

Improvement in dyeing, electro resistivity, and anti-microbial properties of acrylic fibres

Somayeh Baseri^a

Department of Textile Design and Printing, Semnan University, Semnan, Iran

Received 11 April 2016; revised received and accepted 29 November 2016

A simple and low-cost method has been developed to obtain dyed fibres with high electrical conductivity, as well as anti-microbial properties in nature. Fibres are first heat-treated in a solution containing cupric nitrate, sodium sulfide, and sodium hydrogen sulfate. Afterwards the treated fibres are dyed with a cationic dye. Results show that the pretreatment of fibres with conductive layer leads to the improvement in dye uptake, antimicrobial performance of the fibres as well as their reduced electrical resistivity. Using the results obtained from the present study, an appropriate suitable formulation has been developed for application and optimization of dyeing of coated fibres. The coated fibres show excellent fastness properties in terms of electrical conductivity and antimicrobial changes. After dyeing by a cationic dye, the electrical conductivity and antimicrobial properties of the fibres do not decrease. Copper sulfide coating can therefore be claimed as a simple method to produce textiles with good antistatic and antimicrobial properties, while at the same time, having very good fastness properties and laundering durability along with the increased dye ability of the samples.

Keywords: Acrylic fibres, Antimicrobial performance, Cationic dye, Chemical dyeing, Color strength, Electro resistivity coating, Laundering durability

1 Introduction

Synthetic textiles are usually suitable substrate for accumulation of electrostatic charges and also for growth of microorganisms. Accumulation of static electricity on the synthetic textiles leads to attraction of dust, electric shocks, intertwisting, and damages in electronic machines. These effects are of course a severe hindrance during the use of textiles in many applications such as electrically conducting, electronic, electromagnetic shields, and smart clothing.

Textiles possessing inherent antimicrobial functions are expected to be used in several applications such as medical devices, apparel, protective clothing, military, veterinary, automation, construction, decoration, housing, healthcare applications, and a large number of other industries^{1,2}.

To produce electrical conductive textiles, several methods are investigated such as the use of carbon nanotubes and carbon black particles^{3,4}, producing fibres from conductive polymers^{5,6}, coating some textiles with conductive polymers^{7,8}, the use of anti-static spin finishes, and application of nanocomposites containing conductive particles⁹. Several studies have

also been carried out on the antimicrobial activity of textile materials such as grafting of antimicrobial agents on the surface of the textiles, a finishing process, and incorporating agents into spinning solution of regenerated fibres¹⁰⁻¹⁶. The major classes of antimicrobial agents for textile materials include metal compounds such as silver, nickel, and copper salts, phenols, quaternary ammonium salts and organosilicons.

In this context, the question begging an answer is, whether the electrical conductivity and antimicrobial activity occurring simultaneously in one method enables us to further improve our knowledge about the preparation of new textile materials with improved properties. In line with this trend, it seemed likely that coating of textile substrates by copper sulfide is a promising approach to obtain electrically conductive and antimicrobial textiles. This is due to the high electrical conductivity and antimicrobial activity of copper sulfide. Copper sulfide (Cu_xS , $1 \leq x \leq 2$) is an important material which has very useful antimicrobial and electrical conductivity properties, and show several applications in conductive fibre processing, that has been widely investigated¹⁷. Copper sulfide is a low-cost inorganic salt which exhibits a metal-like electrical conductivity and also

^aE-mail: Baseri@semnan.ac.ir

controls the growth of microbes on the surface of textile materials^{17,18}. As a result, it is a good candidate to be used as a precursor for electrical conductive and antimicrobial coatings of textile substrates. Along these lines, the objective was to focus on coating of the acrylic fibres with copper sulfide in an attempt to enhance the electrical conductivity and antimicrobial activity of the samples simultaneously, which also exhibit excellent dye ability and color fastness.

Acrylic is one of the most important commodity polymers that is commonly used in the form of fibres or films. Acrylic has excellent properties such as good elasticity, high strength, horniness, excellent dye ability, relatively insoluble, and also has strong interchain and intrachain interactions through secondary bonding. Acrylic-based carbon fibres have been found to be the most suitable precursors for producing high-performance carbon fibres that are stronger than other types of precursor-based carbon fibres¹⁹. However, acrylic has inherent poor absorbency, accompanied by the high build-up of electrostatic charges, which limits its further development. Acrylic fibre has a strong affinity and adhesion for copper sulfide coatings due to its pendant ligands. As a result, a continuous layer could be formed on the surface of the acrylic fibres.

In the past, chemical bath deposition of copper sulfide thin films has been studied on the surface of poly(ethyleneterephthalate), low-density polyethylene, polysulfone, polymethylmethacrylate, polyimide foils, and polyethersulfone foils²⁰. However, till date no in-depth study has been conducted on the changes induced by copper sulfide in acrylic fibres. Nor has any study been reported about the influence of copper sulfide on the antimicrobial properties in acrylic fibres.

As mentioned earlier, a number of studies have been reported on the use of CuS to produce conductive polymeric materials; however, to the best of our knowledge, no study has been conducted on the changes induced by copper sulfide coating on the dyeing properties of fibres. The other main finding of this work is a detailed investigation of the influence of copper sulfide coating on the dye ability and color fastness properties of acrylic fibres, which was also not found in our literature review. In another attempt to gain a deeper understanding of these issues, a new model for the reaction pathway of copper sulfide layer with the surface of acrylic fibres is also proposed. For this purpose, the work includes the preparation of

copper sulfide coated acrylic fibres to obtain flexible fibres with high electrical conductivity, which also exhibit antimicrobial activity. The effect of conducting and antimicrobial layer on the dye ability of coated acrylic fibres has also been investigated. We studied the different variables involved in the coating and dyeing processes to obtain the optimal conditions for metal coating and then dyeing of coated samples. Also, the color fastness properties and the laundering durability of coating layer are investigated and techniques such as scanning electron microscopy and atomic absorption spectroscopy are used to characterize the metal coated acrylic fibres.

It can be claimed that the coated samples of this research have found several promising applications in many fields, such as medical clothing, floor-covering, fibre reinforcement or fillers in organic resin matrix composites, interior decorative sheets, carpets, gloves or in combination with other fibres. Excellent control over the electrical properties of knitted or woven goods can be obtained by combining the electroconductive fibres of the present work with other nonconductive synthetic yarns. Also because the sulfides have a very good thermal stability, the coated fibres produced by this research work could be incorporated in a melt for the production of molded articles used as electromagnetic shields.

2 Materials and Methods

2.1 Materials

Acrylic fibres with an average diameter of 1503 den were supplied by Polyacryle Co., Iran. Copper (II) nitrate [Cu (NO₃)₂], sodium sulfide (Na₂S), sodium hydrogen sulfate (NaHSO₄) and acetic acid (CH₃COOH) were used. All aqueous solutions were prepared with deionized water.

2.2 Experimental Procedures

Acrylic fibres were first pretreated by washing twice in boiling methanol for 20 min to eliminate spin finish and improve adhesion properties. The fibres were then washed with deionized water and dried. One step dipping method was used to produce conductive acrylic fibres. To determine the effect of chemical materials on the electrical resistivity of acrylic fibres as well as obtaining a suitable formulation for coating bath, the samples were heat-treated in baths containing different concentrations of copper (II) nitrate, sodium sulfide, and sodium hydrogen sulfate. In this study, all aqueous solutions

were prepared with deionized water. Each treatment was carried out for 100 min at 90 °C in an AHIBA 1000 polymath apparatus. The bath temperature was raised gradually from room temperature to 90 °C and the mixture was kept at this temperature for 100 min with constant stirring (a magnetic stirrer was placed in the bath and activated). The samples were washed with deionized water immediately after treatment in the bath, with the solution being repeatedly replaced during each washing. The experiments were carried out three times for each case under similar conditions. The samples thus dyed with a cationic dye [Maxilon Red GRL (C. I. Basic Red 46)] in a bath at 90 °C for 75 min. The pH of the dye bath was adjusted at 4.5-5.5 by adding acetic acid.

2.3 Testing and Analytical Procedures

The surface electrical resistivity measurements were carried out by the two-point probe technique according to the standard method (ASTM D 4496-87) at 20 °C and 65% R.H. The electrical resistivity was determined as the average values of 20 tests on each sample. The morphologies of the coated-acrylic fibres were studied using a Philips XL30 scanning electron microscope and a B5 Motic optical microscope.

The copper ions, extracted from copper sulfide coated samples, were studied using a 2380 atomic absorption spectroscopy (AAS). The dyed samples were subjected to color measurements by using X Rite Sp-64 spectrophotometer. The elemental composition analysis of copper sulfide coated acrylic fibres was determined using an energy-dispersive X-ray spectrometer (EDX) attached to the scanning electron microscope. Gold layer was deposited on the samples before the analysis.

Antimicrobial properties of coated samples were quantitatively evaluated against two types of bacteria according to AATCC 100-2004 test method. The two types of bacteria are *Staphylococcus aureus*, a Gram-positive bacterium (American Type Culture Collection No. 6538) and *Escherichia coli*, a Gram-negative bacterium (ATCC 25922). In this test method, a circular sample swatch with diameter of 4.6 cm was inoculated with 1.0 ± 0.1 mL of bacterial inoculum in a 250 mL container. For both bacteria, suspensions of 10^7 colony forming units (CFU)/mL of microbes were prepared by dilution of the suspension. The control and test swatches were placed in contact with microbes for 24 h and then 100 mL of sterilized distilled water was poured into the vessel and

vigorously shook prior to the dilution of the supernatant to 10^3 mL. After plating the diluted solution aliquots on an agar plate, the samples were incubated at the temperature of 37 ± 1 °C for 24 h. The percentage of reduction in bacterial colonies can be estimated from the following equation:

$$R(\%) = \frac{(A-B)}{A} \times 100 \quad \dots (1)$$

where R is the percentage of reduction rate in bacteria, and A and B are the number of bacterial colonies from initial and copper coated yarns, respectively²¹.

The coated samples were subjected to a repeated washing test according to ISO 105 C03 (1989). Light fastness test for the coated samples was carried out according to ISO 105 BO2 (1989)²².

3 Results and Discussion

3.1 Modification of Acrylic Fibres and Characterization of Metallic Coating

Surface of the acrylic fibres is coated with an insoluble antimicrobial and electro conductive metal sulfide layer by one step coating. Acrylic fibres were heat – treated in a solution containing divalent copper ions [copper (II) nitrate] and a reducing agent (sodium hydrogen sulfate) to reduce the divalent copper ions to monovalent copper ions and a sulfur-containing compound (sodium sulfide), which is capable of converting the adsorbed monovalent ions into copper sulfide.

An investigation of the interaction of acrylic fibres with copper sulfide is found suitable for obtaining the optimal conditions for metal coating. The mechanism of interaction between acrylic fibres and copper sulfide is believed to involve the following²⁰:

- (i) Absorption of divalent copper ions into the fibres;
- (ii) Formation of a covalent bond between the divalent copper ions and the pendant chemical groups on the acrylic fibres;
- (iii) Sulfidation of copper to produce an antimicrobial and conductive layer as a continuous coating on the surfaces of individual acrylic fibres.

It is well known that an insoluble antimicrobial and conducting layer could only be formed if there is a strong adhesive bond between the acrylic fibres and the copper sulfide layer. The acrylic fibres used in this work are produced from acrylonitrile (cyano groups) and methacrylate (oxygen atoms). As a result, they have a strong affinity for divalent copper ions,

ensuring that the adsorbed copper ions are strongly bounded and they can form coordinate bonds with the donor groups in the fibres.

Figure 1 shows schematically the mechanism of binding of copper sulfide on the surface of acrylic fibres. As seen in Fig. 1, coordinate bonds can be formed among the copper ions and the nitrogen atoms in cyano groups and oxygen atoms in methacrylate groups. Some of the divalent copper ions are attached to the oxygen atoms of the functional groups of the fibres with ionic bonds.

Sodium hydrogen sulfate was used as a reducing agent for the reduction of the divalent copper ions attached to the acrylic fibres to monovalent ions. Sodium sulfide provides sulfur atoms and/or ions for reacting with the monovalent copper ions to produce an antimicrobial and conductive copper sulfide layer. Considering the fact that the difference between the electronegativity of divalent copper ions and sulfur ions is more than that of monovalent copper and sulfur ions, the divalent copper ions orbitals overlap more effectively with sulfur ions than the monovalent copper ions. As a result, the energy gap (differences between HOMO and LUMO bands) for Cu_2S seems to be smaller than the gap for Cu_2S_2 . This result is consistent with those reported in the literature that the band gap of Cu_2S_2 is equal to 3.1 eV and band gap of Cu_2S is equal to 1.2 eV (ref. 23).

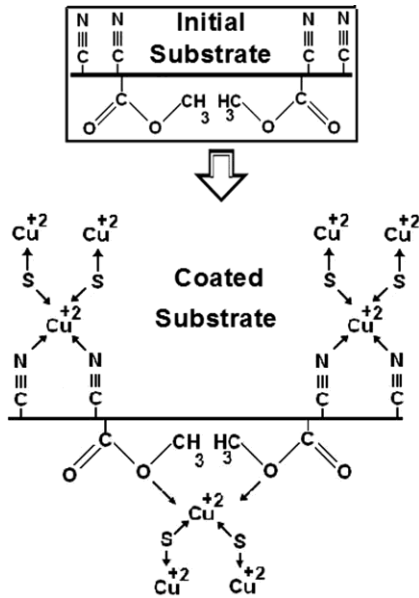


Fig. 1 — Covalent bond formation between special coating layer and acrylic substrate

In order to determine the effect of chemical materials on the electrical resistivity of coated acrylic fibres as well as obtaining a suitable formulation for coating bath, the fibres are coated in solutions containing different concentrations of copper (II) nitrate, sodium hydrogen sulfate and sodium sulfide. A brief study of these parameters has also been carried out and discussed hereunder.

Figure 2 shows the variations in surface electrical resistivity of acrylic fibres in various concentrations of coating bath. It can be noticed that the increase in concentration of each material leads to decrease in surface electrical resistivity of fibres. Also, it is evident that as the concentrations of copper (II) nitrate, sodium sulfide, and sodium hydrogen sulfate increase in the treatment bath, the surface electrical resistivity of the samples is decreased significantly up to 5.1, 9.6, and 5.7 g/L respectively. However, there are no noticeable changes in the surface electrical resistivity above these concentrations. It can be concluded that, for the concentration ranges used in the experiments carried out in this work, the concentrations of 5.1, 9.6, and 5.7 g/L for copper (II) nitrate, sodium sulfide, and sodium hydrogen sulfate are the optimum values. The variations in electrical resistivity (Fig. 2) can be interpreted by the mechanism of interaction between acrylic fibres and copper sulfide layer.

To study the effect of coating temperature on the surface electrical resistivity of the samples, fibres are treated for 100 min with 5.1 g/L copper (II) nitrate, 9.6 g/L sodium sulfide, and 5.7 g/L

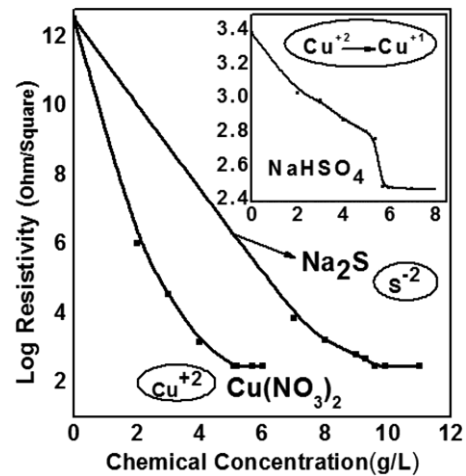


Fig. 2 — Log resistivity of coated samples versus different concentrations of copper (II) nitrate, sodium hydrogen sulfate, and sodium sulfide

sodium hydrogen sulfate at 40, 50, 60, 70, 80, 90, and 100 °C; the log surface electrical resistivity values at these temperatures are 12.539, 12.539, 12.022, 8.251, 4.015, 2.491, and 2.487 Ohm/square respectively.

It is observed that there is no noticeable difference between the electrical resistivity of the uncoated and copper sulfide coated acrylic fibers at 60°C. However, as the temperature increases the electrical resistivity of the samples is decreased obviously till 90 °C after which there is no significant change in electrical resistivity. This could be due to the influence of temperature on the structure and molecular chains of the fibres. By increasing the temperature, a more open structure of the fibres is obtained. Consequently, the number and volume of voids will be greater and more active sites will be available, leading to higher amount of copper sulfide attached to the fibres. The glass transition temperature (T_g) of the acrylic fibers is found about 78°C. It can, therefore, be concluded that the coating of the fibers with copper sulfide is accomplished at a temperature above the glass transition temperature (T_g) of the fibers. As a result, 90 °C is found to be the most suitable coating temperature for the concentration range used in the experiments.

As mentioned above, the optimum condition of coating acrylic fibres with copper sulfide is 5.1 g/L copper (II) nitrate, 9.6 g/L sodium sulfide, and 5.7 g/L sodium hydrogen sulfate at 90°C for 100 min. SEM micrographs of the coated acrylic fibres under these conditions are shown in Fig. 3.

It is evident that the metal coating layer is not limited to the surfaces of the fibres but it has penetrated inside the fibres as well and the coating

layer is uniform along the length of the fibres. In order to investigate the depth of penetration of copper sulfide inside the fibres and determine the composition of the samples, an energy dispersive X-ray (EDX) was carried out during the SEM testing on the cross-section of the coated samples by 2 µm intervals (Fig. 4).

It is clearly noticed from Fig. 4 that the surface of coated fibres contained 32.14 and 19.82 wt. % Cu and S respectively, representing significant loading of copper sulfide on the surface of acrylic fibres. It is also seen that as the depth of probing increases, the amount of these atoms decreases and no evidence of existence of copper and sulfur ions is observed in the depth of 6 µm from the surface of the fibres. Using the result obtained from the present study, copper sulfide coating up to 4 µm through the fibres is estimated.

The percentage amount of the copper content of the coated acrylic fibres was also measured by atomic absorption spectroscopy (AAS). For this purpose, 330 mg of sample was immersed in 25% ammonia solution, and the resulting blue solution was transferred to a 25 mL volumetric flask, and diluted up to the mark by deionized water (solution A). About 5 mL of the solution A was diluted again to 25 mL and the absorption of this solution was measured to be 0.092 by AAS. About 1 mL of the standard solution was also added to a 5 mL aliquot of solution A and was diluted to 25 mL. The absorption of this solution was measured to be 0.237 by AAS. From this, the percentage amount of the copper content of the fibres can be calculated as follows: By using Beer-Lambert law ($A = \epsilon bc$), following equation can be derived:

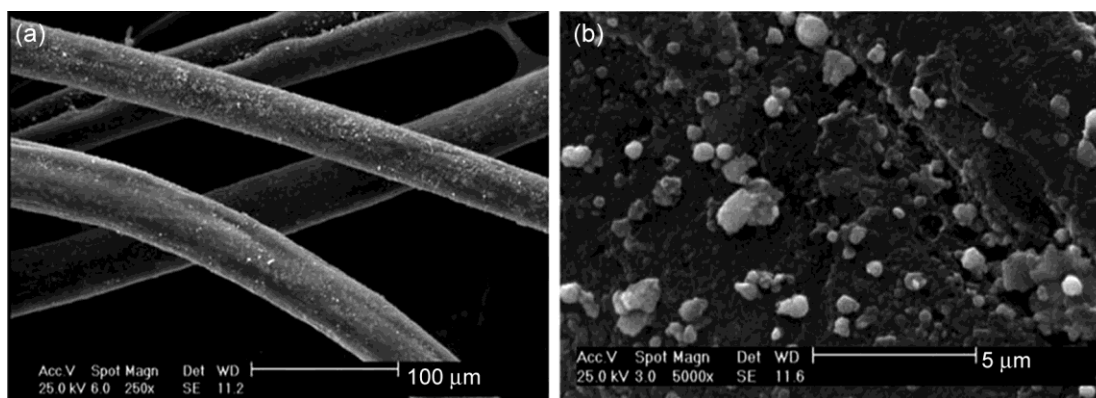


Fig. 3 — SEM photograph of metal coated acrylic fibres at magnifications of (a) ×250, and (b) ×5000

$$C_x = C_S \times \frac{V_S}{V_x} \times \frac{A_x}{(A_{x+S} - A_x)} \quad \dots (2)$$

where the parameters have their general meanings. According to Eq. (2) and the results of the discussion

above, the amount of copper in the coated fibres can be calculated as follows:

$$C_x = 200 \times \left(\frac{0.092 \times (1\text{ml})}{(0.237 - 0.092) \times (5\text{ml})} \right) \Rightarrow C_x = 25.379 \mu\text{g/mL}$$

As the initial volume of the solution for dissolving the coated samples is 25 mL, the amount of copper for this volume is calculated as:

$$25.379 \mu\text{g/mL} \times 25\text{mL} = 634.475 \mu\text{g}$$

From the above calculation, it can be concluded that 1 g of coated acrylic fibres contains 1922.651 μg of copper. The major classes of antimicrobial materials for textiles substrates are metallic compounds such as copper salts. As a result, it seems likely that copper sulfide coated acrylic fibres may have suitable antimicrobial properties. In this scenario, answering the question whether antimicrobial properties occur in copper sulfide coated samples enables us to further improve our knowledge about the preparation of new acrylic fibres with improved properties. In an attempt to gain a deeper understanding of this issue, the effect of copper sulfide layer on the antimicrobial properties of coated acrylic fibres is quantitatively studied according to the AATCC 100-2004 test method (Section 2). The initial acrylic fibres, and the copper sulfide coated samples are screened for their antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* and the percentage reduction in the number of two bacteria after 24 h incubation is shown in Table 1. Also, the results of the inhibition zone test for raw fibres, compared with copper coated fibres against *E. coli* and *S. aureus*, are presented in Fig. 5. It is evident that initial acrylic fibres show no antimicrobial activity, but the fibres coated with copper sulfide show excellent antimicrobial performance. This may be due to antimicrobial property of copper sulfide layer.

Textile materials have been widely subjected to frequent laundering. As a result, durability of electrical resistivity and antimicrobial activity to washing is very important. In order to study the fastness of metal coating, the electrical resistivity and antimicrobial properties of coated acrylic fibres before and after multiple washes are measured and the results are presented in Fig. 6 and Table 2.

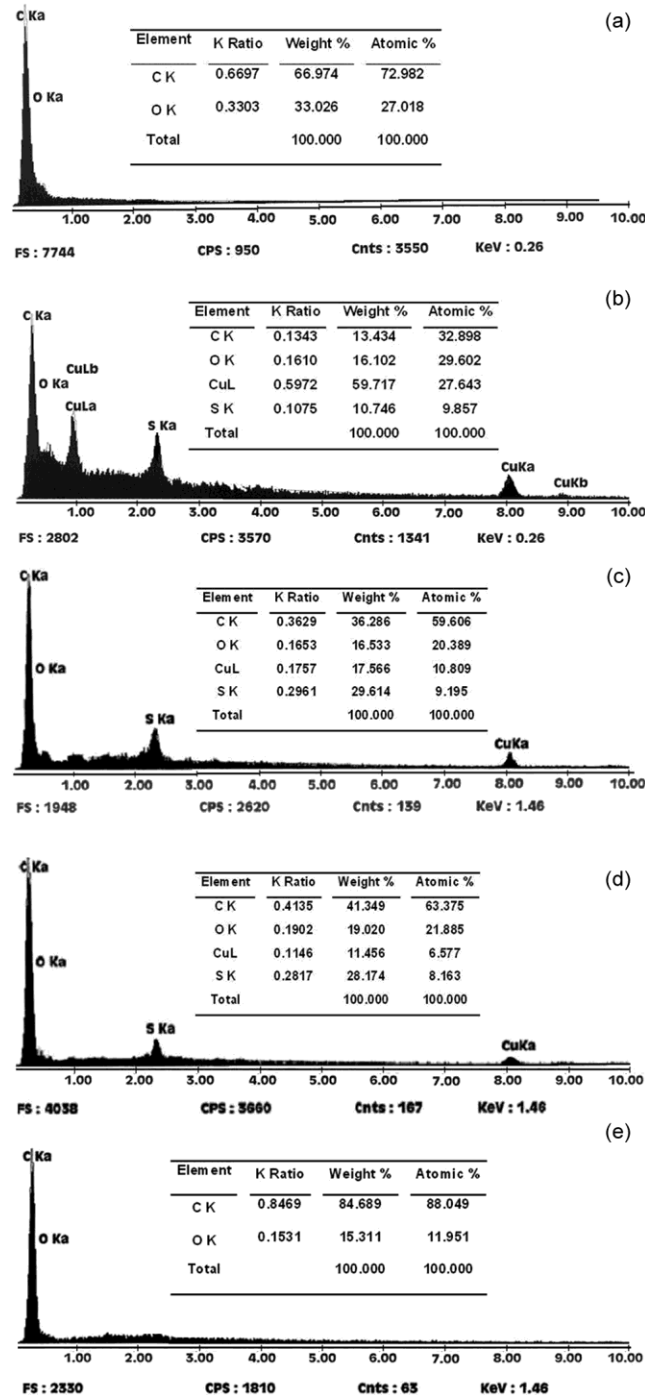


Fig. 4 — An elemental analysis on the cross-section of the coated acrylic fibres by 2 μm intervals: (a) uncoated samples, (b) surface of coated samples, and the depth of 2 (c), 4 (d), and 6 (e) μm from the surface of the coated samples

It is clearly noticed from Fig.6 and Table 2 that the electrical resistivity and antimicrobial activity change very little and it is ascertained that their wash ability is excellent. This could be due to the insolubility of the coating layer and illustrates the presence of strong adhesive bonds between the coating layer and acrylic fibres. The slight increase in the surface electrical resistivity of the fibres can be attributed to the fact that some of the divalent copper ions are attached to the functional groups of the fibres with ionic bonds.

3.2 Effect of Copper Sulfide Coating Layer on Dye Uptake

To study the influence of copper coating on the dye uptake of the acrylic fibres, the samples were dyed with a cationic dye and to determine the most suitable dyeing conditions, the copper coated acrylic fibres, dyed under different conditions and factors, such as dye concentration, electrolyte concentration, pH value, time and dyeing temperature were investigated. So, a brief study of these parameters is presented below.

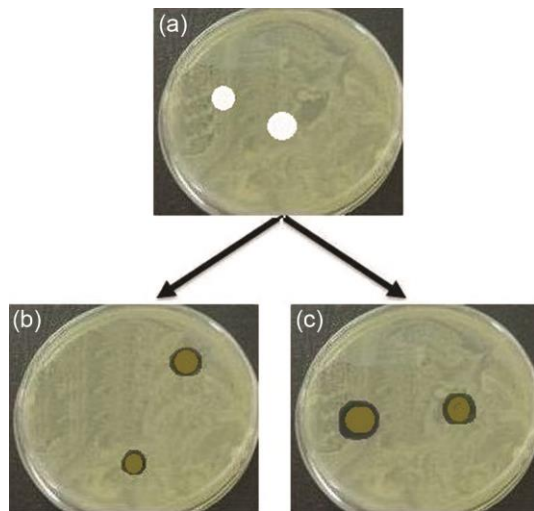


Fig. 5 — Inhibition zone for (a) control fibres, (b) coated fibres against *E. coli*, and (c) coated fibres against *S. aureus*

The effect of dye concentration on the color strength is studied by treating the coated fibres with different concentrations of cationic dye at 90 °C for 75 min. The results are shown in Fig. 7(a). It is found that the dye uptake increases as the concentration of dye increases and the color strength of dyed samples reaches an equilibrium at a concentration of about 2% under the used dyeing conditions in this work. It can be explained by the fact that the amount of acidic groups (-COOH and -SO₃H) on acrylic fibres is limited under fixed dyeing conditions and then dye uptake of the samples limited.

For evaluating the effect of electrolyte concentration on the dyeing process with cationic dye, the samples were dyed with 2% dye using different concentrations of sodium sulfate [Fig. 7(a) (inset frame)]. From this figure, a noticeable decrease in dye uptake is observed with addition of sodium sulfate over 0.5 mol/L; however at concentrations over

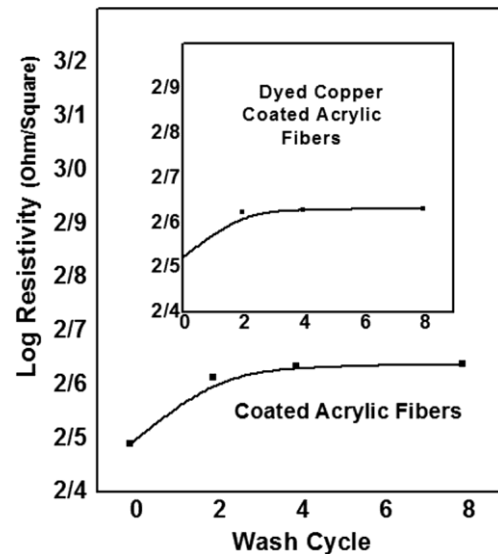


Fig. 6 — Durability of surface electrical resistivity to washing in the coated acrylic fibres before and after dyeing

Table 1 — Surface electrical resistivity and percentage reduction in number of *S. aureus* and *E. coli* bacteria after 24 h incubation

Samples	Bacterial reduction, %		log (surface electrical resistivity) Ohm/square
	<i>S. aureus</i>	<i>E. coli</i>	
Initial acrylic fibres	0	0	12.539
Coated acrylic fibres	99.25	97.82	2.491
Dyed coated fibres	98.95	97.78	2.522

Table 2 — Durability of antimicrobial activity to washing of coated acrylic fibres before and after dyeing

Bacteria	Copper coated samples, %				Dyed coated samples, %			
	0 wash	2 wash	4 wash	8 wash	0 wash	2 wash	4 wash	8 wash
<i>S.aureus</i>	99.25	98.63	98.15	98.13	98.95	98.42	98.14	98.19
<i>E. coli</i>	97.82	97.74	96.32	96.14	97.78	97.51	96.29	96.12

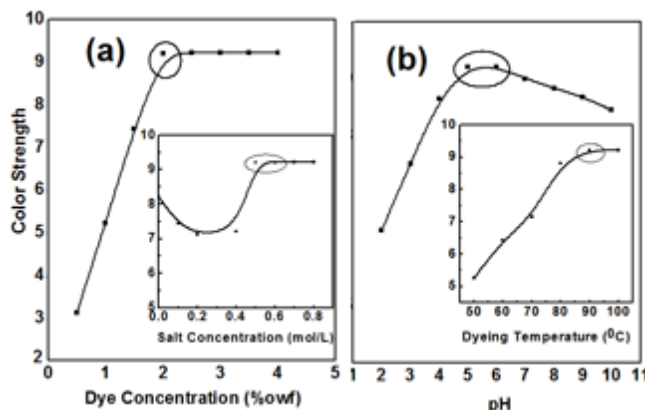


Fig. 7 — [a] Effect of cationic dye concentration on dye uptake of coated fibres (main frame) and effect of salt concentration on dye uptake of coated acrylic fibres (inset frame), and [b] effect of dyeing pH on dye uptake of coated fibres (main frame) and dye uptake of coated fibres versus dyeing temperatures (inset frame)

0.5 mol/L the color strength increases gradually with increasing of sodium sulfate concentration. These two opposite effects of sodium sulfate on dye uptake are explained hereunder.

(i) Acrylic fibres have acidic groups in its structure which leads to exist the negative dye-sites inside the fibres. As a result, there are ionic interaction between cationic dye molecules and acrylic fibres. By increasing the concentration of sodium sulfate, cations of the salt compete with the dye cation for the sorption negative sites inside the acrylic fibres. So sodium sulfate has a retarding effect on the acrylic dyeing process due to an ion-exchange effect at low salt concentration.

(ii) It is understood that ionic interaction is not the only interaction that occurs in acrylic dyeing process. Hydrophobic attraction also has an important role in the cationic dyeing of acrylic fibres²⁴. At high sodium sulfate concentration, sulfate ions can increase the attractive force (hydrophobic interaction) between acrylic fibres and cationic dye, a situation which is characterized by an increasing dye uptake.

In order to study the effect of pH on the dye uptake of acrylic fibres, the samples were dyed at different pH values and under constant conditions of treatment. Figure 7(b) shows the effect of pH value on the dyeing process.

It is evident that the maximum dye sorption is obtained at 5-6 pH, beyond which the dye uptake of coated fibres decreases. The reduction in color strength at acidic conditions (pH<5) can be explained by the fact that hydrogen ions compete with the dye cations for occupying acidic sites within the fibres

(-COOH and -SO₃H), this reducing the sorption of cationic dyes. As a result, it can be said that as the value of dyeing pH decreases, the amount of hydrogen cations increases in the dyeing bath and then the rate of dye uptake decreases.

The decrease in dye uptake over pH 6 can be attributed to the structural features of cationic dyes. It is understood that most cationic dyes (especially benzothiazolyl-azo cationic dyes) are unstable in alkaline conditions and they are decomposed under alkaline solutions²⁵.

To study the effect of dyeing temperature on the dye uptake of the copper coated acrylic fibres, the samples were dyed for 75 min with 2% dye, 0.5 mol/L sodium sulfate, and pH 5 at different temperatures. The dye uptake of samples versus dyeing temperature is shown in Fig. 7(b) (inset frame). It is obvious that the dye uptake of coated samples increases as the dyeing temperature increases till 90 °C. However, there is no significant effect on the dye uptake above this temperature. This may be due to the following two reasons:

(i) By increasing the dyeing temperature, less aggregated dye molecules form in the dye bath and then the solubility of dye molecules is increased.

(ii) Increasing the dyeing temperature, increases the movement speed of polymer chains and subsequently increases the fractional free volumes. Thus, a more open structure is obtained and the amount of available active sites in the fibres increases, thereby increasing interaction of dye molecules with fibres which is followed by an increase in the dye uptake.

It can thus be claimed that raising dyeing temperature leads to facilitate a quick dyeing process and better dye penetration into the fibres. Using the results obtained from the present study, the optimum condition of dyeing with cationic dye is found as 2% dye, 0.5 mol/L salt, and pH 5 at 90°C for 75 min.

To investigate the influence of copper sulfide coating on the dye uptake of the acrylic fibres, the samples were dyed with cationic dye and the color strength, wash, and light fastness properties of the fibres are 4.35, 3-4, and 5-6 respectively for initial fibres and 9.21, 4-5, and 5-6 for copper coated samples. It is observed that the coating of acrylic fibres with copper sulfide improves the dye uptake and more cationic dye is absorbed by the samples. This may be due to the following two reasons:

(i) Acrylic fibres have a strong affinity towards cationic dye due to the formation of electrostatic bonding between the negative charge of acrylic fibres and the positive charge of cationic dyes. The negative charge in acrylic fibres can be attributed to the presence of acidic groups (-COOH and -SO₃H) in its structure. As mentioned earlier, some of oxygen atoms in acidic groups can coordinate to the copper ions in the copper coating pretreatment. So, the amount of anionic sites on the coated samples decreases, which leads to low attraction with cationic dyes. As a result, copper coating will decrease the color strength of samples.

(ii) Since particles of copper sulfide have negative charge, the number of anionic sites in the coated samples is increased as a result of pretreatment with copper sulfide. So, the accessibility and receptivity of copper coated acrylic fibres are increased towards cationic dye, a situation which is characterized by an increase in dye uptake and subsequently the obtained color strength.

The above results suggest that the later (ii) mainly prevails in coated fibres dyed with cationic dye. The color fastness properties of initial and copper sulfide coated fibres dyed with cationic dye show that there is no difference in the light fastness of the samples, but the fastness to wash is improved in the case of copper sulfide coated fibres. This increase may be attributed to the increase in size of the cationic dye molecules when connected to copper sulfide molecules inside the acrylic fibres, followed by more adhesion bonds between the fibre matrix and the dye molecules.

To study the effect of dyeing on the electrical resistivity and antimicrobial activity of the acrylic fibres, these properties are measured in the dyed coated samples and the results are summarized in Table 1. As is evident from Table 1, dyeing of copper coated acrylic fibres with cationic dye has no significant effect on the electrical resistivity and antimicrobial activity of the samples. This may be due to the insolubility of the coating layer, and it confirms the existence of strong, covalent bonds between the copper sulfide phase and the pendant ligands on the acrylic fibres.

4 Conclusion

In this work, a simple and low-cost way to obtain dyed acrylic fibres with high electrical conductivity has been reported, which also exhibit antibacterial properties. Acrylic fibres can be made antimicrobial

and electro conductive by coating with copper sulfide in a bath containing divalent copper ions, a reducing agent, which is capable of reducing the divalent copper ions to a monovalent ions and a sulfur-containing agent. On the basis of the results obtained from the present study, a solution containing 5.1 g/L copper (II) nitrate, 9.6 g/L sodium sulfide, and 5.7 g/L sodium hydrogen sulfate is selected as a suitable formulation for application and optimization of copper sulfide coating of acrylic-based materials. The average thickness of the copper sulfide layer is estimated as about 4 µm. The coated fibres display remarkable fastness properties against multiple washes in terms of electrical conductivity and antimicrobial activity change. Also, the coated samples offer excellent fastness against the light as they have strong adhesive bonds between the fibre matrix and the coating layer. The results show that the pretreatment of acrylic fibres with copper sulfide enhances the dye uptake. The optimum condition of dyeing copper sulfide coated fibres with cationic dye is 2% cationic dye, 0.5 mol/L sodium sulfate, pH 5 at 90 °C for 75 min. The electrical resistivity and antimicrobial activity of the dyed fibres are not found lowered. The fastness properties of washing, and light for dyed copper coated acrylic fibres show good results. Based on these observations, it can be claimed that the coating of acrylic fibres with copper sulfide can produce samples with good electrical conductivity and antimicrobial activity, while at the same time, enhancing wash fastness and dye ability of the starting samples.

References

- 1 Gupta D, *Indian J Fibre Text Res*, 32 (2007) 254.
- 2 Shaki H, Gharanjig K & Khosravi A, *Indian J Fibre Text Res*, 40 (2015) 425.
- 3 Bouchard J, Cayla A, Lutz V, Campagne C & Devaux E, *Text Res J*, 82 (2012) 2106.
- 4 Jellur Rahman M & Mieno T, *J Nanomaterials*, 2015 (2015) 1.
- 5 Stempien Z, Rybicki T, Rybicki E, Kozanecki M & Szykowska M I, *Synthetic Metals*, 202 (2015) 49.
- 6 Deogaonkar S C & Patil A J, *Indian J Fibre Text Res*, 39 (2014) 135.
- 7 Shaikh T N, Chaudhari S, Patel B H & Patel M, *Int J Emerging Sci*, 3 (2015) 11.
- 8 Åkerfeldt M, Strååt M & Walkenström P, *Text Res J*, 83 (2012) 618.
- 9 Hassanpour Dehnavi M, Asgharian Jeddi A A, Gharehaghaji A A, Esmaeil Yazdandshenas M & Rezaei Zarchi S, *Indian J Fibre Text Res*, 38 (2013) 380.
- 10 Nakashima T, Sakagama Y & Matsuo M, *Text Res J*, 71 (2001) 688.

- 11 Bohringer A, Rupp J & Yonenaga A, *Int Text Bull*, 5 (2000) 12.
- 12 Salvio G & Saniewar T, *Chem Fibres Int*, 51 (2001) 34.
- 13 Chen X & Wei L, *J Eng Fibres Fabrics*, 9 (2014) 120.
- 14 Sadeghian M, Montazer M & Rashidi A, *J Eng Fibres Fabrics*, 8 (2013) 68.
- 15 Haji A, Mousavi Shoushtari A & Mirafshar M, *Color Technol*, 130 (2013) 37.
- 16 Kumar V, Bhardwaj Y K, Rawat K P & Sabharwal S, *Radiation Physi Chem*, 73 (2005) 175.
- 17 Chen M, Zhao J & Zhao X, *Electrochimica Acta*, 56 (2011) 5016.
- 18 Janickis V & Ancutiene I, *CHEMIJA*, 20 (2009) 136.
- 19 Purwar R, Sahoo P, Jain M, Bothra U, Yadav P, Juneja J & Srivastava C M, *Indian J Fibre Text Res*, 41(2016) 84.
- 20 Hudson M J & Jacqueline G M, *Solid State Ionics*, 73(1994) 175.
- 21 Sedighi A, Montazer M & Hemmatinejad N, *Cellulose*, 21 (2014) 2119.
- 22 Son Y, Hong J, Lim H & Kim T, *Dyes Pigm*, 66(2005) 231.
- 23 Saraf R, *IOSR J Electrical Electronics Eng*, 2 (2012) 47.
- 24 Yang Y & Ladisch C M, *Text Res J*, 63 (1993) 283.
- 25 Ding M, Ma S & Lui D, *Analytical Sci*, 19 (2003) 1163.