Synthesis and Optimization of Copper Sulfide-Coated Electrically Conducting Poly(acrylonitrile) Fibers

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ABSTRACT: In this research work, coating of acrylic fibers (fibers spun from poly acrylonitrile) with copper sulfide was investigated. Surface of the acrylic fibers were coated with an insoluble conducting copper sulfide layer. One-step dipping method was carried out. Acrylic fibers were treated in a bath containing divalent copper ions, a reducing agent, which is capable of reducing the divalent copper ions to a monovalent copper ions and a sulfur-containing compound. This treatment resulted in a reduction of electrical resistance to 1×10^9 that of an almost infinite resistance for the untreated fibers. The influence of some parameters such as concentration of copper (II) sulfate, hydroxylamine sulfate, sodium thiosulfate, and temperature of treatment bath were also investigated. A second reducing material such as sodium dithionite was used to improve the electrical conductivity of the fibers. The amount of reacted copper was measured by atomic absorption technique. The surface properties of the coated-acrylic fibers were studied using scanning electron microscopy (SEM). Within the experimental conditions, a solution containing 1.2 g/dm^3 copper (II) sulfate, 1.6 g/dm^3 hydroxylamine sulfate, 3.6 g/dm^3 sodium thiosulfate, and 3 g/dm^3 sodium dithionite was selected as a suitable formulation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2579–2586, 2007

Key words: electrical resistivity; semiconductors; copper sulfide; acrylic fibers; coatings

INTRODUCTION

Polymeric materials such as nylon and polyester have revolutionized the fiber and textile industries. Until quite recently, however, there was a significant area of application that these organic polymers could not address. These applications were in the area of electrically conducting, electronic, and magnetic materials.[1] The differences among a conductor, a semiconductor, and an insulator are generally the result of the differences between the HOMO and LUMO bands typically referred as the energy gap. In a semiconductor, the band gaps are not that large so that there is a small energy gap between the HOMO and LUMO levels. However, because of the small gap, electrons can be excited either thermally or electrically over the gap where they are free to delocalize over the LUMO level or, in terms of the solid state physics, the conduction band. Insulator normally has a large energy gap where it is difficult to promote electrons across the gap. For most insulators, the band gap is wide and electrons are localized on atomic centers or a small group of atoms and once promoted are not free to delocalize over extended distances necessary for electrical conduction.[1]

For polymeric materials to become electrically conductive, the energy gap between the valance and conduction bands must be significantly lowered or new bands must be formed in the gap into which electrons can be easily promoted or charge donated.[1] In addition, the molecular orbital must not be localized over single atomic centers or small groups of atoms such as benzene rings, but must allow for significant delocalization of the electron density for a current to be carried.[1]

Accumulation of electrostatic charges on the synthetic fibers leads to attraction of dust, intertwisting, electric shocks, and damages in electronic machines. These effects are of course a severe hindrance to the use of polymer fibers in many applications.[2] Also conductive polymer fibers are intended for use in creating conductive yarns and realizing connections in smart clothing or producing conductive fabrics, which can be used as electromagnetic shields.[3] To overcome these problems and to produce conductive polymer fibers, several methods are studied, such as producing fibers, from electrical conductive polymers,[4,5] coating some synthetic fibers with conductive polymers,[6–8] the use of carbon nanotubes and carbon black particles in fibers,[9–11] the use of antistatic spin finishes, and application of nanocomposites containing conductive particles in fibers.[12]

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During the last few years, several works have dealt with the modification of polymeric surfaces to improve their mechanical adhesion, wettability, dyeing, and other properties.[13] For instance, when a metallic sulfide is deposited onto polymeric surface, the resulting composite presents an association of the flexibility and the mechanical robustness of the polymer with the electro-optical properties of the sulfide.[14] Copper sulfide stands out because of its low electrical resistance, its technological applications, and to its occurrence in a variety of stoichiometries. Impregnated onto a polymeric membrane, this metal sulfide finds applications in areas, such as electrochemistry in the development of selective microelectrodes.[13,14] Covellite porcelain, a CuS polymorph, has special interest because of its metal-like conductivity at very low temperatures and the ability of producing or impregnating it *in situ* onto electrically charged polymers surfaces.[14]

In the past, chemical bath deposition of semiconductor thin films on polymer substrates has been reported:

Cu_2Se on polyester (polyethyleneterephthalate, PET)[15];
CuS on PET[16];
CuS on low-density polyethylene[13];
CuS on polysulfone[14];
CuS on acrylic or modacrylic (polymethylmethacrylate, PMMA)[15,17,18–22];
CuS on polyimide foils[23];
CuS on polyethersulfone foils[24]; etc.

The aim of this work was the preparation of copper sulfide-coated acrylic fibers (fibers spun from polyacrylonitrile) to obtain flexible fibers with low electrical resistance, which also exhibit antibacterial properties in nature. These conducting acrylic fibers having superior conductivity are obtained without the need for special pretreatment of fibers, while in the case of other fibers and films such as polysolfone films, a previous treatment of the polymer surface with modifiers is needed to provide adherence.[13–15]

The copper sulfide acrylic fibers produced in this work can lend itself to numerous applications in many fields. It can be used alone or in combination with other fibers to produce woven or knitted fabrics for electric blankets, electrically heated clothing, and other similar applications. Excellent control over the electrical properties of knitted or woven goods can be obtained by combining the electrically conductive fibers of the present work with other nonconductive synthetic fibers. Also, spun yarns can be produced from mixtures of the electrically conductive fibers of the present work with other synthetic fibers in the form of staple fibers.

The main difference between the results presented by this research work in comparison with the results shown in Ref. 17 are based on changes in formulation used in the coating bath. In addition to the chemicals used in the coating formulation of Ref. 17, sodium dithionite was added and its optimum concentration was determined. This addition showed a significant improvement in the electrical conductivity of the fibers. The other main finding of this work was a detailed investigation into the mechanism of decreasing electrical resistivity of the fibers, which was not found in our literature review.

In this work, we studied the different variables involved in the coating process to optimize the amount of copper (II) sulfate, hydroxylamine sulfate, sodium thiosulfate, and a second reducing agent such as sodium dithionite in the formulation and temperature of the treatment bath.

On the basis of the statistical experimental planning, the optimal conditions for copper sulfide coating were reported. Also, techniques such as scanning electron microscopy (SEM) and atomic absorption spectroscopy (AAS) were used to characterize the copper sulfide-coated acrylic fibers.

EXPERIMENTAL

Materials

Acrylic fibers used in this work were supplied by Isfahan Polyacryl Company. These fibers were produced from 94% acrylonitrile, 5% methylcrylate, and a trace of acrylamidomethylpropeosulfate.

The molecular weights of these fibers are $\overline{M}_w = 120{,}000$ and $\overline{M}_n = 70{,}000$.

Chemical materials used in this work are listed in Table I.

Pretreatment of fibers

Prior to metal deposition, to eliminate spinfinish and improve adhesion properties, the fibers were pretreated by washing twice in boiling methanol for 20 min. Fibers were then washed with deionized water and dried.

Coating of fibers

To investigate the influence of the ingredients concentration in the coating bath on the surface electrical resistivity of the acrylic fibers, different concentration of

TABLE I
Chemical Materials Used for Coating

Chemical	Formula	Company
Copper sulfate	$CuSO_4.5H_2O$	Merk
Sodium thiosulfate	$Na_2S_2O_2.5H_2O$	Merk
Hydroxylamine sulfate	SO_4NH_4OH	Merk
Sodium dithionite	$Na_2S_2O_6.5H_2O$	Merk

TABLE II
Variation of Concentrations in Coating Process

1	Copper(II) sulfate (g/dm^3)	0.5	1	1.2	1.3	1.4	1.5	1.7
	Sodium thiosulfate 3.6 (g/dm^3)			Hydroxylamine sulfate 1.6 (g/dm^3)				
2	Sodium thiosulfate (g/dm^3)	0	1	2	3.6	5	–	–
	Copper(II) sulfate 1.2 (g/dm^3)			Hydroxylamine sulfate 1.6 (g/dm^3)				
3	Hydroxylamine sulfate (g/dm^3)	0	0.5	1	1.6	1.9	2.3	–
	Copper(II) sulfate 1.2 (g/dm^3)			Sodium thiosulfate 3.6 (g/dm^3)				
4	Sodium dithionie (g/dm^3)	0	1	2	3	4	5	–
	Copper(II) sulfate 1.2 (g/dm^3)			Sodium thiosulfate 3.6 (g/dm^3)				
		Hydroxylamine sulfate 1.6 (g/dm^3)						
5	Copper(II) sulfate 1.2 (g/dm^3)	Various temperatures 70, 80, 85, 90, 95, and 100°C						
	Sodium thiosulfate 3.6 (g/dm^3)							
	Hydroxylamine sulfate 1.6 (g/dm^3)							

copper (II) sulfate, sodium thiosulfate, hydroxylamine sulfate, and sodium dithionite were chosen (Table II). Each treatment was carried out for 90 min at 85°C. Treatments were carried out in an AHIBA 1000 polymath apparatus made by Data Color Company. Prior to each treatment, the fibers were washed with deionized water and dried. Deionized water was used to dissolve the chemical materials and the experiments were carried out thrice for each case under similar conditions.

Characterization of the fibers

The surface electrical resistivity measurements were carried out by the two-point probe technique according to the standard method (ASTM D 4496-87).[25]

All of the measurements were carried out at 20°C and 65% R.H. The morphologies of the coated-acrylic fibers were studied using a Philips XL30 scanning electron microscope and a B5 Motic optical microscope.

The copper ions, extracted from copper sulfide-coated acrylic fibers, was studied using a 2380 Atomic Absorption Spectroscopy (AAS).

A sample of coated-acrylic fibers (330 mg) was immersed in 25% ammonia solution, and the resulting blue solution was transferred to a 25-mL volumetric flask, and diluted 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 0.052 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 0.141 by AAS. From this, the percentage amount of the copper content of the fibers was calculated.

Statistical methods

SPSS 9 for windows computer program was used for the statistical analysis of the data. Two methods were selected Kruskal-Wallis and Mann-Whitney U tests. These test methods are nonparametric tests and their validity does not depend on the data being drawn from any particular distribution. The advantage of the nonparametric method is that they can be used with any set of data with their distribution being unknown.[26]

RESULTS AND DISCUSSION

Mechanism of the interaction of acrylic fibers with copper sulfide

The mechanism of interaction between polymeric fiber substrate and copper sulfide is believed to involve:

1. Absorption of aqueous copper (II) ions into the fiber;
2. Formation of a strong, covalent bond between the copper(II) and the pendant groups on the fibers;
3. Sulfidation of copper to produce an insoluble conducting copper sulfide phase as a continuous coating on the surfaces of the individual fibers.[18]

It is believed that a continuous conducting layer could only be formed if there was a strong adhesive bond between the fiber matrix and the conductive phase.[17]

Coordinating copolymers with pendant ligands, which have a strong affinity for copper (II) ensure that the adsorbed copper is strongly bounded.[17]

The extraction of copper ions by the fibers appears to involve:

1. Primary sorption of copper ions;
2. Diffusion of copper ions into the fiber;
3. Secondary sorption.[18]

The acrylic fibers used in this work was produced from 94% acrylonitrile, 5% methylcrylate, and a trace of acrylamidomethylpropeosulfate.The fibers were treated in a bath containing divalent copper ions (copper (II) sulfate), reducing agent(hydroxylamine
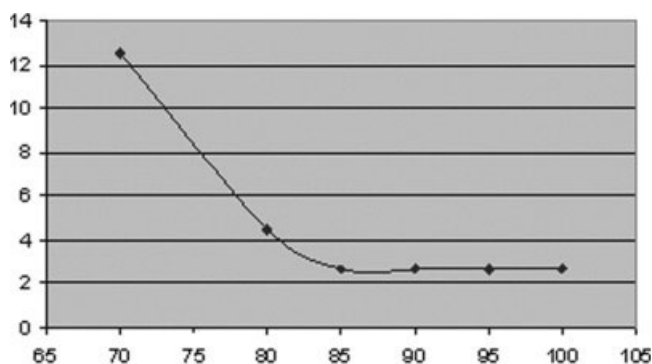
Figure 1 Surface electrical resistivity of coated-acrylic fibers versus temperatures of coating bath. X label: temperature (°C); Y label: log surface electrical resistivity (Ω/square).

sulfate) and a sulfur-containing compound (sodium thiosulfate).

Considering the electron orientation of copper ions in the form of [Ar] $3d^{10}$ and [Ar] $3d^9$ for copper (I) and copper (II), respectively. The nitrogen atoms in cyano groups and oxygen atoms in methylcrylate groups can coordinate to the copper ions (Fig. 1). Some of the copper (II) ions are attached to the oxygen atoms of the pendant ligands of the acrylic fibers with ionic bonds.

The reducing agent is capable of reducing the copper (II) ions attached to the acrylic fibers to copper (I). Sulfur-containing compound, which provides sulfur atoms and/or sulfur ions for reacting with the copper (I) ions is needed to produce insoluble copper sulfide layer.

Influence of the coating bath temperature on the electrical conductivity of the fibers

To study the effect of coating bath temperature on the electrical resistivity of the studied acrylic fibers, acrylic fibers were coated for 90 min at temperatures 70, 80, 85, 90, 95, and 100°C respectively, as shown in Table II, Section 5. The measured electrical resistivity of fibers versus bath temperatures is shown in Figure 2.

It is evident that there is no difference between the electrical resistivity of the untreated (2.89×10^{12} Ω/square) and treated fibers at 70°C. However, as the bath temperature increases the electrical resistivity of the fibers is decreased significantly up to 85°C, and above this temperature there is no noticeable changes. The mechanism for this reduction is related to the effect of temperature on the structure of the fibers. By increasing the temperature, a more open structure of the fibers is obtained, and hence more active sites are available. Consequently, more copper (II) ions react, resulting in more copper sulfide attached to the fibers. The glass transition temperature (T_g) of the fibers was about 78°C. It can 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. Statistical analysis (Kruskal-Wallis and Mann-Whitney tests) carried out shows that there are no meaningful differences in the electrical resistivity of the fibers treated at temperatures 85, 90, 95, and 100°C. Optimum bath temperature of 85°C was selected for the coating time of 90 min.
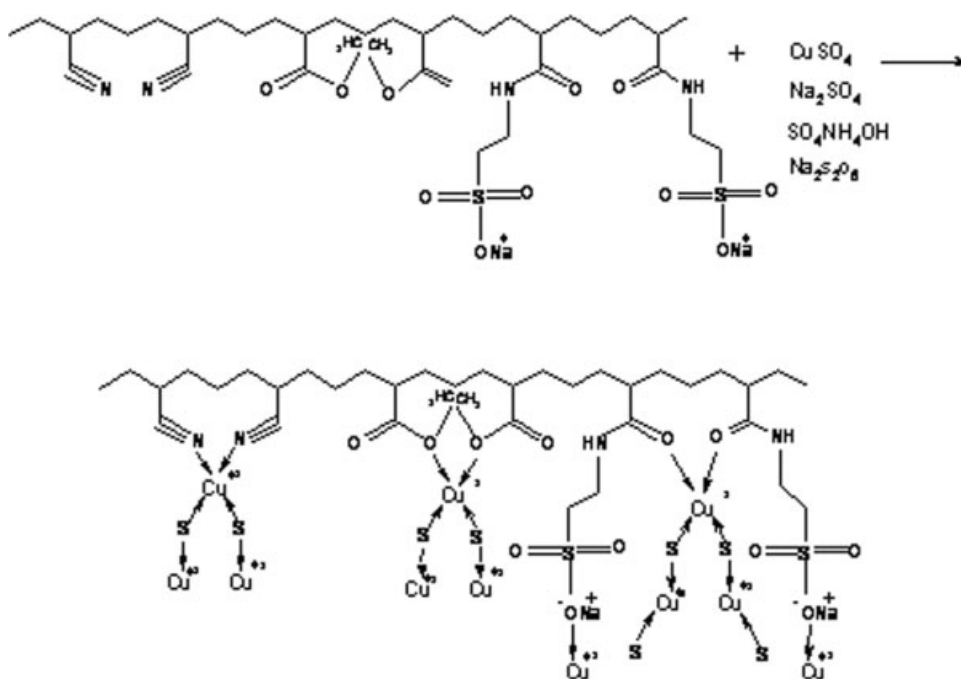

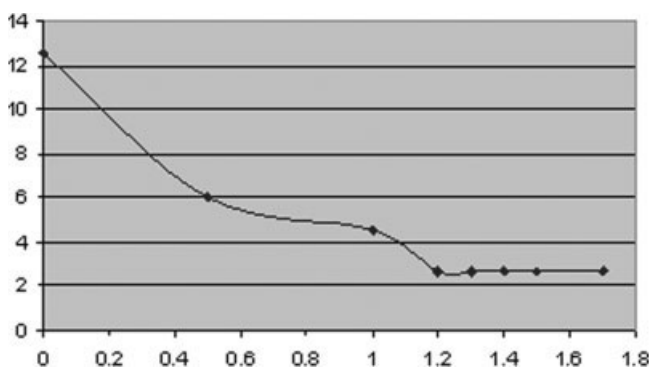**Figure 2** The mechanism of interaction between acrylic fibers and copper sulfide.

Figure 3 Surface electrical resistivity of coated-acrylic fibers versus various concentrations of copper (II) sulfate in treatment bath. X label: copper (II) sulfate (g/dm^3); Y label: log surface electrical resistivity (Ω/square).

Copper (II) sulfate concentration effect on the electrical resistivity of acrylic fibers

Previous works show that the electrical resistivity of textile fibers and films decreases as the concentration of copper (II) sulfate content of the coating solution increases.[17–22] The results obtained for the surface electrical resistivity of the coated-acrylic fibers for different concentrations of copper (II) sulfate are presented in Figure 3.

As is evident from Figure 3, the electrical resistivity of fibers decreases as the concentration of copper (II) sulfate increases in the coating bath. There is a fast decrease in electrical resistivity with increasing copper (II) sulfate concentration up to 1.2 g/dm^3. However, there is no significant effect on the electrical resistivity above this concentration. This can be explained by the fact that in the low copper (II) sulfate concentration of the coating bath, less copper (II) ions will be available to react with the active sites of the pendant ligands. As the copper (II) ions concentration increases in the coating bath, more copper sulfide can be formed on the surface of the acrylic fibers, and the electrical resistivity will decrease. As the con-
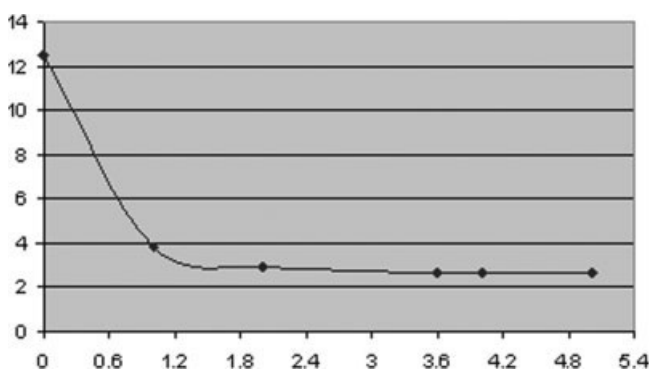
centration of the copper (II) sulfate is increased in the treatment bath, a more uniform continuous layer is formed, and the concentration effect is maintained to the final stage of the continuous layer formation (concentration 1.2 g/dm^3). No concentration effect is observed beyond this value. Statistical analysis shows that for concentrations between 1.2 and 1.7 g/dm^3, the concentration has not any significant influence on the electrical resistivity. It can be concluded that, for the concentration range used in the experiments carried out in this work, the concentration of 1.2 g/dm^3 for copper (II) sulfate is the optimum to be selected.

Sodium thiosulfate concentration effect on the surface electrical resistivity of acrylic fibers

The results obtained for surface resistivity of the coated acrylic fibers for different concentrations of sodium thiosulfate are presented in Figure 4.

Sodium thiosulfate was chosen to provide sulfur atoms or sulfur ions for reacting with the copper ions to produce copper sulfide on the fibers. The results presented in Figure 5 show that the absence of sodium thiosulfate in the treatment bath will prevent the development of electrical conductivity in the fibers. This result is in accordance with the published reports[22] show that using copper (II) sulfate alone in the treatment solution has no effect on improving the conductivity of the fibers. Sodium thiosulfate is a source of sulfur for sulfidation of copper ions attached to the fibers. Its concentration has a significant influence on the electrical resistivity of the fibers, which is effective up to 3.6 g/dm^3. The statistical analysis of the experimental data confirms the results shown in Figure 4.

Reducing agent effect on the surface resistivity of the acrylic fibers

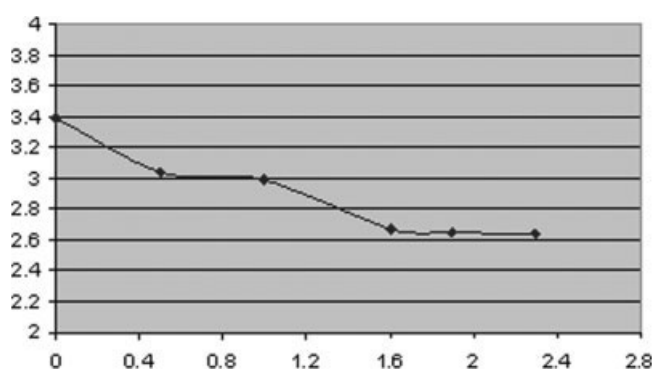Hydroxylamine sulfate was used as a reducing agent and the effect of its concentration on the surface resis-

Figure 4 Surface electrical resistivity of coated-acrylic fibers versus various concentrations of sodium thiosulfate in treatment bath. X label: sodium thiosulfate (g/dm^3); Y label: log surface electrical resistivity (Ω/square).

Figure 5 Surface electrical resistivity of coated-acrylic fibers versus various concentrations of hydroxylamine sulfate in treatment bath. X label: hydroxylamine sulfate (g/dm^3); Y label: log surface electrical resistivity (Ω/square).
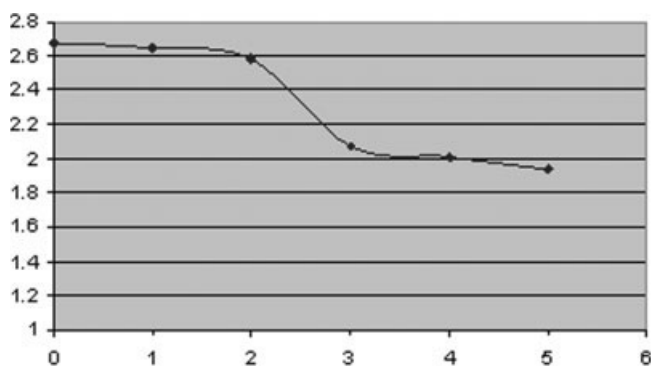
Figure 6 Surface electrical resistivity of coated-acrylic fibers versus various concentrations of sodium dithionite in treatment bath. X label: sodium dithionite (g/dm^3); Y label: log surface electrical resistivity (Ω/square).

tivity of the coated acrylic fibers is presented in Figure 5.

As the concentration of the hydroxylamine sulfate is increased in the treatment bath, the surface resistivity of coated fibers is decreased. The effective concentration of hydroxylamine sulfate in the treatment bath appears to be 1.6 g/dm^3. Hydroxylamine sulfate is a reducing agent for the reduction of copper (II) ions attached to the fibers to copper (I). Considering the electronic configuration of copper ions as [Ar] $3d^{10}$ and [Ar] $3d^9$ for copper (I) and copper (II) respectively, the difference between the electronegativity of Cu^{+2} and S^{-2} ions is more than that of Cu^{+1} and S^{-2} ions. Consequently, the Cu^{+2} orbitals overlap more effectively with S^{-2} than Cu^{+1} ions. Therefore, the energy gap for Cu_2S seems to be smaller than the gap for Cu_2S_2 as the data obtained from literature shows that band gap of Cu_2S_2 is equal to 3.1 eV and band gap of Cu_2S is equal to 1.2 eV.[27]

It can be claimed that as the concentrations of the sulfur ions and/or atoms and the reducing agent are increased in the treatment bath simultaneously, more reduction and sulfidation of copper (II) ions attached to the fibers are obtained and more Cu_2S is formed in the coating layer.

As an alternative reducing agent, sodium dithionite (which contains sulfur ions and/or atoms) was used in the treatment bath and the effect of its concentration on the surface resistivity of the coated fibers is presented in Figure 6.

As the concentration of the sodium dithionite increases, the electrical resistivity of the fibers is decreased significantly up to 3 g/dm^3, and above this concentration, no noticeable changes are observed. Statistical analysis confirms the results shown in Figures 5 and 6.
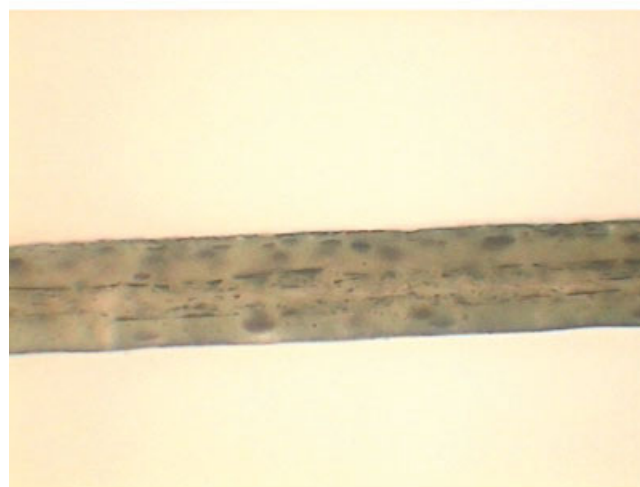
Microscopical observations

Images of cross section of uncoated and coated-acrylic fibers with copper sulfide are shown in Figures 7(a,b)
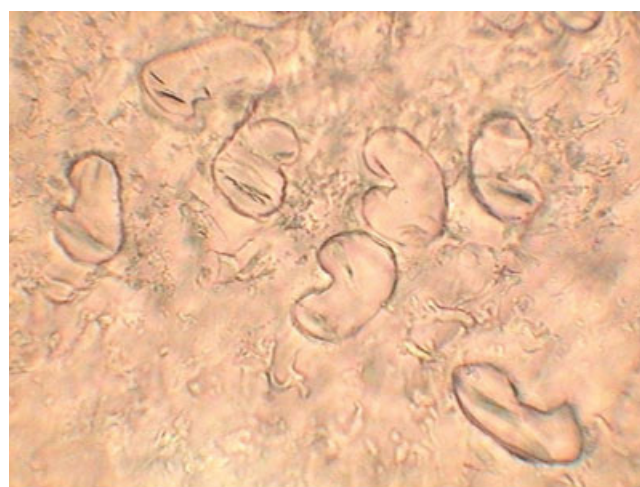
(a)
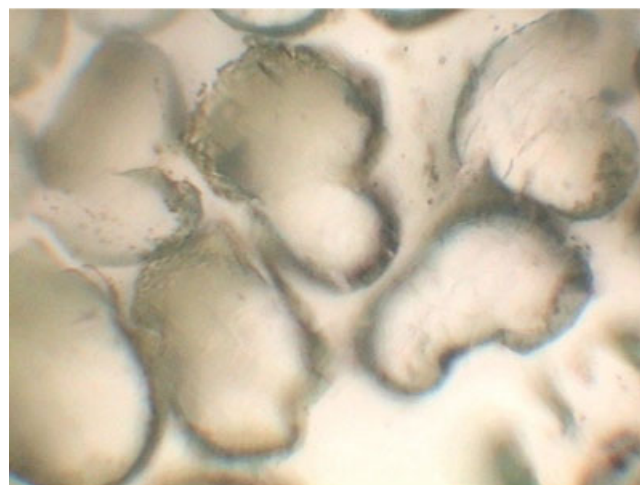
(b)

(c)

Figure 7 Optical microscope images of acrylic fibers (a) cross section of uncoated fibers, (b) cross section of coated-acrylic fibers, and (c) longitudinal surface of coated fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
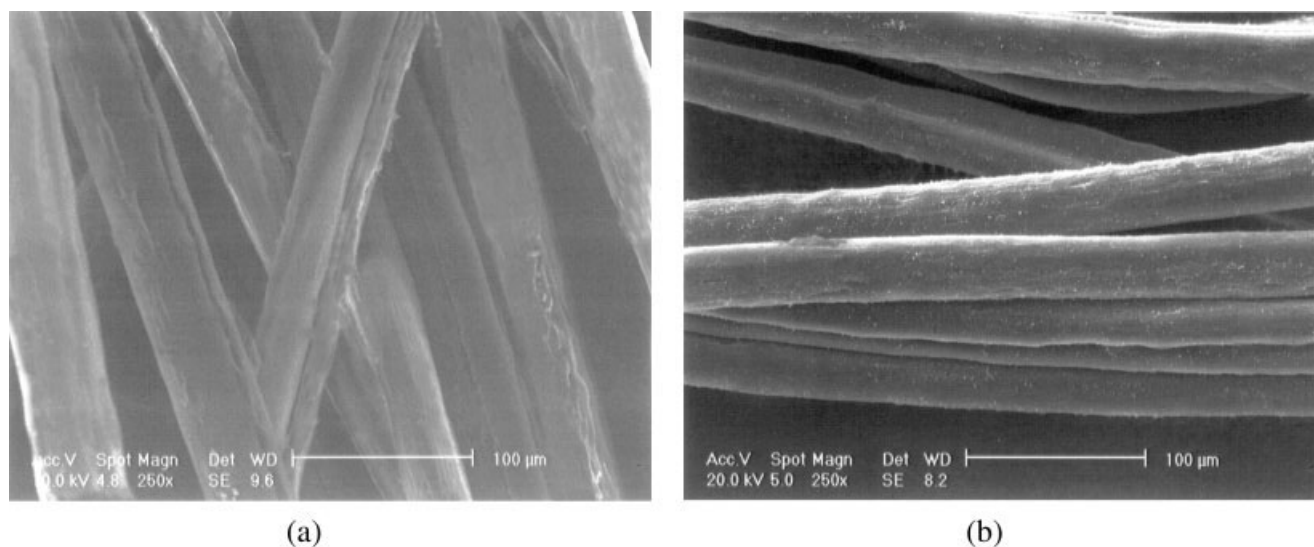
Figure 8 Magnification SEM micrographs of acrylic fibers (a) before coating and (b) after copper sulfide coating.

respectively. Figure 7(c) shows the longitudinal surface of the coated-acrylic fibers. These micrographs were taken by optical microscope with 400 magnitudes.

The micrographs obtained show that the formed coating layer is not limited to the surfaces of the fibers but has penetrated inside the fibers as well. For further study of the coating layer, SEM was used. Figures 8(a,b) show that the low magnification SEM micrographs of acrylic fibers without and with the copper sulfide coating, respectively.

Fibers used had a linear density of 16.7 dTex and several centimeters in length. As is evident in Figure 8(b), the copper sulfide coating is nearly uniform. Figures 9(a,b) show high magnified SEM micrographs of

the individual fibers. Figure 9(a) shows the individual uncoated acrylic fiber. Figure 9(b) shows the fiber after the copper sulfide deposition.

Figure 9 shows that the coating is relatively uniform with the presence of a number of nucleating copper sulfide centers, which are formed during the deposition process.

A cross-sectional micrograph of coated-acrylic fiber with copper sulfide was prepared to study the depth of copper sulfide penetration into the coated fiber (Fig. 10).

An elemental analysis was carried out on the cross section of the fiber by 2-μm intervals. Copper sulfide coating up to the depth of 4 μm through the fibers was observed.
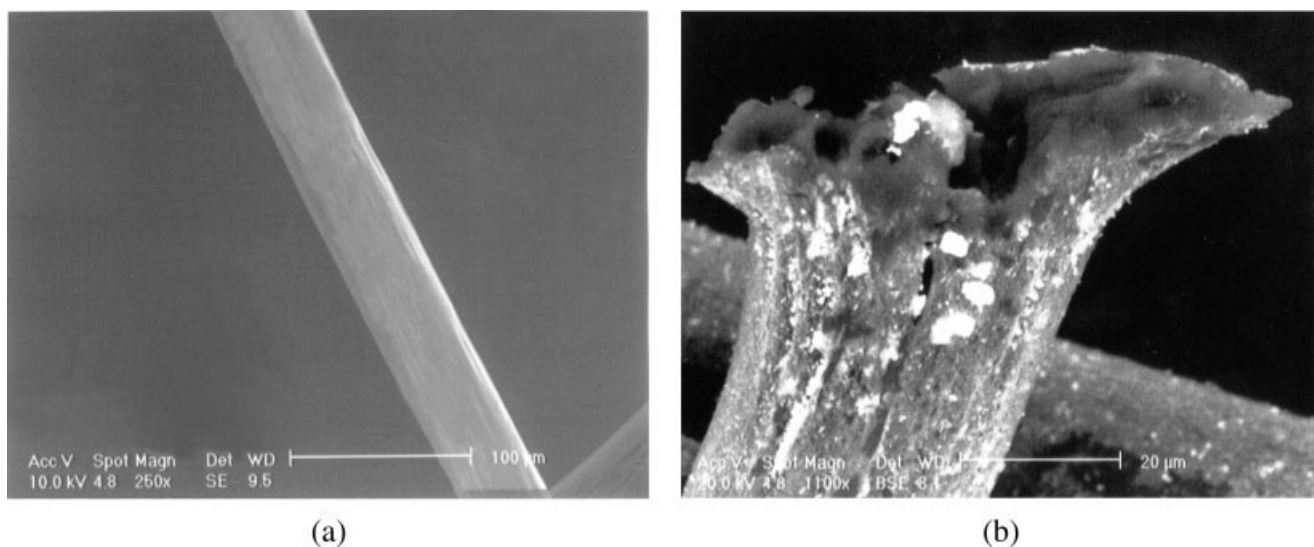

Figure 9 Magnification SEM micrographs of individual acrylic fiber (a) uncoated fiber and (b) after copper sulfide coating.
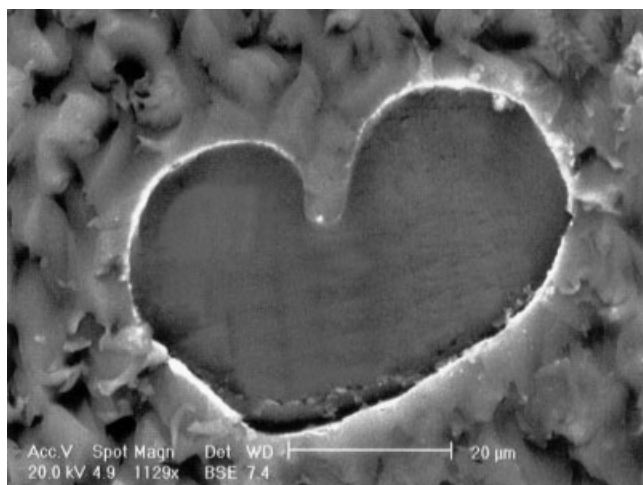
Figure 10 A cross section micrograph of coated-acrylic fiber.

Atomic absorption spectroscopy observations

To determine the amount of copper in the coated fibers, atomic absorption spectroscopy (AAS) measurement was carried out. By using Bear-Lambert law shown in eq. (1), the eq. (2) can be derived:

$$A = \varepsilon bc = kc \qquad (1)$$

$$C_x = C_s \left[\frac{A_x V_s}{(A_{x+s} - A_x)V_x} \right] \qquad (2)$$

The parameters in these equations have their general meanings. According to eq. (2) and the results discussion under Characterization of the fibers Section, the amount of copper in the coated fibers can be calculated as follows:

$$C_x = 200 \left[\frac{(0.052)(1\,\text{mL})}{5\,\text{mL}(0.141 - 0.052)} \right] = 23.371\,\text{ppm}$$

As the initial volume of the solution for dissolving the coated fibers was 25 cm³, the amount of copper for this volume is calculated as follows:

$$23.375\,\mu g/mL \times 25\,mL = 584.27\,\mu g$$

From the above calculation, it can be concluded that 1 g of coated-acrylic fibers contains 1770.51 μg of copper.

CONCLUSIONS

It can be concluded that acrylic fibers can be made conductive by coating with copper sulfide in a treatment bath with formulation of 1.2 g/dm³ copper (II) sulfate, 3.6 g/dm³ sodium thiosulfate, 1.6 g/dm³ hydroxylamine sulfate, and 3.0 g/dm³ sodium dithionite at 85°C temperature for 90 min.

The fibers obtained have an average surface resistivity of 10^2 Ω/square in comparison with the untreated acrylic fibers, which have the resistivity of 10^{12} Ω/square. It is clearly shown that the main parameters for making conductive acrylic fibers are the concentrations of copper (II) sulfate, hydroxylamine sulfate, sodium thiosulfate, sodium dithionite, and temperature of treatment bath. The average thickness of the continuous, copper sulfide coating is about 4 μm.

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