes, like enzyme, plasma and biopolymers in place of chemical treatments. Besides escape potential chemical pollutants and their effluents as a result of chemical processes, bulk properties of fabric can be protected. Chitosan is a renewable polysaccharide-based cationic biopolymer. It is derived from the chitin component of the shells of crustaceans. It holds promise for replacement of some synthetic polymers having desirable properties that consist of nontoxicity, biocompatibility, biodegradability, antimicrobial activity and chemical reactivity. It can be used mainly for the purpose of shrink resistance, dyeability, antimicrobial effect in wool finishing treatments. In order to reduce wool damage, chitosan application before enzyme treatment is used in many studies [29-32]. Due to its polycationic character, it has an interaction with oppositely charged molecule or surfaces of enzymes and wool fibers. Whereas, it can be removed partially from the fabric surface based on conditions of washing. The suitable treatment coupled with chemical agents can prove advantageous to offer the stability against multiple washings. New investigations have been directed on nano sized chitosan particles so as to achieve more merits of chitosan. The use of nano chitosan is a relatively new concept in textile industry. The unique properties of nano-particles include large ratio of surface to volume, surface-active multi centers and high surface reactivity. The merits of chitosan and nano-materials have arisen as nano chitosan having outstanding physicochemical characteristics. It is bioactive and frequently used in many industrial areas including textiles [33-37]. Enzyme treatments offer the prospect of environmentally acceptable processes for treating protein fibers. To modify the surface of wool by enzymatic treatments, proteases have been widely used due to their ability to catalyze the hydrolysis of peptide bonds in wool scales. Wool treated with protease can remove the lipid layer and also result in some oxidation of peptide links to a particular extent [38,39]. Plasma treatment seems a prospective option to impart new functional properties like water repellence, hydrophilicity, mechanical, antibacterial properties, and so on because of the nano scaled modification on textile fibers. At the same time, the natural aspect of fiber properties as well as the handle of the material

remains unaffected. For wool fabrics, plasma treatments are replacing chemical textile treatments to achieve shrink-resistance and improved dyeability substantially. In addition, other effects can be obtained like modification of the cuticle layer, generation of new hydrophilic groups due to hydrocarbon chain oxidation, decrease of the chain length of fatty acids, enhancement of surface wettability, dyeability, fiber cohesion, and shrink resistance. In the case of large scale applications, atmospheric plasma treatments exhibit considerable merits with regard to the expense, time and space, than that of the vacuum plasma applications. Bulk chitosan and nano chitosan particles have been used in the study considered. The treated fabrics have been assessed with regard to their antimicrobial effect, dyeing by acid dyes, air permeability, and tensile strength and surface morphologies. In the case of antibacterial treatments, silver loaded chitosan particles have also been synthesized. Various treatments (enzyme, plasma and enzyme + plasma combinations) have been given to modify the wool surface to improve biopolymer particles effect and to achieve required properties.

Because of its many unique properties, the applications of chitosan in textiles have received very good focus in many investigations. The penetration of chitosan polymer into the fibre is restricted by its large molecular size and high viscosity. Hence, only surface deposition occurs and it results in deterioration in handle and appeal of the fabric. Reducing the particle size of chitosan to nano level increases the extent of penetration into fiber structure and maintains inherent properties of cotton fiber [40].

A limited literature is available relating to the application of nano formed chitosan in textile industry [41-46]. For the investigation concerned, chitosan nanoparticles and chitosan-silver nanoparticles have been synthesized. In the case of wool fabrics, enzyme and plasma treatment contributions of nanochitosan treatments have been studied with regard to different properties. Studies have also been carried out on comparison of chitosan and nano-chitosan in dyeing, antimicrobial effect, tensile strength, and surface morphology and air permeability properties. Addition of chitosan on the wool surface creates additional functional groups that result in hydrophilicity. Protease enzyme has hydrolytic effect on wool fibers and the diffusion barrier to water and dye molecules can be overcome. The capillarity is improved by plasma treatment through oxidation and etching reactions. Taking into account all such aspects; dual effects of enzyme, plasma and chitosan exhibit significant improvements while triple effects yield the best results [47]. Upon assessment of dyeing results, it has been observed that chitosan, enzyme and plasma treatments alone increase dye uptake of wool by various mechanisms to a large extent than that of the control sample. Before chitosan treatment, enzyme and plasma treatments enable dye diffusion. Such influence is more prominent in case of combination of enzyme, plasma, chitosan and is found to be 2.5 times higher in K/S values than untreated one with good fastness properties. Nano-chitosan showed better properties due to its large surface area and smaller size when compared with bulk chitosan [48]. When antibacterial effects are concerned, chitosan showed 93.98% effect against gram

negative bacteria with combined treatments of enzyme and plasma. Chitosan silver nanoparticles showed the highest antibacterial effect on fabrics up to 97.66%. Almost complete antibacterial influence has been obtained through enzyme and plasma pretreatments before chitosan-silver nanoparticle application. There has been loss of tensile strength due to enzyme treatment but within acceptable limits. But, enhanced tensile strength and protective effect has been observed by post application of chitosan or nano chitosan. There has been a reduction in permeability to some extent by enzyme, plasma and chitosan considering air permeability test. Chitosan and nanochitosan in particular possess lower values in comparison with untreated one. The chemicals used in conventional textile finishing processes can be replaced by chitosan and nano chitosan particles. Findings have shown that ecological processes like enzyme and plasma improve their effect substantially without deteriorating bulk properties of wool fabrics. For finishing of wool, nano-sized chitosan and its application with ecological processes appears to be more feasible and prospective from the sustainability point of view in the textile industry.

Nano silver treatment of silk

As silk is susceptible to attack by bacteria that can adhere easily and grow on it, and can result in its degradation and deformation, its use is greatly hindered by hard conditions of storage [49]. Hence, it is much preferable to modify silk fabrics to show the antimicrobial activity in order to widen its scope of end uses.

Antibacterial finishes are applied to textiles for three major reasons, namely,

- To prevent the spread of disease and avoid the danger of injury-induced infection
- To limit the development of odour from perspiration, stains and soil on textile materials, and
- To prevent the deterioration of textile caused by mildew, particularly fabrics made of natural fibre [50]

In comparison with conventional chemical, physical, physio chemical modifications, nano technology is considered as the futuristic approach for improvement in the performance of textiles [51-55]. In textile area, the major emphasis has been towards use of nano size substances and generating nano structures during finishing and manufacturing processes to impart anti-bacterial, water and oil repellency, soil resistance, anti-static, flame retardancy and enhanced dyeability properties. Silver nano particles are considered typical nano materials having wide range of anti-bacterial properties on Gram positive as well as Gram-negative bacteria. Nano particles were dispersed in the polymer (binder) matrix or coated/impregnated and finally become immobilized in the cotton fibre matrix. The polymeric materials have been found to be suitable to form composite dressings with silver nano particles because of their structure, tailorability and flexibility. A number of techniques have been reported for polymer immobilization in antimicrobial coatings based on their particular characteristics, viz as stabilizers during synthesis of

silver nano particles for prevention of the aggregation of the nano particles, and as linkers for silver nano particles which are directly loaded or *in situ* synthesized in antimicrobial composite coating and enable regulated release of silver nano particles by both alteration of the interaction between polymer and nano particles and their concentration.

Silk fibre has been coated with silver nano particles in order to achieve antimicrobial properties [55]. Two kinds of approaches have been evolved to design silver nano particles functionalized on silk fibres. The first approach involves coating of silk surface using pre synthesized silver nano particle that has been immobilized by exhaust technique by means of impregnation. The second approach involves direct synthesis of silver nano particles *in situ* onto silk fibres. Silver ions are attached on silk fibres by means of electrostatic adsorption or ion exchange, followed by a reduction step to produce silver nano particle. The method of *in situ* synthesis was superficial and enabled strong binding between silver nano particle and the fibres and has been used for coating on silk [56]. Different polymers like polyamide network polymer, poly(vinyl pyrrolidone) and polyacrylic acid ha polyamide network polymer, poly(vinyl pyrrolidone) and polyacrylic acid have been used to functionalize the surface of silk in order to enhance the extent of adsorption of silver ions in the *in situ* modification method [57,58]. Chemical reducing agents like hydrazine, glucose, sodium borohydride and citrate have been used to consequently reduce the silk absorbed silver ions to silver nano particle [59,60]. When silk fabric has been coated with the silver nano particle produced by chemical method through reduction of silver nitrate it showed good antimicrobial activity against *S. aureus*. After five wash cycles the fabrics showed up to 80% antimicrobial activity [61]. The antimicrobial mechanism of silver nano particle has been proposed to be related to the formation of free radicals on the surface of silver nano particles (positive charges) as confirmed by ER investigations followed by free radical-induced membrane damage [62]. It was finally confirmed that the antimicrobial activity of silver nano particle and silver nitrate was by NAC (N-Acetyl cysteine) [56-68]. It has been reported that the treatment of silver with silver nano particles by reduction of silver nitrate with hydrazine and glucose as reducing agents and with PVP as a dispersing and protecting agent [63]. Exhaust technique has been used for the application of silver nano particles. The exhaust method of application has been used to study the antibacterial properties of silk fibres against *Staphylococcus aureus* and *Escherichia coli* regarding the effects of nano sized silver colloids [64]. Silver nano particles have been coated on silk using sericin as capping agent after synthesizing by the reduction of silver nitrate with sodium borohydride in an aqueous solution [65]. Investigations have been conducted on silk base wound dressings by incorporation of silk nano particle at low concentrations on electro-spun silk fibroin mats and it has been found that there is considerable antibacterial activity against *S. aureus* [66]. Investigation has been carried out relating to the green chemistry method to synthesize silk sericin capped silver nano particles under alkaline conditions (pH 11) with silk sericin as a reducing and stabilizing agent in

place of toxic chemicals [67]. The antimicrobial behaviour of silk has been studied after synthesizing the silver nano particles *in situ* using silver nitrate and multi amino compound [68]. But, the agglomeration of silver nano particles occurs in one step mixing of the compounds mentioned. Cotton fabric has been finished with commercial silver nano particles [69]. SEM studies have been used to investigate the morphology of the silver nano particles finished cotton and it has been found that nano silver particles distribution was partially uniform and they were clustered while adhering to the fabric. The commercial nano silver particles have also shown to be spheroids having an average diameter of 20-90 nm. There have been reports relating to the findings on the bacteriostatic efficacy of chosen silver nano particles in the finishing of cotton textiles by the padding squeezing method with silver compounds in the resin matrix. When the silver finished fabrics have been observed using SEM it showed that silver compounds were well dispersed on the fabric surface. However, in certain cases, they form agglomerates of single particles. The treatment has proved good and durable in the case of *Bacillus subtilis* (Gram positive) as well as *E. coli* (Gram negative).

Previous investigations have pointed out that the application of silver nano particles has been effected by exhaust method or by *in situ* synthesis of silver nano particles in the fibre matrix. But it is to be noted that pad dry cure technique is adopted for most of the textile finishing processes. Thus, efforts have been taken for application of silver nano particles with self-cross linking binders by pad dry cure method to simulate the current finishing technique used in the industry. Application parameters were optimized and relevant physical, structural and antimicrobial properties were evaluated to find out the effect of treatment as well as mechanism of binding of silver nano particles by adopting standard test method and analytical techniques.

By means of impregnation and coating self-cross linking acrylic binder enables the entrapping of silver nano particles. There seems to be no chemical binding between silk fibroin and silver nano particles [70]. Morphological studies (SEM), FTIR studies, and X-ray diffraction studies have revealed that the treatment is predominantly impregnation followed by binding in the amorphous region of silk. Antimicrobial properties of the treated silk fabric are good and durable to dry cleaning. Because of the agglomeration of the silver nano particles, there has been a slight change in whiteness index of the treated silk fabrics.

Eco friendly application of nano-silver on special silk

During the past few years, the techniques of green synthesis have prompted the continually increasing interest [71]. Hence, an understanding of present environmental problems prompts for the green synthesis of nanoparticles. The synthesis of nanoparticles from a green chemistry point of view is related with the following aspects.

- Selection of the solvent medium

- Use of an eco-friendly reducing agent, and
- Stabilization of nano particles by means of a source of non-toxic material.

The green preparation of nanoparticles by means of natural polymers such as chitosan, soluble starch, polypeptide, heparin, and hyaluronan used as reducing and stabilizing agents have been reported by some researchers [72]. Recently, polysaccharide-based materials have been related to the synthesis of green silver nano particles by the use of an eco-friendly benign solvent; i.e., using water and polysaccharides as capping agents [73]. Sodium alginate is a type of polysaccharide polymer that is isolated from marine algae and consists of β -D-mannuronic (M) and its stereoisomer α -L-guluronic (G) acid that forms a kind of linear block copolymer of branched chains. Owing to its outstanding cytocompatibility and biocompatibility, biodegradation, sol-gel transition properties, and chemical versatility which renders it more suitable with regard to modifications for design its properties, it is considered ideal for use [74,75]. Many free hydroxyl and carboxyl groups from its backbone permit it to dissolve well in water because of a negatively-charged carboxyl group. In the synthesis of sodium alginate (Na-Alg)-assisted AgNPs, the reaction between Na-Alg and Ag⁺ possibly leads to the formation of a Na-Alg complex [Ag (Na-Alg)]⁺, which is responsible for the formation of AgNPs by silver ion reduction in the presence of alginic acid regeneration. It has been reported that use of glucose can reduce silver ions to metallic silver to form silver nano particles, and through this process it is oxidized to gluconic acid [76]. Owing to their remarkable properties alginates exhibit better stability than chitosan, which include being water-soluble that covers gel formation in the absence of heating or cooling, and also has crucial function in trapping molecules that remain free to migrate by diffusion, based on their size by means of capillary forces. Such features render alginates perfectly suited for the stabilization of silver nanoparticles so as to satisfy the need for the eco-friendly or green synthesis approach. Nowadays, the modification of silk material with AgNPs has attracted a good deal of interest for diverse applications in the clinical, safety, and production engineering, water technology, clothing, lightweight creation, and automotive industries [77]. Rajshahi silk is the name given to the silk produced in Rajshahi, Bangladesh. It is a famous name in the clothing and textiles sector. Although the situation of the Bangladesh textile market is presently dominated by synthetic products, the charming features of Rajshahi silk allow it to maintain its celebrated position [78]. Rajshahi silk is an aerial fibre that is flexible and is made from the cocoons of silkworms; it is covered by means of a protein called sericin which has wide application in textiles over many years owing to its inherent luster, notable flexibility, eco friendliness, and unique mechanical strength [79]. The study on the chemical structure of silk has shown that the sericin protein is consists of 18 amino acids which mainly have sturdy polar moieties that comprise of hydroxyl, carboxyl, and amino groups which are adequate to bind charged functional group of natural or inorganic substances. Considering that silk is a natural protein fiber, it has structural resemblance of a human skin having easy, breathable, tender, non-itchy, and antistatic properties.

Such distinct properties render silk an ideal material in the selective adhesion of metal ions [80]. But, so far little research has been done relating to the advancement of "Rajshahi silk" fiber properties in order to retain their traditional position through a functionalization approach. In all possibilities, it is the first attempt of the surface treatment on Rajshahi silk fabric using green-synthesized silver nitrate by using Na-Alg as a reducing as well as stabilizing agent.

An innovative approach to the functionalization of "Rajshahi silk fabric" by an exhaustive technique through the green synthesis of silver nitrate has been proposed. The presence of the functional groups has been confirmed through FTIR spectra, while the good crystalline structures of synthesized silver nitrate have been shown by TEM image and XRD data [80]. The investigations of SEM ha chemical reducing agents such as hydrazine, glucose, sodium borohydride and citrate revealed that the silver nitrate have been well-deposited on the fiber surface, while the residue weight observed in the TGA experiment further proved the successful synthesis of silver nitrate on the silk fiber surface. The effects of pH, time, and temperature were also studied while AgNPs were applied on silk, where optimized conditions were determined at pH 4, and 40°C for 40 min. AgNPs treatment enhanced the color strength of silk and also improved the fastness towards light and washing, which suggests this method can overcome the limitations of traditional dyeing processes. Treatment using silver nanoparticles is found to enhance the tensile properties of and crease recovery angle of the fabric, with nearly no influence on the rigidity of the material. The findings from the bacterial test confirmed that the proposed technique proves very effective for antibacterial action, since the antibacterial activity increased with increasing concentration of silver nano particles on the surface of fiber.

Conclusion

Recently, many eco-friendly nano finishing processes have been developed. The developments relating to the nano finishing of the protein fibre finishing have been highlighted. In order to enhance the deposition of titanium dioxide nanoparticles plasma treatment, considered as an eco-friendly process is used to prepare wool/PET fabric. The cross linking agent used is citric acid. SEM observation has revealed improved deposition. Investigation has been carried out relating to the self-cleaning property of the coated fabric. In the case of fabric samples treated using titanium dioxide after UV-radiation, the changes in color differences of samples have revealed that an appropriate discoloration has been obtained. Nanochitosan particles have been synthesized, applied on wool fabrics and compared with bulk chitosan with regard to different characteristics. Silver loaded chitosan nanoparticles have also been synthesized and studied with regard to its antibacterial activity by various techniques of application. It has more than 95% antibacterial effect against gram positive and negative bacteria. The influences on hydrophilicity, antibacterial activity, dyeing, air permeability, surface morphology and tensile strength were studied. Enzyme and atmospheric plasma treatments were used both alone and

combined treatments before application of chitosan/nanochitosan to increase their effects. It was noticed that enzyme and plasma treatments showed significant contributions on chitosan and nanochitosan in all investigated properties. From surface observations, it was seen that especially combined treatments caused a smoother surface on wool fabrics. Therefore improved hydrophilicity and dyeability properties could be obtained by ecological methods. As a result of dyeing process, the synergetic effect of enzyme, plasma and nanochitosan treatments led to 2.5 times higher K/S values than that of untreated fabric. Moreover, all treatments had no detrimental effects on bulk properties of fabrics. Silver nano particles are fixed on the silk fibroin either by entrapping in the binder matrix or due to the adhesive force involved. The antimicrobial activity due to the treatment is found to be good and fast to dry cleaning with loss in strength well within the industrial norms. Sodium alginate assisted green silver nano particles have been applied on traditional rajshahi silk. The green silver nanoparticle coated traditional silk shows multifunctional characteristics and holds vast scope in the textile industry. In the case of wool, treatments like chemical, enzymatic, cyclodextrin, sericin, and plasma treatments can be used to overcome shrinkage (felting) and pilling which are considered as two major disadvantages.

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