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Synthesis of spray dried polyvinyl pyrrolidone coated silver nanopowder and its application on wool and cotton for microbial resistance

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Silver nanoparticle - polyvinyl pyrrolidone (PVP) composite containing 100 ppm of silver has been synthesized in powder form for textile applications, using sono-chemical method comprising sonication and reduction with trisodium citrate followed by spray drying. The synthesized PVP coated silver nanopowder is then characterized by UV-Visible spectra, atomic absorption spectra, transmission electron microscope and energy dispersive analysis of X-rays. The results indicate the presence of silver particle of the size 50-60 nm in the synthesized powder. The silver nanopowder has been applied on cotton and wool to impart antimicrobial efficacy by exhaustion method. The treated cotton fabric shows a clear microbial resistance with 35-40 mm zone of inhibition in the agar diffusion test against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. The treated wool fabric shows 100%, 97% and 99% antimicrobial efficacy in the quantitative AATCC 100 test against the above-mentioned microorganisms respectively.

Keywords: Antimicrobial finish, Cotton, Polyvinyl pyrrolidone, Silver nanoparticle, Sonication, Spray drying, Wool

1 Introduction

The textile materials are good media for generation and spreading of microorganisms. Proteins present in keratinous fibres and carbohydrate in cellulose fibres can act as nutrients for the growth of microorganisms. The growth of microorganisms in the textile material causes unpleasant smell, staining, loss of mechanical strength, and can also create health related problems to the wearer. Hence, it is necessary to give antimicrobial finishing for textile materials to avoid infections to the wearer from the harmful microorganisms. Several antimicrobial agents, like polyhexamethylene biguanide (PHMB), quaternary ammonium salts and nano silver have been used for textile applications[1]. Among them, silver nanoparticles have potential antimicrobial activity against many pathogenic microorganisms. The silver nanoparticles are able to kill the microorganisms by interacting with their sulfur containing proteins present in the cell wall and inhibiting their metabolism[2,3]. It is reported in the literature that the silver nanoparticles are applied on cotton[4], wool[5] and silk[6] fabrics to impart antimicrobial efficacy.

There are some limitations associated with the use of silver nanoparticles for textile applications. Recent studies have shown that silver nanoparticles with less than 50nm size, which are normally used for textile finishing, can cause toxic effects on human health and environment[7,8]. Hence, it is necessary to produce silver nanoparticles of > 50nm size for textile applications. Another limitation of the silver nanoparticles is their inherent ability to agglomerate in solution. The silver nanoparticles are stable only for few weeks in solution and then tend to agglomerate due to the reduction of electrostatic repulsive forces and increase in the attractive van der Walls forces between the nanoparticles. The agglomeration process leads to precipitation of silver in silver sulfide (Ag_2S) form and the disappearance of original yellow colour of nano solution due to broadening of optical extinction of silver[9]. The agglomeration of nano silver leads to loss of its antimicrobial property and can also stain the fabric during application. Hence, the stability of the silver nanoparticle in solution is very much essential for textile applications. It is reported in the literature that the silver nanoparticles can be coated with different polymers like 4-mercaptomethylstyrene, poly (methyl methacrylate) and silicon dioxide in order to circumvent the agglomeration problem[10]. However, such prepared polymer- silver nanocomposites are

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water insoluble in nature and have to be applied on the textile materials only during the final stage of finishing operation by pad-dry-cure method.

Based on the above, attempts have been made to synthesize water soluble polyvinyl pyrrolidone (PVP) coated silver nanoparticles in powder form with 50-60 nm average size by a sono-chemical method followed by spray drying for textile application. The development of such nanopowder will address the earlier discussed limitations of silver nanoparticles, such as agglomeration during storage in solution state, requirement of complex pad-dry-cure process for application and possible damage to human beings and environment due to nanoparticles of < 50nm size. The synthesized nanopowder is water soluble and can be incorporated into the fabric by simple exhaustion method instead of complex pad-dry-cure process at any stage of wet processing. The synthesized nanopowder has been characterized by UV-Visible spectra, transmission electron microscope (TEM), atomic absorption spectra (AAS) and energy dispersive analysis of X-rays (EDAX). The nanopowder is then applied on wool and cotton fabrics to find out its antimicrobial efficacy against three common infectious microorganisms, namely *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*.

2 Materials and Methods

2.1 Chemicals and Fabrics

Analytical grade silver nitrate and trisodium citrate purchased from M/s SD Fine Chemicals and polyvinyl pyrrolidone (PVP) from M/s HiMedia Laboratories, India were used as such. The bleached, plain woven wool and cotton fabrics having 350 and 100 g/m^2 weights respectively were used for this study.

2.2 Preparation of Silver Nanoparticles

A sono-chemical method was used for synthesizing silver nanoparticles. All solutions were prepared in deionized water. In a typical recipe, 1×10^{-3} M silver nitrate solution containing 2% PVP was sonicated in a 20 kHz, 130 watts ultra sonicator (Model VX 130; M/S Sonics, USA) for 3 h. The sonicated solution was then immediately heated to boil followed by drop by drop addition of 1% trisodium citrate till the colour of the solution turns yellow. The appearance of yellow colour in the solution indicates the formation of silver nanoparticles.

2.3 Spray Drying

The synthesized silver nanoparticle solution was converted into powder form using a laboratory spray dryer (Model – LU222 Advanced; M/S Lab Ultima, India) operated in the co-current mode. The liquid feed rate was 2mL/min through 0.7 mm diameter nozzle at 3 psi air pressure. The atomization was done in the aspirator with the vacuum of 35 mm water column. Spray drying was performed at an inlet air temperature (T_{inlet}) of 135°C, corresponding to an outlet air temperature (T_{outlet}) of 90°C. The spray drying solution contained 2% w/v of total dissolved solids. The powder was collected from I & II cyclones of the spray dryer and stored in airtight container for further applications.

2.4 Characterization

UV-Visible spectrum was used to qualitatively confirm the presence of silver in nanometer size in the prepared nanopowder using Shimadzu UV-1601 spectrometer. Silver in nanometer size has the ability to produce absorption peak in the wavelength region of 400-440 nm. Atomic absorption spectrum was used to find out concentration of silver in the synthesized powder using Varian SpectrAA 220. TEM analysis was carried out to determine the size of silver nanoparticles in the nanopowder using Philips CM 200 model machine by drop coating method. The nanopowder was dissolved in water and drop-coated on the copper grids for TEM analysis. The elemental analysis on the individual nanoparticle was done using EDAX facility attached with the TEM itself.

2.5 Application on Textile Material

The silver nanopowder was dissolved in water to a concentration of 50 ppm of silver content and applied on wool and cotton fabrics by exhaustion method. The materials were treated for 45 min at boiling condition followed by washing with normal water. The durability of the finished samples was determined after 5, 10 and 20 washes as per AATCC 124-2001 method using IFB washing machine.

2.6 Assessment of Microbial Resistance

The antimicrobial efficacy[11] of the treated cotton and wool fabrics along with their different washed samples was determined using qualitative agar diffusion method [SN 195920-1992 (Swiss Norm)] and quantitative AATCC 100 method against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. In the agar diffusion method, the evaluation was made on the basis of absence or presence of bacterial effect in the contact zone under the specimen and the possible formation of a zone of inhibition around the test specimen. The area of inhibition zone in mm was a measure of antimicrobial effectiveness. In the AATCC 100 method, the efficiency of the antimicrobial treatment was determined by comparing the reduction in bacterial concentration of the treated sample with that of the control sample expressed as a percentage reduction in standard time.

3 Results and Discussion

3.1 Mechanism of Producing PVP Coated Silver Nanopowder

The silver nanoparticles are produced from silver nitrate dispersed in polyvinyl pyrrolidone by two stage process namely sonication and chemical reduction. During sonication, the cavitations, in other words the creation, growth and collapse of bubbles (so called hot spots), are formed in the liquid. The cavities fluctuate in size, but when the cavity reaches a certain size, it cannot retain its shape. When this happens, the cavity collapses, creating an extremely high temperature of 5,000°C, pressures of about 500 atmospheres, and heating / cooling rates greater than 10^9 K/s. Millions of these bubbles are created and collapsed every second. The generation of such high temperature and pressure during ultrasonic irradiation leads to the decomposition of water molecules into hydrogen and hydroxyl free radicals[12,13]. The hydrogen free radical thus produced reduces the silver nitrate to silver. During this process, the colour of the solution turns pale yellow. This process is followed by chemical reduction with trisodium citrate at boiling condition. During this process, silver nitrate is completely reduced to elemental silver as per the following equation[14]:

$$4AgNO_3 + C_6H_5O_7Na_3 + 2H_2O \longrightarrow 4Ag^0 + C_6H_5O_7H_3 + 3Na\,NO_3 + + HNO_3 + O_2\uparrow$$

The PVP used in this process is acting as dispersing agent as well as stabilizing agent. It forms weak coordinate bond with silver by supplying lone pairs of electron of its both nitrogen and oxygen atoms in aqueous solution. Silver ions – PVP complex is more easily reduced than pure silver ions because PVP promotes the nucleation of the metallic silver owing to the fact that silver ions receive more electronic clouds from PVP than from water[15,16]. Atomic absorption spectrum shows that the prepared silver nano solution contains 100 ppm of silver. The PVP coated silver nano solution is then converted to powder using laboratory spray dryer. The recovery of solid materials is 80%. The colour of obtained powder is light brown with slightly sticky nature. There is no major drop in the outlet temperature during spray drying process, which indicates smooth drying process.

3.2 UV-Visible Spectra

The UV-Visible spectra of the produced PVP coated silver nanoparticles in both solution and powder form are shown in Figs 1a & b respectively. Both the spectra show a clear absorption peak at 430 nm wavelength region due to the presence of silver nanoparticles. The UV-Visible spectroscopy is considered as a proven analytical method to confirm the formation of silver nanoparticles in the solution. Silver nanoparticles produce an intense absorption peak at 400 nm due to the surface plasmon excitation. Surface plasmon excitation describes the collective excitation of conduction electrons in a metal.

3.3 TEM and EDAX Studies

The TEM image of PVP coated silver nanopowder is shown in Fig. 2. It is found that the size of PVP coated silver nanoparticles is in the range of 50-60 nm. The figure also shows the presence of few big agglomerates of PVP coated silver of the size 100 nm and 200 nm. The formation of these agglomerates may be due to thermal migration of the nanoparticles during drying process in the spray dryer. The elemental analysis on different sizes of nanoparticles present in TEM image is done using EDAX. The spectrum taken at a place without any particle is shown in Fig.3a and that at the places where 55 nm, 100 nm and 200 nm nanoparticles are found is shown in Figs 3b-d respectively. All the four spectra confirm the presence of silver (Ag) in the synthesized powder. The low intensity peak related to silver at the place without any nanoparticle (Fig. 3a) is due to the presence of traces of silver in the polymer matrix. The peak related to copper (Cu) in all the spectra is due to the use of copper grids in the TEM analysis.

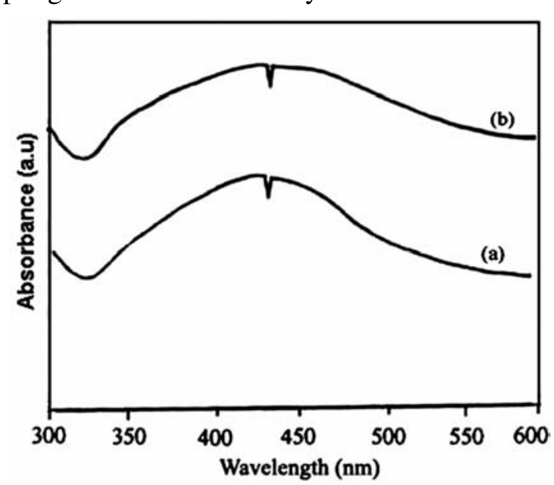

Fig. 1—UV –Visible spectra of PVP coated silver (a) nanoparticle (b) nanopowder

3.4 Application on Textile Fabrics and Testing of Antimicrobial Efficacy

The synthesized PVP coated silver nanopowder is easily dissolved in water due to the use of water soluble PVP polymer. The water soluble nature of nanopowder provides several operational advantages during application on textile materials. The textile materials can be finished by simple exhaustion method instead of conventionally used pad-dry-cure method. Delicate fabrics, wound dressing bandages, bed linens, knitted fabric and small lot of fabrics, for which pad-dry-cure type of processing is not possible, can be provided durable antimicrobial finishing by simple exhaustion method using the synthesized silver nanopowder.

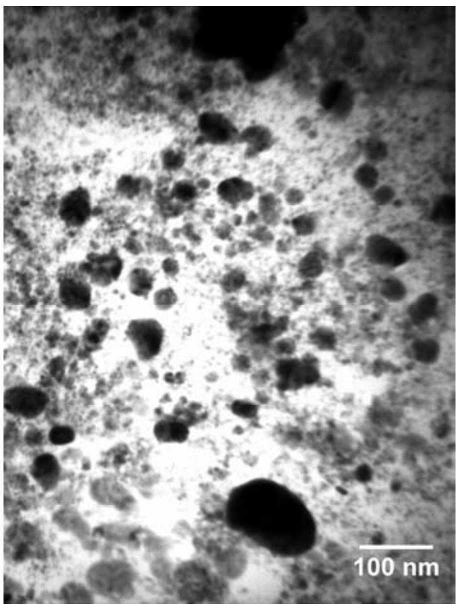

Fig. 2—TEM image of PVP coated silver nanopowder (×2, 30,000)

The results of agar diffusion test carried out for treated cotton fabric and its differently washed fabrics to determine the microbial resistance in terms of zone of inhibition are shown in Figs 4a-c and Table 1. The results indicate the presence of clear zone of inhibition (35-40 mm diameter) in the treated fabrics against all the three selected microorganisms. The

Table 1 —Agar diffusion test for treated and washed cotton fabrics

Sample	Zone of inhibition [a]		
	S. aureus	*E. coli*	*P. aeruginosa*
Control	Nil	Nil	Nil
Silver nanopowder treated			
Without washing	38	41	37
After 5 washes	37	40	35
After 10 washes	37	40	35
After 20 washes	35	38	35

[a] Diameter of the control sample is 20mm.

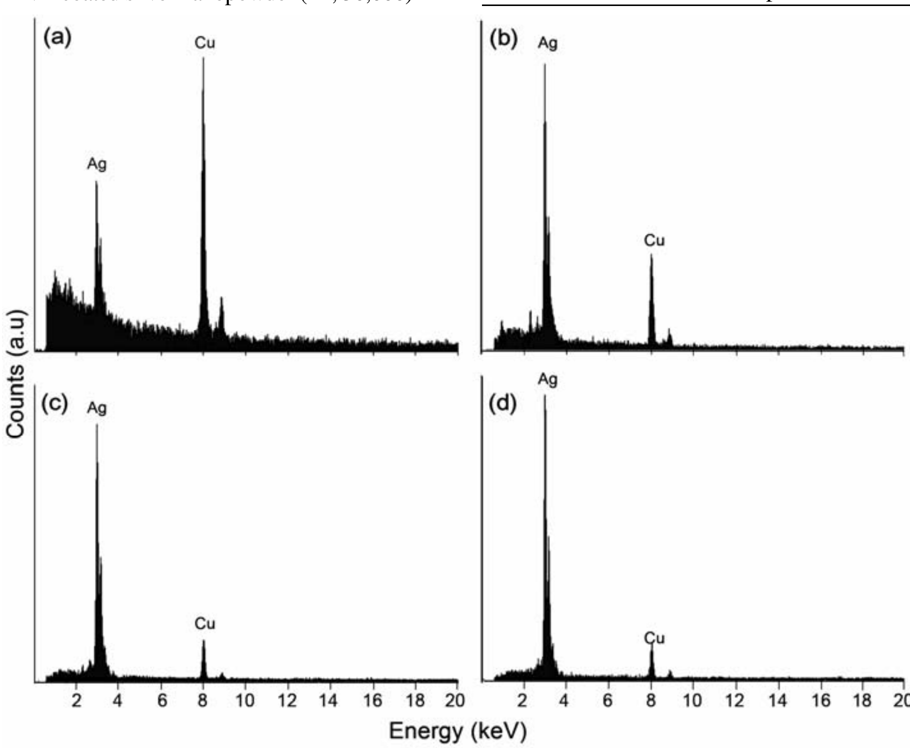

Fig. 3—EDAX spectra of (a) polymer matrix without nanoparticle, (b) at 55 nm size nanoparticle, (c) at 100 nm size nanoparticle, and (d) at 200 nm size nanoparticle

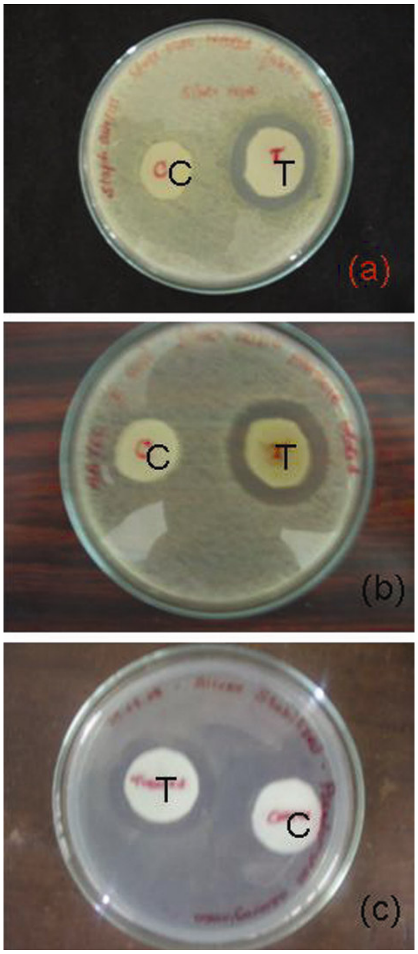

Fig. 4—Agar diffusion test on treated cotton fabrics. Zone of inhibition against (a) *S. aureus*, (b) *E. coli* and (c) *P. aeruginosa*

zone of inhibition is observed in the treated cotton fabrics even after 20 washes. The results of the quantitative test to determine the microbial resistance of treated wool are given in Table 2. The results indicate that the treated wool fabric has 100%, 97% and 99% efficacy against *S. aureus*, *E. coli* and *P. aeruginosa* respectively. The antimicrobial efficacy is present in the treated wool fabric even after 20 washes. The increased durability of the finish may be due to the ability of PVP present in the silver nanopowder to form hydrogen bond with the hydroxyl groups of the cotton and wool and coordinate bond with the silver nanoparticles. Thus, the developed silver nanoparticles in powder form with PVP can be used to provide durable antimicrobial finishing to textiles in addition to the operational benefits such as easy handling, simple method of application and assured presence of nanoparticles without agglomeration.

Table 2—Percentage reduction in bacterial count after 24 h incubation (AATCC100)

Bacteria	Sample	At 0 h	After 24 h	% Reduction
S. aureus	Control	1.78×10^{6}	8.6×10^{6}	Nil
	Silver nanopowder treated			
	Without washing	5.6×10^{5}	3.4×10^{3}	99.96
	After 10 washes	5.2×10^{5}	3.3×10^{3}	99.96
	After 20 washes	5.07×10^{5}	3.27×10^{3}	99.96
E. coli	Control	7.3×10^{6}	4.3×10^{7}	Nil
	Silver nanopowder treated			
	Without washing	6.5×10^{6}	1.36×10^{6}	96.83
	After 10 washes	6.22×10^{6}	1.33×10^{6}	96.90
	After 20 washes	6.39×10^{6}	1.37×10^{6}	96.81
P. aeruginosa	Control	2.5×10^{6}	3.9×10^{7}	Nil
	Silver nanopowder treated			
	Without washing	2.1×10^{6}	2.5×10^{5}	99.35
	After 10 washes	2.08×10^{6}	2.62×10^{5}	99.32
	After 20 washes	2.2×10^{6}	2.8×10^{5}	99.28

4 Conclusions

The silver nanoparticles in composite with PVP have been synthesized in powder form for the textile applications. The UV-Visible spectrum of the powder confirms the presence of silver in nanometer size. The atomic absorption spectroscopic results show that the synthesized powder contains 100 ppm of silver. The TEM analysis indicates the presence 50-60 nm size of silver nanoparticles in the synthesized powder. The EDAX results further confirm the existence of silver in the synthesized powder. The treated wool and cotton materials by simple exhaustion method show durable antimicrobial efficacy against the three common infectious bacteria, namely *S. aureus*, *E. coli* and *P. aeruginosa*. The synthesized PVP coated silver nanopowder is useful for application on delicate fabrics, home textiles, knitted goods, wound dressings, etc.

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