

Surface Modification of Nylon 6 Multifilament Yarns with 3-Aminopropyltriethoxysilane and Study of its Special Properties

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Abstract

The aim of the research was the solvent-based impregnation of poly(lactic acid) (PLA) with The present work developed a new and simple method for producing engineered nylon yarns by two-step coating. The nylon yarns were first immersed in a solution containing a silane coupling agent (3-Aminopropyltriethoxysilane) to improve the adhesion properties. Then the modified samples were heat-treated in a solution containing cupric nitrate, hydroxylamine sulfate, and sodium pyrosulfite. Microstructural imaging of the coated surfaces shows a homogeneously formed coating layer without any microscopic cracks or discontinuity in the sample surface. Results showed that this two-step coating can produce nylon yarns with good electrical conductivity and anti-microbial properties. The coated samples displayed very good light fastness and washing fastness to multiple washes in terms of electrical conductivity changes and anti-microbial activity.

Key words: nylon yarns, 3-aminopropyltriethoxysilane, electroconductive coating, anti-microbial activity, mechanical properties.

Introduction

Nylons are a group of aliphatic polyamides that consist of polyethylene segments $(CH_2)_n$ separated by peptide units (NH-CO). Nylon polymers are some of the most commercially important thermoplastic materials, mostly used as yarns and films of different levels of thickness and crystallinity as well as different degrees of orientation in textiles and numerous other technical applications [1-5]. These fibres have excellent properties, such as stiffness, toughness, lubricity, fatigue, resistance to abrasion, and a degree of crystallinity, which can be controlled over a wide range. Nylon 6 and nylon 6,6 are two of the most common nylon materials in the market, especially for carpets and garments [2].

Nylon is one of the leading synthetic yarns due to its excellent properties, such as high strength, good elasticity and excellent dye-ability. However, its inherent poor absorbency, accompanied by the high build-up of electrostatic charges, limits its further development [6]. The accumulation of static electricity on synthetic yarns leads to the attraction of electric shocks, dust, intertwisting, and damage to electronic machines. These effects are, of course, a severe hindrance to the use of polymeric yarns in many applications, especially for electrically conducting, electronic, and magnetic materials. Furthermore, conductive polymeric yarns are intended for use in creating conductive yarns and realising connections in smart clothing or producing

conductive fabrics, which can be used as electromagnetic shields.

For polymeric materials to become electrically conductive, the energy gap between the valance and conduction bands must be significantly lowered or new bands formed in the gap into which electrons can be easily promoted or charge-donated [7]. Several methods have been studied by a number of researchers to produce conductive polymer textiles [8-13]. One example is conductive yarns produced from electrical conductive polymers [14 and 15]. Other approaches to produce conductive polymeric textiles are via coating some synthetic yarns with conductive polymers [16-18], the use of carbon nanotubes and carbon black particles in textiles [11-12], the use of antistatic spin finishes, and the application of nanocomposites containing conductive particles in yarns [19]. Copper sulfide (Cu_xS , $1 \leq x \leq 2$) is an important material with scientifically relevant optical and electrical properties, and has several interesting applications in conductive fibre processing [20, 21]. The coating of polymeric substrates with copper sulfide layers is a novel and challenging approach to obtain electrical conductive materials.

It is well known that good adhesion is necessary at the interface between the coating and polymeric substrate. Nylon yarns have a weak affinity and adhesion to copper sulfide coatings due to the lack of polarity of the polymer. The term "polarity of polymer" is defined as the low interfacial tension and poor wetting be-

haviour of the nylon yarns on the metal. Several methods have been studied to improve the polarity of the polymer surface. For instance, chemical changes at the polymer interface, metal surface modification, introduction of polar groups into the polymer, and application of adhesion promoters [22].

Adhesion promoters may improve adhesion at the polymer/adhesive interface, which is employed as an alternative to the application of a surface primer [23]. An important class of adhesion promoters and primers are silane coupling agents. The utility of these agents to enhance adhesion can be attributed to the fact that they can interact with both the adhesive material and the polymer, typically through diffusion, covalent bonding, or other interactions, such as hydrogen bonding [23, 24]. 3-Aminopropyltriethoxysilane (APTES) is a silane coupling agent which can further activate the surface of a polymer using various cross-linkers [24, 25]. A number of techniques have been used to characterise the structures of silane coupling agents on glass and polymeric substrates. Furthermore, several procedures have also been developed employing these silanes to promote the covalent linkage of organic complexes to a modified surface [23, 24]. However, none of these studies reported about the effect of silica multilayers for applications as an electrical conductive coating of nylon yarns.

A number of studies have been reported on the use of copper sulfide to generate

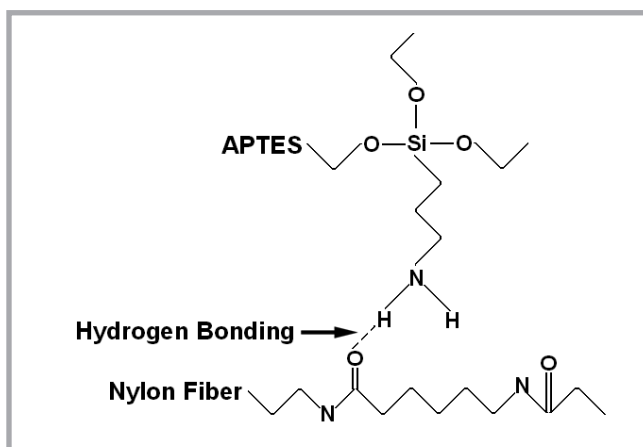


Figure 1. Physisorption of APTES molecules to the nylon surface.

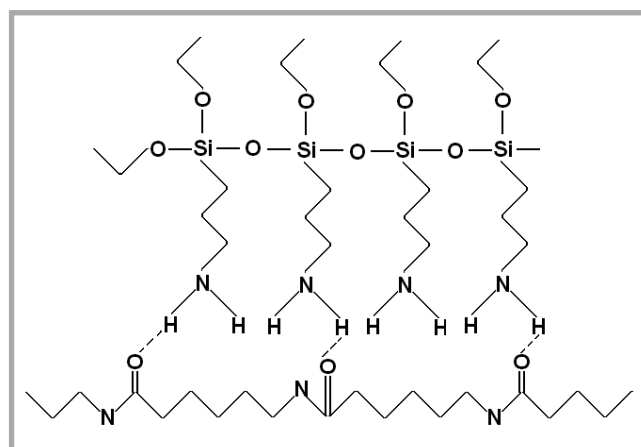


Figure 2. Siloxane bond formation to the nearest neighbors.

electrical conductive yarns; however, up until now, no study has been conducted on the changes induced by copper sulfide layers in nylon yarns. In this scenario, answering the question whether electrical conductivity and anti-microbial properties occur in APTES modified nylon yarns coated with copper sulfide enables us to further improve our knowledge about the preparation of new polymeric materials with improved properties. The electrical conductivity and transparency of the modified nylon yarns of the present study allow their use as fibre reinforcement or fillers in organic resin matrix composites, interior decorative sheets, carpets, clothing, and gloves or in combination with other yarns because of their excellent electrostatic resistance and affinity for dyes. Excellent control over the electrical properties of knitted or woven goods can be obtained by combining the electroconductive yarns of the present work with other nonconductive synthetic yarns. Additionally, sulfides have very good thermal stability, and therefore the power of coated yarns may be incorporated in a melt for the production of moulded articles used as electromagnetic shields. It can be claimed that the coated samples of this research have found several promising applications in many fields.

In the present study, nylon 6 yarns were considered as the substrate, and their surface adhesion properties were improved by a silane coupling agent (APTES). Then the modified nylon yarns were heat-treated in a solution containing cupric ions, a reducing agent, and a sulfur-containing compound to prepare antistatic and antimicrobial yarns. The reaction route, surface morphology, electrical conductivity, anti-microbial performan-

ce, mechanical properties, and wash and light fastnesses were also investigated.

Materials and methods

Fully drawn oriented polyamide 6 yarns were used throughout this paper, namely FDY (20 denier/10 filaments). These yarns were obtained from the Alyaf Company, Tehran, Iran. All other chemicals, including cupric nitrate ($\text{Cu}(\text{NO}_3)_2$), hydroxylamine sulfate ($\text{SO}_4\text{NH}_4\text{OH}$), sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$), acetic acid (CH_3COOH), sodium acetate (CH_3COONa) and sodium hydroxide (NaOH) were analytic grade and used without further purification. Deionised water was also utilised to prepare all aqueous solutions.

Nylon yarns were washed in a bath containing 1 g/l of a nonionic surfactant at 60 °C for 20 minutes, and then rinsed with deionised water in order to remove any impurities and improve the adhesion properties. Prior to metal deposition, the nylon yarns were modified with the 3-aminopropyltriethoxysilane (APTES) reagent. A reaction with APTES was performed using 1% v/v anhydrous toluene solution in a nitrogen atmosphere. The reaction was heated to 75 °C in an oil bath and kept for 72 h. The modified nylon yarns were washed by immersion in copious amounts of flowing toluene and then dried at reduced pressure. The one step dipping method was used to produce conductive modified nylon yarns. For this purpose, the modified yarns were heat-treated in a solution containing 35 wt. % of cupric nitrate, 15 wt. % of hydroxylamine sulfate, and 18 wt. % of sodium pyrosulfite, with pH = 4-5, at 80 °C. The yarn to bath ratio was 1:15 and the process was kept at this temperature for

2 h with constant stirring with a magnetic stirrer placed in the bath. Finally, the coated yarns were washed with deionised water and dried at room temperature.

Surface electrical conductivity measurements were carried out by the two-point probe technique according to the standard method (ASTM D 4496-87). All of the electrical conductivity measurements were performed at 20 °C and 65% R.H. The electrical conductivity was determined as the average values of 20 tests for each sample. A Philips scanning electron microscope (XL-30, The Netherlands) was used to investigate the surface morphology of samples. Anti-microbial properties of the coated samples were quantitatively evaluated against two types of bacteria according to the AATCC 100-2004 test method. The two types of bacteria used were *Staphylococcus aureus*, a gram-positive bacterium (American Type Culture Collection No. 6538), and *Escherichia coli*, a gram-negative bacterium (ATCC 25922). The coated samples were subjected to a repeated washing test according to AATCC 61 (2A)-1996. The stability of the copper sulfide coated samples was studied by means of the surface electrical conductivity and anti-microbial measurements after 0 and 30 washings with a nonionic detergent [26]. A light fastness test of the coated samples was carried out according to ISO 105 BO2 (1989) [27].

The mechanical properties were tested by means of a FAFEGRAPH instrument according to the standard test methods of DIN 51221, 53816 and ISO 5079. The measurements were performed under standard conditions (24 °C, 52%). The specimen length and crosshead speed were 20 mm and 20 mm/min, respectively.

vely. The elongation at break and tensile strength were determined as the average values of 30 tests for each sample.

■ Results and discussions

Chemical interaction of nylon yarns with APTES and coated layer

APTES is an amino-functional trialkoxy silane (a silane coupling agent) which has been commonly used to provide surface protection and improve adhesion promoters. APTES is envisioned to be comprised of four reactive functional groups: an amino end group (-NH₂), and three ethoxy head groups (-OC₂H₅).

On the basis of previous studies, a new model for the reaction route is proposed in order to investigate the effects of various factors on the coating step. When nylon yarns come in contact with APTES, the hydrogen bonding between the APTES and nylon may influence the conformation of the APTES molecules at the interface, and a three step formulation of a thin continuous multilayer on the nylon surface occurs [23, 24, 31].

(1) The first step in this process is the initial adsorption (physisorption) of APTES to the nylon surface. In this step, the amino end groups of APTES are oriented toward the nylon surface, while the ethoxy head groups are directed toward the silane bulk. As a result, hydrogen bonding is formed between the nylon surface carbonyl groups and the amino protons of the APTES molecules (**Figure 1**). The formation of hydrogen bonding between the nylon surface and APTES reagent can enhance the physical adhesion [23].

(2) The second step is subsequent lateral bond formation through the ethoxy head groups with neighbors H-bonded to the surface of the nylon yarns (**Figure 2**).

(3) The final step in the surface modification of nylon yarns is multilayer formation through lateral cross-linking (**Figure 3**). The second and third steps can be performed concurrently.

The modified nylon yarns have a strong affinity for cupric ions since only a small amount of the silane coupling agent can bind or adsorb a sufficient amount of cupric ions. In general, the mechanism of interaction between the polymeric material and the copper sulfide layer is believed to involve three sections: firstly,

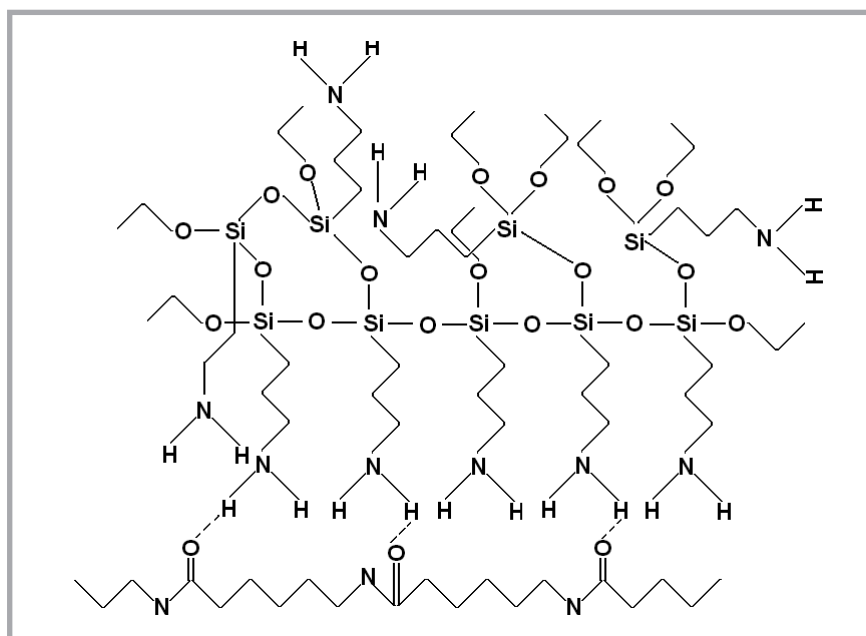


Figure 3. Multilayer formation through lateral cross-linking.

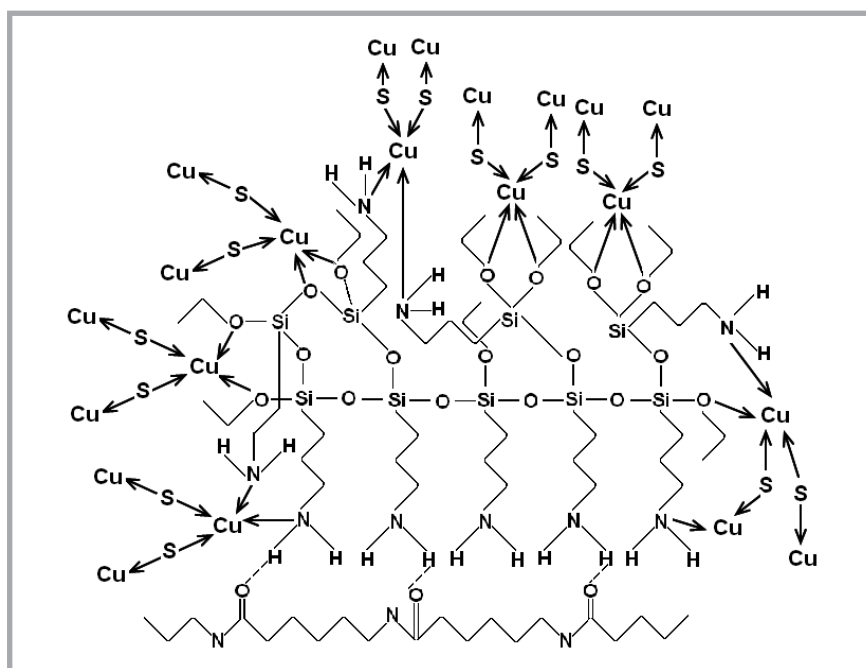


Figure 4. Schematic diagram of covalent interaction between modified nylon yarns and coating layer.

the absorption of aqueous cupric ions into the samples; secondly, the formation of a covalent bond between the cuprous ions and pendant groups on the samples, and finally, the sulfidation of cuprous ions to produce an insoluble conducting copper sulfide phase as a continuous coating on the surfaces of the individual samples [32]. It is suggested that a continuous coating could only be formed if there is a strong adhesive bond between the polymeric matrix and the conductive phase [33]. In this paper, the modified

nylon yarns were treated in a bath containing cupric ions (cupric nitrate), a reducing agent (hydroxylamine sulfate) and a sulfur containing compound (sodium pyrosulfate). Considering the electron orientation of cupric ions in the form of [Ar] 3d⁹, the nitrogen atoms in amino groups and also oxygen atoms in ethoxy groups can form coordinate bonds with the cupric ions. As a result, two reactive functional groups of the APTES reagent are able to form a strong covalent bond with cupric ions (**Figure 4**).

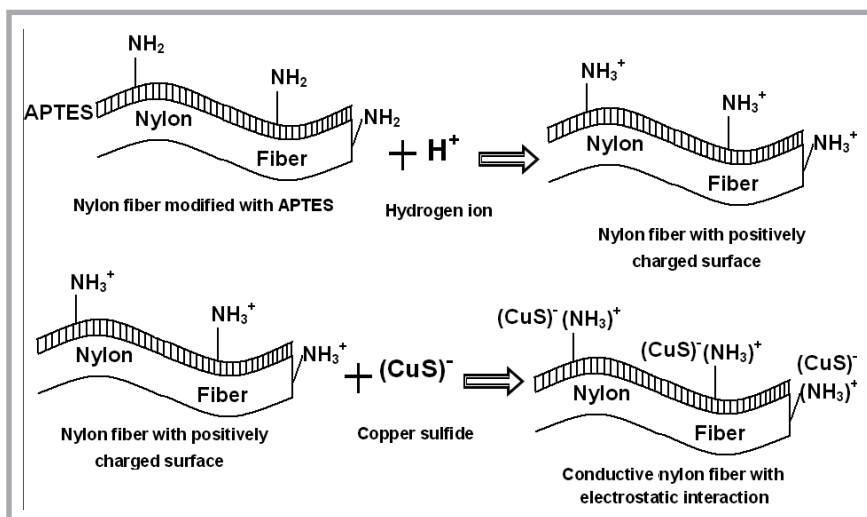


Figure 5. Schematic diagram for the electrostatic interaction between modified nylon yarns and the coating layer.

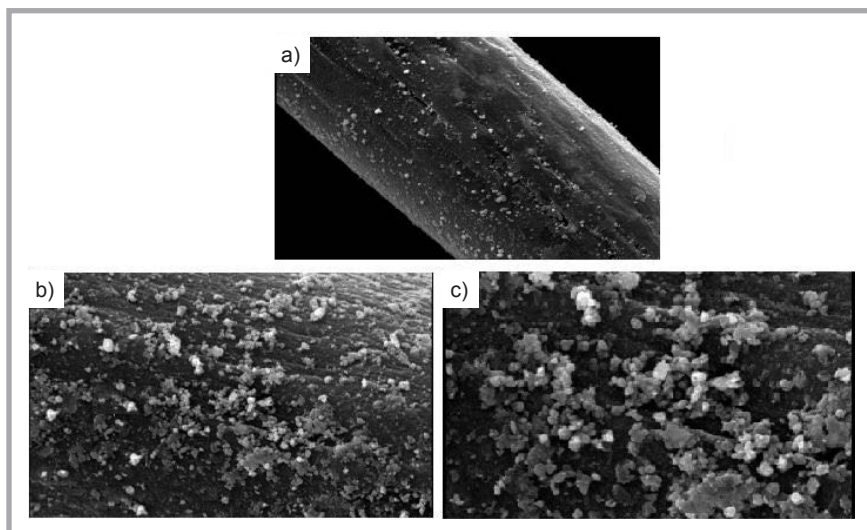


Figure 6. SEM photograph of copper coated nylon yarns at magnifications of a) 1250X, b) 2500X, and c) 5000X.

In addition to the dominant covalent bonds, electrostatic interaction plays an important role in the bonding between the cupric ions and nylon yarns. As mentioned earlier, coating was carried out in acidic conditions of pH = 4-5. The amino end groups in APTES molecules and the terminal amino groups of nylon yarns undergo partial protonation under the acidic conditions, as shown in **Figure 5**. Therefore, a positively charged surface is formed, and copper sulfide particles which have negative charges [20] are absorbed on the modified surface through electrostatic forces.

Scanning electron microscopy (SEM)

Microstructural imaging of the electrical conductive surfaces was conducted using a scanning electron microscope at magnifications of 1250X, 2500X, and 5000X (**Figure 6**).

The micrographs obtained show a homogeneously formed coating layer without any microscopic cracks or discontinuity in the fibre surface. It is also clear from **Figure 6** that the electrical conducting coating was relatively smooth and uniform along the length of the samples even at high magnification. This may be attributed to the presence of a strong bond between the modified nylon yarns and the coating layer. As mentioned earlier, it is believed that a continuous coating layer could only be formed in the presence of a strong bond between the polymeric matrix and the coating layer.

Anti-microbial efficiency

Inherent anti-microbial functions of textiles possessing are expected to be used in several applications, such as medical devices, apparel, protective clothing, mili-

tary, veterinary, automation, construction, decoration, housing, healthcare (including disposable) appliances, and a large number of other industries [34-36]. The major classes of anti-microbial agents for textiles include metal compounds such as silver, nickel, copper salts, phenols, quaternary ammonium salts and organo-silicons. Therefore, it seemed likely that modified nylon yarns coated with copper sulfide may have suitable anti-microbial properties and are an ideal substrate for future scientific investigations.

In this scenario, answering the question whether anti-microbial properties occur in modified nylon yarns coated with copper sulfide enables us to further improve our knowledge about the preparation of new polyamide materials with improved properties. In an attempt to gain a deeper understanding of this topic, we investigated the influence of copper sulfide on the anti-microbial properties of coated modified yarns. For this purpose, anti-microbial properties of the copper sulfide coated samples were evaluated against two types of bacteria, known as gram-positive (*Staphylococcus aureus*, ATCC 6538) and gram-negative (*Escherichia coli*, ATCC 25922). The percentage reduction in the number of the two bacteria after 0 and 3 h incubation on the surface of the control samples, samples modified with APTES, and copper sulfide coated samples is shown in **Table 1**.

As seen in **Table 1**, the control samples and samples modified with APTES showed no anti-microbial activity, whereas the yarns coated after APTES pretreatment showed an efficient anti-microbial effect against *E. coli* and *S. aureus* bacteria. This may be due to the anti-microbial property of the copper coated layer. The anti-microbial activity of copper salts has been attributed to the binding of copper particles to the bacteria cell wall and further penetration within the cell, which firstly destroys the bacteria cell wall until final degradation of the cytoplasm takes place [26]. As a result, the bacteria cell is easily killed, and a situation which is characterised by increasing values of bacterial reduction occurs. The percentage of bacterial reduction can be estimated from the following equation:

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

Where A and B are the number of bacterial colonies from initial and modified nylon samples, respectively. Another

important point to note in **Table 1** is that at a zero contact time, the copper coated modified yarns showed an ability to kill bacteria.

Electrical resistivity and fastness properties

The average conductivity of the coated modified nylon yarns measured was about 94.57×10^{-3} (S/m), indicating that these samples have good antistatic performance. Since textiles are subjected to frequent laundering, the durability of electrical conductivity and anti-microbial activity to washing may have a strong effect on the final application and properties of coated nylon yarns. In order to investigate the durability of electrical conductivity and anti-microbial activity to washing, the coated samples were washed in a Launder-Ometer according to the AATCC 61-1996 (No. 2A) test method. One cycle of washing in a Launder-Ometer is considered equivalent to five home washes at 38 °C. The surface electrical conductivity of the coated modified samples was investigated before and after 30 washes (section 2), the results of which are shown in **Table 2**.

The results show that the coating of modified nylon yarns with copper sulfide exhibited good wash fastness properties to multiple washes in term of shade change. No staining towards the adjacent multi-fibre strip was observed. Additionally, different washing cycles show no significant influence on the electrical conductivity properties of the samples, and it was ascertained that its washability remained good (**Table 2**). This can be attributed to the insolubility of the conducting layer, and also indicates the existence of strong bonds between the copper sulfide molecules and the surface of the modified nylon yarns. This result is consistent with those observed in the microscopic micrographs.

The anti-microbial behaviour of the coated modified samples against *S. aureus* and *E. coli* bacteria was investigated after 3 h exposure under different conditions, including 0 and 30 washes. The results are presented in **Table 2**.

It is evident that the coating of modified nylon yarns with copper sulfide shows excellent durability for anti-microbial performance against washing. The different washing cycles have no considerable effect on the anti-microbial activity of the samples.

Table 1. Bacterial reduction in the number of the two bacteria after 0 and 3 h incubation on the surface of the control, modified, and coated modified nylon yarns.

Samples	Anti-microbial efficiency, %			
	<i>Escherichia coli</i>		<i>Staphylococcus aureus</i>	
	0 h	3 h	0 h	3 h
Control	0	0	0	0
Modified with APTES	0	0	0	0
Coated modified yarns	97	100	94	100

Table 2. Anti-microbial efficiency and surface electrical conductivity of coated modified nylon yarns before and after radiation and multiple washes.

		Wash fastness		Light fastness
		0	30	
Anti-microbial efficiency, %	<i>E. coli</i>	100	95.63	100
	<i>S. aureus</i>	100	97.81	100
Electrical conductivity ($\times 10^{-3}$), S/m		94.57	63.41	94.57

Table 3. Mechanical properties of various nylon yarns.

Samples	Mechanical properties			
	Tensile strength, g/den	Standard deviation	Elongation at break, %	Standard deviation
Control	5.7	0.2	50.2	3.1
Coated modified yarns	5.3	0.1	44.4	1.6

The surface electrical conductivity and anti-microbial activity of coated nylon yarns before and after the samples were radiated by an xenon lamp (Xenotest 150S, section 2) were measured in order to investigate the fastness of the coating treatments against light. The results are shown in **Table 2**.

The results indicate that the coated samples have excellent light fastness. As is evident, there is no difference between the electrical conductivity and anti-microbial behaviour of the samples before and after the radiation. It is also known that the coating layer-fibre bond serves as a bridge for transferring excitation energy between the coating layer and fibre. As mentioned earlier, there is a strong bond between the modified nylon yarns and the coated layer, and therefore the transfer of excitation energy from the coating layer to the fibre chain is more pronounced. Consequently, the light fastness properties are not compromised and remain the same.

Mechanical properties

To find out how copper sulfide coating affects the physical properties of modified nylon yarns, the tensile strength and elongation at break, which are both important characteristics for textile material, were measured. **Table 3** presents mechanical properties of the initial and modified nylon yarns coated with copper sulfide.

As is evident from **Table 3**, the tensile strength of the coated nylon yarns slightly decreased. It appears that thermal degradation and mechanical actions may have slightly damaged the yarns. Also, it is seen from **Table 3** that coating nylon yarns leads to a reduction in breaking elongation, which can be explained by two events. First, as a result of the penetration of copper sulfide into the yarns, lateral forces existing between the polymeric chains are increased. This leads to a decrease in the flexibility of the chains. Second, copper sulfide particles are rigid and have a higher modulus than the polymeric chains; therefore, deformation of its particles is generally much less than that of the polymer chains. As a result, coated modified yarns gain increased stiffness, whereby a loss of flexibility of the polymeric chain at the particle surface causes the breaking elongation to decrease.

Conclusions

In this research, APTES was used to improve the adhesion promoters of nylon 6 yarns, and then they were successfully coated with a copper sulfide layer. The results of the experiments in this study revealed that metal coating of the modified nylon yarns led to the formation of a continuous anti-microbial and antistatic layer. A new model for the reaction route was proposed to gain an understanding of the effects of various factors on the

coating step. SEM imaging showed the formation of a homogeneous coating layer without any microscopic cracks or discontinuity on the fibre surface. Repeated washing had no significant effect on the electrical conductivity of the coated modified samples, demonstrating excellent durability of the samples against washing. Additionally, the coated modified nylon yarns offer excellent fastness again in light due to the strong bonds between the fibre matrix and the coating layer. Moreover, the coating of modified nylon yarns showed a high performance in the quantitative anti-microbial test against *E. coli* and *S. aureus*. High stability of the coated samples even after 30 washes confirmed the presence of a strong covalent bond between the modified nylon yarns and the coating layer.



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