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Antimicrobial treatment of silk with silver nanoparticles using acrylic binder

Vinay G Nadiger & Sanjeev R Shukla[a]
Department of Fibres and Textile Processing Technology
Institute of Chemical Technology, Matunga, Mumbai 400 019, India

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Application of silver nanoparticles with self cross-linking binders by pad-dry- cure method has been attempted in this study. 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. Silver nanoparticles are fixed on the silk fibroin either by entrapping in the binder matrix or due to the adhesive force involved. FTIR studies prove that there is no chemical binding of silver nanoparticles involved. SEM image shows that the binder is impregnated in the interstitials with some amount of adherence as coating. Based on X-ray diffraction studies, the treatment is observed to be predominately in the amorphous region. The antimicrobial activity due to the treatment is found to be good and fast to drycleaning with loss in strength well within the industrial norms.

Keywords: Antimicrobial properties, Acrylic binder, Silk, Silver nanoparticles, Self cross-linking binder, Pad-dry-cure mothed

1 Introduction

Silk[1] is one of the world's most favoured textile materials and has been known as the "queen of textiles" due to its superior properties. Clothes made from silk are distinctly luxurious and have many excellent qualities including lustre, wearing comfort, fine and smooth texture, soft handle and excellent draping quality. Natural silk has been conventionally used in textiles for thousands of years due to 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[2]. However, 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[3]. The use of silk is greatly hindered by its stringent storage conditions, since bacteria can easily adhere and grow on the silk, thereby causing deformation and even degradation[4]. Thus, it is highly desirable to modify silk fabrics to exhibit the antimicrobial activity for enlarging its spectrum of applications.

Antibacterial finishes are applied to textiles for three major reasons, namely (i) to prevent the spread of disease and avoid the danger of injury-induced infection, (ii) to limit the development of odour from perspiration, stains and soil on textile materials, and (iii) to prevent the deterioration of textile caused by mildew, particularly fabrics made of natural fibre[5]. Nanotechnology[2-9,10] is considered as the futuristic approach as against the conventional chemical, physical or physiochemical modifications, to enhance the performance of textiles. In the field of textile, use of nanosized substances and generating nanostructures during manufacturing and finishing processes to impart anti-bacterial, water and oil repellency, soil-resistance, anti-static, flame-retardancy and improved dyeability properties is the main focus[6-8]. In the recent past, the immobilization of silver nanoparticles in the fibre matrix for multifunctional textiles has attracted the attention of researchers since silver nanoparticles are typical nano-materials with broad-spectrum antibacterial characteristics on both Gram-negative and Gram-positive bacteria. Nanoparticles were dispersed in the polymer (binder) matrix or coated/impregnated and finally become immobilized in the cotton fibre matrix. It is reported that polymeric materials are good candidates to form composite coatings with silver nanoparticles due to their structure, tailorability and flexibility. Different methods are reported for polymer immobilization in antimicrobial coatings depending on their specific properties, viz as stabilizers during synthesis of silver nanoparticles for prevention of the aggregation of the nanoparticles,

[a]Corresponding author.
E-mail: srshukla19@gmail.com

and as linkers for silver nanoparticles which are directly loaded or *in-situ* synthesized in antimicrobial composite coating and facilitate controlled release of silver nanoparticles by changing the interaction between polymer and nanoparticles as well as their concentration[9].

Silver[10] nanoparticles have been utilized to coat silk fibre for antimicrobial properties. Two types of approaches have been developed to fabricate silver nanoparticles functionalized on silk fibres. In the first approach, silk surface is coated with pre-synthesized silver nanoparticle and immobilized by exhaust method through impregnation. In the second approach, silver nanoparticles are directly synthesized *in situ* onto silk fibres. In this, silver ions (Ag+) are attached on silk fibres via electrostatic adsorption or ion exchange, followed by a reduction step to produce silver nanoparticle. The facile *in situ* synthesis approach provided strong binding between silver nanoparticle and the fibres and has been adopted for coating on silk [11]. To increase amount of adsorption of Ag+ in the *in situ* modification approach, various polymers such as polyamide network polymer, poly (vinyl pyrrolidone) and polyacrylic acid were employed to functionalize the silk surface[12,13]. The silk-adsorbed silver ions were subsequently reduced to silver nanoparticle using chemical reducing agents such as hydrazine, glucose, sodium borohydride and citrate[14,15]. The silver nanoparticle produced using chemical method by reducing silver nitrate was applied on silk fabric and good antimicrobial activity was observed against *S.aureus*. The fabrics maintained upto 80% antimicrobial activity after 5 cycles of washing[16]. Kim *et al.*[17] suggested that the antimicrobial mechanism of silver nanoparticle is related to the formation of free radicals on the surface of silver nanoparticles (positive charges) established by ESR studies and subsequent free radical-induced membrane damage; it was finally confirmed[11-23] that the antimicrobial activity of silver nanoparticle and silver nitrate was by NAC (N-acetyl cysteine). Gulrajani *et al*.[18] reported the treatment of silk with silver nanoparticles by reduction of silver nitrate with hydrazine and glucose as reducing agents and with PVP as a dispersing and protecting agent. The application of silver nanoparticles was done by exhaust method. Atousa Moazami *et al*[19]. also reported the effects of nanosized silver colloids on the antibacterial properties of silk fibre against two kinds of bacteria such as *Staphylococcus aureus* and *Escherichia coli* using exhaust method of application. Silver nanoparticles were synthesized by the reduction of silver nitrate with sodium borohydride in an aqueous solution by Bhat *et al* [20]. and applied on silk with sericin as capping agent. Uttayarat *et al.* [21] studied the silk-based wound dressings by incorporation of silver nanoparticle at low concentrations on electro-spun silk fibroin mats and observed significant antibacterial activity against *S. aureus*. Paramwit *et al.*[22] studied the green chemistry approach to synthesize silk sericin (SS)-capped silver nanoparticles under alkaline condition (*p*H 11) using SS as a reducing and stabilizing agent instead of toxic chemicals. Zhang *et al* [23]. synthesized the silver nanoparticles *in situ* with $AgNO_3$ and multi-amino-compound (RSD-NH_2) and studied the antimicrobial behavior of silk. However, it was noted that agglomeration of silver nanoparticles took place in one step mixing of the above compounds. Chen *et al*[24]. conducted the finishing of cotton using commercial silver nanoparticles. The morphology of the silver nanoparticles finished cotton was examined under the SEM and it was revealed that nanosilver particles distribution was partly uniform and they were clustered while adhering to the fabric, as shown in SEM at higher magnification. It was also revealed that the commercial nanosilver particles were spheroids with an average diameter of 20-90nm. Matyjas–Zgondek *et al.*[25] have reported the results on the bacteriostatic efficacy of selected silver particles, viz nano Ag, submicron Ag, and AgCl in the finishing of cotton textiles by the padding squeezing technique using silver compounds in the resin matrix. SEM images of the silver finished fabrics indicated that silver compounds were well dispersed on the fabric surface, but in some cases, they form agglomerates of single particles. The treatment was good and durable for both Gram positive (*Bacillus subtilis*) and Gram negative (*E .coli*).

Based on the earlier works, it is remarked that the application of silver nanoparticles is done either by exhaust method or by *in situ* synthesis of silver nanoparticles in the fibre matrix. It may, however be noted that most of the finishing operations on textiles are done by pad-dry-cure method. Hence, application of silver nanoparticles with self-cross-linking binders by pad-dry- cure method has been attempted to simulate the current finishing technique adopted 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 nanoparticles by adopting standard test method and analytical techniques.

2 Materials and Methods

2.1 Materials

Mulberry silk fabric, ready for dyeing (denier: warp 34.4 & weft 68.2; EPI 114; PPI 105.4; and GSM 50) was prepared using organzine as warp and tram as weft on a power loom. Prior to weaving, the warp and weft yarns were pre-treated to make them suitable for piece dyeing. Mono-disperse silver nanoparticles that are free from agglomeration were used to make them ideal for research, development, and use in antimicrobial applications. The nanoparticles were characterized by using transmission electron microscopy (TEM) images, dynamic light scattering (for particle size analysis), zeta potential measurements, and UV/Visible spectral analysis to ensure that the consistent materials were supplied by M/s Sigma Aldrich [Sigma (No.576832-Ag)]. According to Sigma Aldrich specification, the particle size was < 100nm with a thermal resistance of 1.59 Wm/cm at 20°C and a specific surface area of 5.0m^2/g. Silver nanoparticles (99.5% purity based on trace metal analysis) was taken in different proportion 150ppm, 200ppm, 250ppm in ultra-pure water. Self cross- linking acrylic binder was procured from L. N. Chemicals Pvt. Ltd. India.

2.2 Methods

2.2.1 Fabric Pretreatment

Mild scouring was done using soap (1%) and soda (0.5%) for 30 min with 1:30 material- to- -liquor ratio (MLR) at 60°C to remove lubricants and contaminants deposited on silk fabric during twisting and weaving processes. The fabric was hydro-extracted and dried at 80°C for 45 min.

2.2.2 Preparation of Silver Nanoparticles and Acrylic Binder solutions

Silver nanoparticles were taken in different concentrations for the treatment.

Acrylic binder solution (7%) was prepared in ultra pure water and the solution was stirred using magnetic stirrer at 25° C for 30 min to get homogeneous solution.

2.2.3 Treatment of Silk with Silver Nanoparticles

Silver nanoparticle solution of different concentrations prior to treatment was mixed in 7 % (w/w) solution of acrylic binder. The solution thus prepared was sonicated for half an hour at 30°C. Acidic *p*H 4-4.5 of the solution was noted. Silk fabric samples were soaked in the resultant solution with material – to-liquor ratio of 1:20 for 45 min. It was squeezed and loaded on the padding mangle under pressure of 1kg/cm^2 to achieve pick-on pick-up of the treatment liquor with the tune of 95% and to get uniform application of the finish throughout the body of the fabric. The fabric was dried at 65°C for 35 min and finally cured at 145°C for 2 min. Treated silk fabric samples were washed using mild acidic soap solution at 30°C followed by cold water wash to remove unfixed finishing chemical and other ingredients. The fabric was oven dried at 80°C for 30 min.

2.2.4 Physical Properties of Silk

Silk fabrics after silver nanoparticles treatment were tested for various properties, namely add-on(%), EPI/PPI, GSM, tensile strength, crease recovery angle, abrasion resistance, moisture regain, bending length and whiteness index as per standard methods/ procedures given in (Table 1).

2.2.5 SEM, FTIR and XRD and Whiteness Index Analysis

SEM studies were carried out using SEM model Philips XL 30, the Netherlands. The samples of various treated silk fabrics were prepared on the metallic stub and coated with platinum by sputter coating unit SC7640, POLARON make, UK to make the surface conducting[26-28]. These samples were observed under SEM for evaluating the morphological changes due to the treatment at an accelerating voltage of 10kV at different magnifications. FTIR analysis was done using FTIR Spectrophotometer model ABB Bomen instrument Canada MB 3000.

Table 1 — Characterization carried out for treated silk and the standard test

Parameter	Standard method/procedure
Add-on% (owf)	Gravimetric method over the weight of fabric
Thread density (EPI/PPI)	IS:1963-1981
GSM	IS: 1964-2001
Tensile strength	IS:1969-1985
Crease recovery	IS: 4681-1981
Abrasion resistance by Martindale method	ISO:12947-1:1998
Moisture regain	IS: 199-1989
Fabric stiffness	ASTM D 1388-08
Color fastness to drycleaning	AATCC Test Method 132-2009
Antimicrobial Properties	AATCC Test Method 100-2012
Whiteness Index	ASTM E313 standard

The untreated and treated silk fabric samples were cut into fine powder, sieved, dried at 100°C for 2 h and cooled to 25°C through desiccation in P_2O_5. Dried sample powder (2mg) was dispersed in 198mg of spectroscopic grade dried KBR and made into pellet [29]. The KBR pellet was used for recording the transmission FTIR spectra. X- Ray diffractograms (XRD) of untreated and treated silk fabric samples were recorded using X' Pert PRO MPD X-Ray Diffractometer supplied by M/s PANalytical BV, the Netherland. Untreated and treated silk fabrics/fibres were cut into fine powder with the help of a Wiley Mill. Fine powdered sample was made into a rectangular pallet and mounted onto a rectangular sample holder using back loading method. The Cu Kα X- rays were generated using 40 kV at 30mA on copper target. XRD scans thus obtained were analyzed using X'Pert High Score X-ray diffraction analysis software. Order factor which is directly related to the degree of crystallinity was estimated as per the procedure reported [29]. Whiteness index of the untreated and treated silk sample was evaluated using computer colour matching system (M/s Premier Color Scan Macbeth Model CE 3100, India).

2.3 Antimicrobial Property

Antimicrobial properties of silver nanoparticles treated silk fabric were evaluated quantitatively by AATCC 100 method for both *Staphylococcus aureus* ATCC 6538 (Gram positive) and *Klebsiella pneumoniae* ATCC 4352 (Gram negative) bacteria. Per cent reduction of bacteria due to the specimen treatments was calculated by the following formula:

$$R(\%) = \frac{100[(A-B)]}{A}$$

where R is the per cent reduction; A , the number of bacteria in the control sample at time t=0 (cfu/sample); and B, the number of bacteria in the treated silk sample after time t= 24 h (cfu/sample). The reduction in bacteria count over 99% was considered as the highest level.

3 Results and Discussion

3.1 Add - on % on Silk Fabric

Add on % on silk fabric due to silver nanoparticles treatment for 150, 200 and 250 ppm is found to be 8.19, 8.60 and 9.43 respectively. It is observed that add on (% owf) increases as the silver nanoparticles concentration is increased at 7% acrylic binder in the recipe.

3.2 Effect of Silver Nanoparticles Treatment on Physical Properties

Table 2 shows various physical properties of untreated and silver nanoparticles treated silk samples at 150, 200 and 250ppm concentrations. It may be seen from Table 2 that EPI does not change due to the treatment. However, PPI and GSM increase with the increase in add-on (% owf). Further, shrinkage (%) in weft direction does not change significantly, however the shrinkage (%) in the warp direction increases due to the treatment and there has been marginal decrease in the shrinkage (%) as the concentration of the silver nanoparticles is increased. This may be due to deformation processes involved with regard to addition of silver nanoparticles in the binder matrix. Warp tensile strength is decreased by 1.5 -10% due to the treatment. Likewise, weft tensile strength decreases by 7.7-22%. The loss of strength in the weft direction is higher than that in the warp direction. The loss of weight (%) due to abrasion is reduced after the treatment and hence abrasion resistance is improved due to the treatment. This implies that the coating with good adhesion of the binder and silver nanoparticles has yielded better abrasion resistance and is deemed as superior features of the treated silk fabric as compared to the untreated silk fabric both in terms of wear properties and durability of the treatment. Likewise, the moisture regain is decreased due to the treatment, thereby blocking the hydrophilic groups contributing to the reduction in moisture regain (%). It may be remarked that the decrease in moisture regain (%) is mainly due to the binder add on (% owf) and cross-linking processes involved as compared to the increase in concentration of silver nanoparticles. The bending length decreases due to the treatment in both warp and weft direction and the decrease is statistically significant. Crease recovery angle increases due to the treatment in both warp and weft direction and the increase in crease recovery angle is found significant. It may be pointed out that the cross-linking of binder might have led to improve the crease recovery and decrease in stiffness apart from entrapping of silver nanoparticles. Further, the entrapping of silver nanoparticles in the fibroin lattice has not made the silk fabric stiff, thereby increasing the crease recovery angle. It is reported[30, 31] that the strength loss in the finishing is mainly due to inter and intra

Table 2 — Effect of Ag nano particles treatment on different physical properties (mean values) of silk

Property	Silk treated with				't' value paired		
	0 ppm (Untreated)	150 ppm	200 ppm	250 ppm	150 ppm	200 ppm	250 ppm
EPI	114	113	113	113	-	-	-
PPI	86	91	90	89	-	-	-
GSM	58.4	64.7	64.3	62.3	-	-	-
Shrinkage, %							
weft	1.00	0.87	0.87	0.87	-	-	-
warp	0.5%	5.8	4.65	3.48	-	-	-
Tensile strength, N							
warp	668.0	603.1	639.1	658.2	8.5	5.33	1.36
weft	445.2	348.5	410.8	399.7	8.54	2.03	3.08
Abrasion resistance (as wt. loss), %	6.5	4.1	3.5	2.25	-	-	-
Moisture regain, %	9.64	7.34	7.44	7.71	-	-	-
Bending length, cm							
warp	2.4	1.76	1.77	1.8	8.83	14.5	14.9
weft	2.64	2.07	2.13	2.15	8.16	10.06	10.04
Crease recovery, deg							
warp	85	96	98	101	3.82	9.3	6.77
weft	108	118	117	115	10.88	9.97	3.4

macromolecular cross linking and due to the acidity of the treatment solution which leads to an irreversible de-polymerization of the macromolecules during the high temperature curing step. Further, the maximum decrease in tensile strength is around 10% in warp and 22% in weft for the treated silk with silver nanoparticles. It is reported that the finishing in certain cases reduce the strength by about 20% and the observed loss of strength is well within the reported values which is accepted in the industry[30, 31].

3.3 Effect of Silver Nanoparticles Treatment on Resistance against Microbes

The resistance against bacterial attack of untreated silk and silver nanoparticles treated silk samples has been evaluated with respect to Gram positive (*Staphylococcus aureus ATCC 6538*) and Gram negative (*Klebsiella pneumoniae ATCC4352*) bacteria. Table 3 gives the data on antimicrobial properties of control silk and silver nanoparticles treated silk fabric. Control silk fabric shows no reduction in the count of the bacteria and hence it is not antimicrobial. On the other hand, silver nanoparticles treated silk fabrics show antimicrobial characteristics at different concentrations satisfactorily. Ahmed *et al*.[32] reported that the acrylic polymer based dentures and orthodontic appliances do not have effective antimicrobial material and requires antimicrobial treatment to contain with the same. Likewise, Oei *et al*[33]. reported that polymethyl methacrylate (PMMA) is widely used to treat traumatic head injuries (cranioplasty) and orthopedic injuries (bone cement), but there is a problem with implant-centered infections. Hence, the reported antimicrobial activity on the treated silk fabrics is mainly due to the treatment with silver nanoparticles only.

Table 3 — Antimicrobial properties of different treated silk

Silk treated with	Wash cycles	% Reduction	
		S.aureus	*K.pneumoniae*
0ppm (Untreated)	-	0	0
150ppm	-	94	92
150ppm	1	93	90
150ppm	3	89	86
150ppm	5	86	84
200ppm	-	98	94
200ppm	1	97	92
200ppm	3	93	92
200ppm	5	90	90
250ppm	-	98	97
250ppm	1	96	97
250ppm	3	93	92
250ppm	5	93	92

It is well known that silk fibre loses its strength by 30-40% and becomes more ductile under wet condition[34]. Hence poor dimensional stability will be persisting and any mechanical force applied on the fabric during wet washing can mechanically deform/ degrade the fibre and can lead to loss of wear and tear properties. Silk is dyed with acid, basic and reactive dyes. It is found that the wash fastness property of silk is vulnerable when it is dyed with acid or basic dyes due to acidic/basic properties of soaps/detergents. Hence, the wet washing is not advisable for silk textiles dyed with acid dyes. Even in the case of silk dyed with reactive dyes, it is not advisable to have washing with water, as mechanical deformation may lead to loss of wear and tear properties. In view of the above facts, the silk textiles are drycleaned in the industry and also at consumer end. Hence, the retention of antimicrobial properties of the treated silk fabrics has been evaluated after drycleaning using perchloroethylene up to 5 cycles. It may be observed from Table 3 that antimicrobial properties (over 80%) of the treated fabric are retained after 5 cycles of drycleaning for 150, 200 and 250ppm silver nanoparticles treated fabric, indicating that the treatment is durable at different concentrations of silver nanoparticles used in the present study. The observed phenomenon may be due to adhesive forces of binder with that of silver nanoparticles as seen in terms of improvement in abrasion resistance apart from crosslinking of the acrylic binder with fibroin creating the trap for the silver nanoparticles to exhibit durable treatment features.

3.4 Characterization Techniques

3.4.1 SEM Study

Figures 1 (a) and (b) show the SEM photomicrographs of untreated and 250ppm silver nanoparticles finished silk fabrics respectively. As could be seen in the figure, the surface of the untreated fabric is smooth and no extraneous deposition is observed. However, the micrograph of silver nanoparticles treated fabric shows the deposition on the surface, indicating that the silver nanoparticles are deposited unevenly. It may be mentioned that the SEM photographs at high magnification have been analyzed to find out the distribution of nanoparticles in the binder matrix on the surface and it is observed that the particles are partly evenly distributed. Similar observations were made by Chen *et al*[24]. while conducting the finishing of cotton using commercial silver nanoparticles supplied by M/s Sigma Aldrich. The morphology of the silver nanoparticles finished cotton has been examined with the SEM and it is revealed that nanosilver particles distribution is partly uniform and they are clustered while adhering to the fabric, as can be seen under SEM at higher magnification. Further, it is revealed that nanosilver particles are spheroids with an average diameter of 20-90nm. Since the antimicrobial properties are fast to drycleaning, it is pointed out that silver nanoparticles may be impregnated in the interstitials of the fibre matrix, leading to durability of the treatment. It is reported that binder contributes to chemical binding through cross-linking between the molecular chains of fibroin and also leads to somewhat coating apart from impregnation, thereby improving some of the properties. Hence, the morphological changes are likely to be attributed to binding of acrylic polymer[35]. As such, cross-linking of acrylic binder may lead to a network trap for entrapping silver nanoparticles. In the light of the above, the predominant mechanisms are both cross-linking and impregnation.

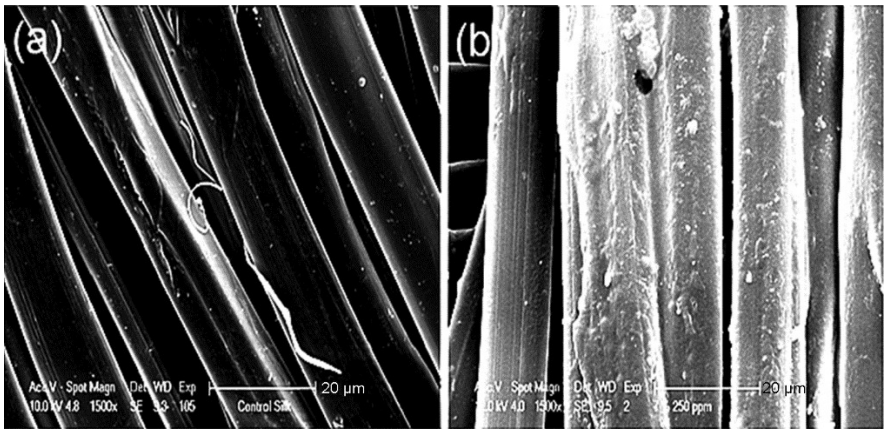

Fig. 1 — SEM micrographs of (a) untreated and (b) 250ppm nano-silver finished silk fabrics

3.4.2 FTIR Studies

Figures 2 (a) and (c) show the FTIR spectra of untreated and silver nanoparticles treated silk fabrics. It may be seen that the band at about 1700± 5 cm^{-1} corresponds to carboxylic group and the band at 2970cm^{-1} corresponds to CH_3 asymmetric group. The carboxylic band has potential to have crosslinking with the poly acrylic acid groups of acrylic binder and is likely to be influenced by chemical binding in the treatment. On the other hand, CH_3 band at 2970cm^{-1} is invariant to the treatment. Since the new absorption band owing to the treatment is not observed, it is decided to define index of chemical binding of acrylic binder through crosslinking in the treatment (A_{1700} cm^{-1}) by considering the ratio of the optical density of band at 1700+ 5 cm^{-1} and the optical density of the band at 2970cm^{-1} ($A_{2970cm-1}$). Accordingly, the index of chemical binding ($A_{1700\ cm-1)}$ / $A_{2970cm-1}$) was calculated for different concentrations of silver nanoparticles. It is observed that the index of chemical binding decreases due to the treatment with control silk exhibiting ratio as 10.80 and the treated

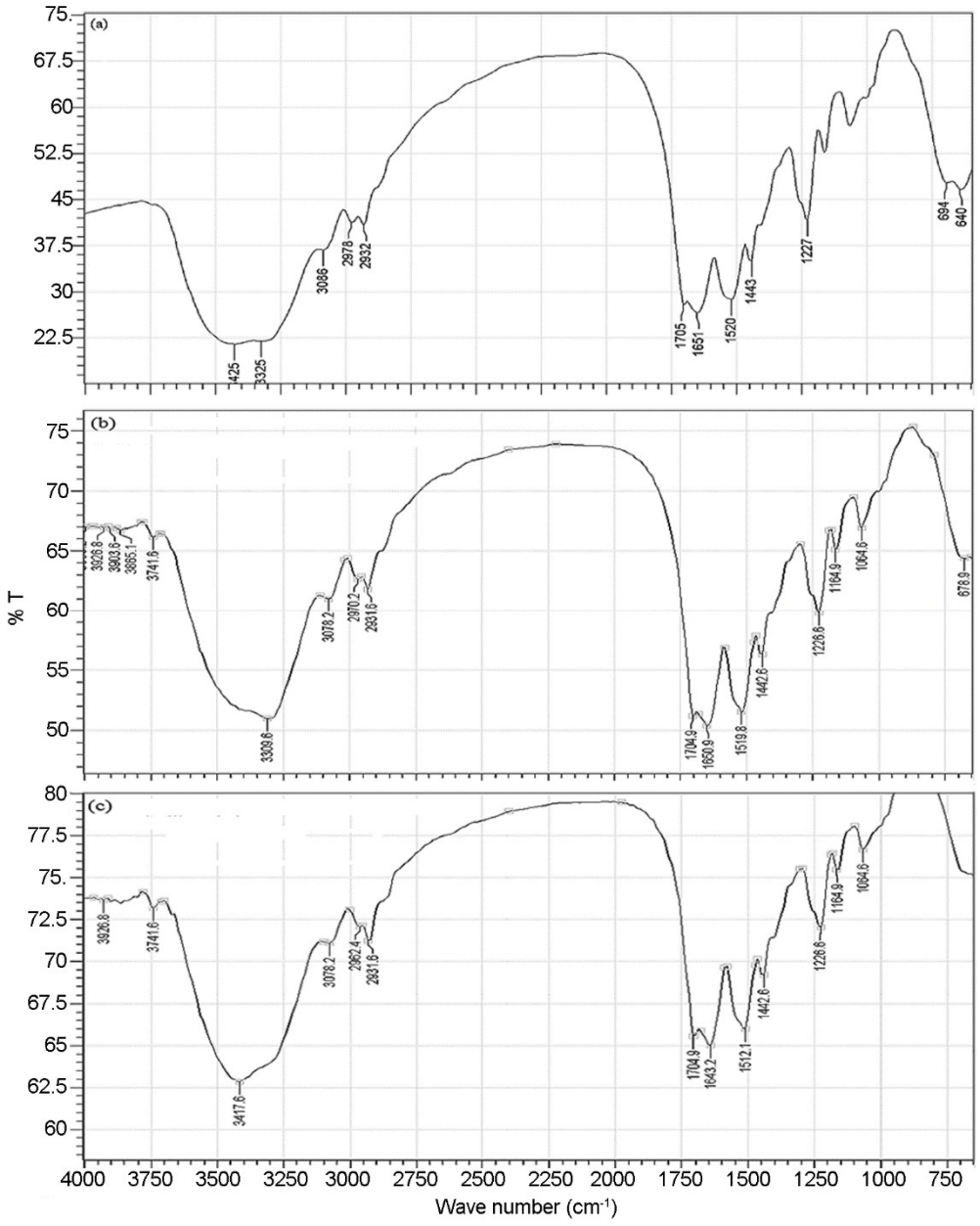

Fig. 2 — FTIR spectra of (a) untreated silk fabric, (b) 250ppm (warp faced) nano-silver treated silk fabric and (c) 250ppm (weft faced) nano-silver treated silk fabric

silks show 7 - 8.51. It is pointed out that the decrease in index of chemical binding is not proportionate to the concentration of silver nanoparticles. The observed phenomena may be attributed to the chemical binding of acrylic binder with the silk fibroin and a very little role of silver nanoparticles. In other words, silver nanoparticles do not contribute in the process of chemical binding. However, they are fixed with the fibroin due to either entrapping or adhesive forces involved in the treatment.

3.4.3 X-Ray Diffraction Studies

Silk fibroin is known to be semicrystalline and gives rise to X-ray diffraction pattern. The determination of crystallinity by X-ray diffraction has been attempted by various workers for polymeric materials such as nylon, PET, and cellulose. Various formulas have been suggested to compute the crystallinity index on the basis of relative intensities of peaks as well as the integrated area under the diffraction profile. In the present work, the formula reported by Venkatraman[36] is adopted to determine the resolution factor (R_f). Using the following equation for resolution factor, the lateral order factor is estimated for untreated and various treated silk fabric samples:

Lateral order factor (Lo) = 1- R_f = [1-2 (m_1- m_2)]/ (h_1+ h_2+ h_3)

where L_o is the lateral order factor; h_1, h_2, and h_3 are the respective peak heights; and m_1 and m_2 are the respective heights of minima between the two peaks representing amorphous contribution.

It may be seen from Fig. 3 that X- ray diffractograms of the untreated silk and treated silk fabrics with silver nanoparticles are more or less similar and hence crystalline structure remains invariant. It is further substantiated from the estimation of the order factor determined by the method developed by Venkatraman[36]. The order factor for untreated silk and treated silk fabric with 250ppm silver nanoparticles is found to be 0.80 only. This leads to the hypothesis that the treatment is not affecting the crystalline region. It may also be pointed that amorphous region is having high disorder chain conformation with reactive amino acids like serine and tyrosine, and leads to distorted morphological structure thereby facilitating easy access to the binder for impregnation, to facilitate fixing up of the nanoparticles in the fibre matrix for obtaining the desired antimicrobial properties. Further, silver nanoparticles concentration used in the treatment is low and does not exhibit its own diffraction pattern in the X-ray diffraction, and hence it does not contribute for the super lattice formation as no new diffraction peak is seen in diffractograms.

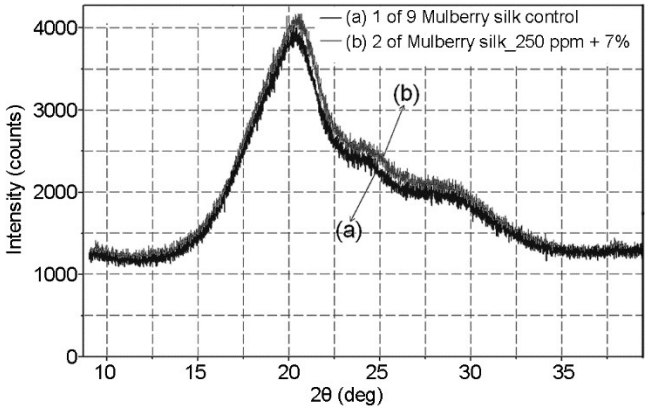

Fig. 3 — X ray diffractograms of (a) untreated silk fabrics and (b) 250ppm silver nanoparticles treated silk

3.4.4 Whiteness Index

During silver nanoparticles treatment of textiles, it is reported that the fabric gets discolored or loses its whiteness due to conglomeration of nanoparticles[20, 23]. In order to evaluate the effect of treatment, visual assessment of lustre whiteness index has been done. It is observed that the difference in lustre of the control and treated silk fabrics is marginal. We have also determined the whiteness index of the control and treated silk fabrics and the whiteness index of silk fabric changed from 45 to 38 (CIE) due to the treatment at 250ppm silver nanoparticles concentration. Hence, it is inferred that the treatment is not adversely affecting the whiteness of the fabric due to the agglomeration of nanoparticles.

4 Conclusion

4.1 Self crosslinking acrylic binder facilitates the entrapping of silver nanoparticles through impregnation and coating. Silver nanoparticles appear to have no chemical binding with silk fibroin.

4.2 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.

4.3 Antimicrobial properties of the treated silk fabric are good and durable to drycleaning.

4.4 Whiteness index of the treated silk fabrics changed marginally due to the agglomeration of the silver nanoparticles.

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