

Production of Electroconductive, Superhydrophobic and Flame-Retardant Cotton Fibers via Pad-Dry-Cure Process using Silicone Rubber and Ammonium Polyphosphate

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Research Article

Keywords: Cotton-nickel blend, Ammonium polyphosphate, Silicon rubber, Flame-retardant, Electroconductive, Superhydrophobic

Posted Date: March 11th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-270637/v1>

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Abstract

Although pyrovatex has been widely utilized as commercial flame-retardant material, the discharge of poisonous formaldehyde is still a major concern. On the other side, fluorine-based materials have been successfully used to impart superhydrophobic textile surfaces, but they are highly expensive and extremely toxic. Based on these challenging concerns, we report a simple one-step method for the production of flame-retardant and water-repellent coating onto an electroconductive cotton-nickel (Cot-Ni) blend fabric. Firstly, the electroconductive cotton was prepared by weaving nickel strip twisted around cotton core yarns, which were then weaved with pure cotton yarns to introduce Cot-Ni blend fabric. Secondly a composite comprising ammonium polyphosphate (APP) and room-temperature vulcanized silicone rubber (RTV) was applied onto the electroconductive cotton fabrics via one-step pad-dry-cure technique. Results showed that the flame-retardant effect of cotton was enhanced due to the high binding of RTV with both APP and cotton fibers. Thus, different concentrations of APP were implemented in the composite to establish that only 100 g/L of APP with RTV presented an improved fire-retardancy. The surface of Cot-Ni fabric displayed different hierarchical morphologies relying on the concentration of APP. Moreover, RTV further enhanced the superhydrophobic nature of cotton surface. Importantly, the superhydrophobic activity was characterized by static water contact angle of the coated Cot-Ni blend. The CIE Lab colorimetric measurements of the coated Cot-Ni blend were also explored. The comfort characteristics of the coated Cot-Ni blend were assessed by measuring their air permeability and stiffness. Ultimately, these multifunctional cotton-nickel (Cot-Ni)/RTV-APP treated fabrics could be suitable for diverse applications, including firefighters' wear, car seat mats, and grain storage containers.

1. Introduction

Textile flammability has been a severe danger for human safety. Therefore, researchers have been incessantly looking for flame-retardant treatments with the ability to improve a fabric resistance to flame (Li et al. 2019; Wu et al. 2019). In the meantime, governments are upsetting due to the health and environmental risks generated from the application of hazardous flame retardants and superhydrophobic fluorinated agents (Villamil Watson and Schiraldi 2020; Yang et al. 2020). Textile industries have been a broad manufacturing sector with innovative applications being reported on a daily basis (El-Naggar et al. 2018; Hebeish et al. 2019; Sharaf and El-Naggar 2019). A technical textile product can be identified as a fibrous material created for non-aesthetic application, where its purpose is the major criterion to improve people safety, such as flame-retardant, electroconductive, superhydrophobic and antimicrobial textiles (Maity and Chatterjee 2018; Sharaf and El-Naggar 2018; Yang et al. 2018; Xu et al. 2019; El-Naggar et al. 2021). Electrically conductive textiles have been broadly utilized in a variety of applications, such as electromagnetic interference shielding, flexible electronics, electrostatic discharge clothes, heating panels, actuators and sensors. The most electroactive materials are metals, such as nickel, steel, silver, gold and copper. Composites of these metals can be applied directly by coating onto conventional textiles to generate electrically conductive technical textiles, which can be also produced by inserting metal yarns or

filaments woven within the fibrous matrix to establish a superior electroconductivity in comparison to the coated textile substrates (Chatterjee et al. 2017; Cohen David et al. 2017; Krishnanand et al. 2017).

Cotton is an extremely flammable material in the presence of heat and oxygen transforming its contents to gaseous volatile products, which may lead to severe damaging to the fabric-containing product, such as house, automobile, furniture and more considerably individual life. There are a variety of reasons that may lead to cotton flammability, such as cigarettes, cooking domestic devices, open flame appliances, electric spark, as well as wrong handling of flammable gases and liquids. Thus, flame-retardant treatment of cotton products has been highly valuable and can be accomplished by chemical methods to result in obstruction of the undesirable flaming course (Visakh et al. 2019; Lazar et al. 2020). There has been a diversity of renowned fire-retardant substances that have been applied on a diversity of substrates. Treatment of textile surface has been an efficient and appropriate method to impart flame-retardancy to flammable textiles. Most of flame-retardant materials are typically intensified at the fabric surface to reach the highest protective value (Tongue et al. 2019; Yue et al. 2019). Flame-retardant materials on a fabric surface should not alter their mechanical or comfort properties of the treated textiles. Additionally, an immobilization of a flame-retardant on a fabric surface can be integrated with additional functional contents to achieve multifunctional textiles, such as superhydrophobicity and antimicrobial activity (Al-Noaimi et al. 2014; Liu et al. 2019).

Both flammability and hydrophilicity significantly decrease the applications range of technical textiles, especially in packaging crafts and transportation (Revaiah et al. 2019). The development of superhydrophobic surfaces, induced with the lotus phenomenon, has been a significant research for the latest few years. With a slide angle less than 10° and a contact angle more than 150° , the water-repellent surfaces typically exhibit an astonishing waterproof ability, self-cleaning nature, and antifouling activity (Zahid et al. 2019; Dalawai et al. 2020; Pakdel et al. 2020). The low surface energy, as well as both nano/micro-hierarchical surface roughness can be monitored as excellent heuristic models to accomplish a superhydrophobic character, which is a key function to construct water-repellent clothing. However, the surface energy reducing agents are typically fluorinated substances, which are extremely poisonous and costly (Shao et al. 2020). There are a number of chemical and physical techniques that have been described recently for the assembly of superhydrophobic surfaces, such as self-assembled nanofibers, electrospun nanofibers, plasma or chemical etching, sol-gel technology, deposition of chemical vapor and lithography (Chen et al. 2017; Al-Enizi et al. 2018, 2019; Aljumaily et al. 2018; Kumar and Gogoi 2018; Nakajima et al. 2018; Yan et al. 2018; Lin et al. 2019; Torasso et al. 2019). However, these techniques usually necessitate multiple-step sophisticated procedures and instrumentations, as well as being expensive and time-consuming. The pad-dry-cure method has been utilized as an easy, inexpensive and non-contact method for textile coating under ambient conditions (Riaz et al. 2019).

The most suitable fire-retardant substances utilized for cellulose substrates depend on organophosphorus derived materials, which are able to generate a protective char layer to avoid further burning. Both of tetrakis(hydroxymethyl)phosphonium chloride ($(\text{HOCH}_2)_4\text{P}^+\text{Cl}^-$; THPC) and *N*-hydroxymethyl-3-dimethylphosphonopropionamide (Pyrovatex CP) have been known as the most

commercial organophosphorus derived flame-retardant for cotton [32]. Nonetheless, they are harmful to both environment and human health. For instance, a chamber of ammonia gas is essential for successful application of THPC onto cotton substrates. Additionally, Pyrovatex necessitates the presence of trimethylol melamine as a cross-linker to improve the durability and flame-retardant efficiency of the treated cotton. However, formaldehyde is utilized in the manufacture of trimethylol melamine; and consequently, the inclusion of trimethylol melamine into a Pyrovatex formula leads to discharging high levels of formaldehyde [33]. Unfortunately, there are severe toxic issues associated with formaldehyde, such as skin and eye irritation, harmful damages to respiratory system and carcinogenicity. Thus, formaldehyde-free substitutes, such as ammonium polyphosphate (APP), have been examined as an environmentally friendly flame-retardant material. However, it is also required to introduce a fire-retardant treatment characterized with high efficiency and durability at low cost (Abdelrahman and Khattab 2019; Paul 2019). Room temperature vulcanized (RTV) silicone has been a class of silicone rubber materials, which can be cured under ambient conditions in the presence of a catalytic agent, such as dibutyltin dilaurate. RTV is characterized with high resistance against ageing, acid/base conditions, temperature and chemicals, as well as high-quality mechanical properties and thermal stress, low shrinkage, high-quality hardness and low viscosity. RTV has been utilized in aviation, printing technology and electronics. It has been also applied in the casting of various materials, such as polyester and epoxy resins, wax, gypsum, alloys and urethane (Hamadi et al. 2020; Wang et al. 2021). Recently, extremely hard research has been taken to establish an eco-friendly process for the development of flame-retardant cotton fibers.

Herein, we develop an inexpensive and formaldehyde-free procedure for the development of superhydrophobic, electroconductive and flame-retardant cotton fibers using ammonium polyphosphate in the presence of room temperature vulcanized silicone rubber (RTV) as a cross-linking and superhydrophobic agent to get better durability and flame retardancy to cotton fibers. The morphologies of the pad-dry-cured cotton-nickel blends were studied with SEM, CIE Lab colorimetric measurements, FT-IR and EDX. The superhydrophobic activity was explored by determining the static water contact angle of the coated Cot-Ni blend. The comfortability of the coated cotton-nickel blends were also evaluated by studying their stiffness and air permeability.

2. Experimental

2.1. Materials

Ammonium polyphosphate (APP) and petroleum ether (AR Grade; 60–80°C) were supplied from Sigma-Aldrich. Electroconductive woven cotton-nickel (Cot-Ni) blend was supplied from Misr ElMahalla Co., Egypt. The electroconductive cotton-nickel blend fabric was generated from a pure nickel strip twisted around a pure cotton core yarn. The produced Cot-Ni filament was then woven with pure cotton yarns. The electroconductive blend was prepared utilizing the core spun yarn technique (Rajendrakumar and Thilagavathi 2013). Room temperature vulcanized silicon rubber (Decoseal RTV-2540) was purchased from ADMICO Chemical Industries, Egypt.

2.2. Preparation of multifunctional cotton-nickel blend fabric

As shown in Fig. 1, a solution of silicone rubber (RTV) in petroleum ether was prepared at a total content of 15 g/L. The solution was stirred mechanically for one hour. Ammonium polyphosphate (APP) was added to the generated solution with vigorous mechanical stirring for one hour; and then subjected to ultrasonication at 25 kHz for one hour to ensure better homogeneous dispersion. APP was added at different concentrations, including zero, 25, 50, 75, 100, 125 and 150 g/L, which were represented by RTV-APP-0, RTV-APP-1, RTV-APP-2, RTV-APP-3, RTV-APP-4, RTV-APP-5 and RTV-APP-6, respectively. Cotton-nickel blend fabrics (50 g/L) were pad-dry-cured for 5 minutes in each mixture of the generated RTV-APP composites. The treated fabrics were then placed on a clean flat surface for 10 minutes to completely evaporate petroleum ether from the sample under ambient conditions. The samples were then rinsed under tap water.

2.3. Characterization methods

2.3.1. Field-emission scan electron microscope (FE-SEM)

Both morphologies and elemental composition of the Cot-Ni fabrics coated (and uncoated) with RTV-APP were examined with Quanta FEG-250 SEM with field emission gun (Czech Republic) coupled with energy-dispersive X-ray analyzer (TEAM-EDX). The average size of particles was measured by Image J software accessible on SEM.

2.3.2. Fourier-transform infrared spectra (FT-IR)

FT-IR spectroscopy (transmission mode) was explored in the range of 400–4000 cm^{-1} using Nexus-670 (Nicolet, USA).

2.3.3. Contact angle

Both slide and static water contact angles [32] of Cot-Ni fabrics coated (and uncoated) with RTV-APP were measured on OCA-15EC (Dataphysics GmbH, Germany). Triple distilled water (10 μL droplets) was utilized to measure both slide and static water contact angles, whereas the sample was attached by an adhesive tape to glass cover slip.

2.3.4. Flammability testing

Flammability of Cot-Ni fabrics was evaluated by standard BS 5438 (1989) method (Verma and Kaur 2012).

2.4.5. Electroconductivity

The electrical conductivity of Cot-Ni fabrics coated (and uncoated) with RTV-APP were studied by HIOKI 3522-50 LCR HiTester (Japan) (Marzec and Olszewski 2019).

2.3.6. Bending length

The bending stiffness (Khattab et al. 2019) of both blank and treated Cot-Ni fabrics was assessed on Shirley stiffness testing machine using standard British 3356(1961) procedure.

2.4.7. Air-permeability

The tests of both blank and treated fabrics were carried out a pressure gradient of 100 Pa using Textest FX-3300 at a pressure of 100 Pa using ASTM D-737 standard method (Abdelrahman and Khattab 2019; Khattab et al. 2019).

2.4.8. Durability assessment

To examine the durability of the treated Cot-Ni fabrics (5 x 15 cm), they were washed for different numbers of laundering rounds, including 1, 3, 6, 9, 12, 15, 18 and 21 rounds, using AATCC 61(1989) standard methodology. The pad-dry-cured Cot-Ni samples were placed in a launder-o-meter laundry appliance. The fabrics were washed in an aqueous solution of a detergent (66 mL for each washing cycle) at 40°C for 45 minutes. Then, the char length was measured as an indicator for the durability testing. Each washing round involved pre-wash, main wash, rinse and spin.

2.4.9. Colorimetric studies

The colorimetric variations of the pad-dry-cured Cot-Ni fabrics were determined on Ultra Scan PRO Hunter Lab (United States) by measuring the three dimensional CIE Lab parameters; where L^* represents shades from white (100) to black (0), a^* represents green (-) to red (+) color ratio, and b^* represents blue (-) to yellow (+) color ratio.

3. Results And Discussion

3.1. Fabrication of multifunctional Cot-Ni blend

The main objective of the present research is to produce electricoconductive cotton-nickel (Cot-Ni) blend fabrics with flame-retardant and superhydrophobic surface utilizing a composite of ammonium polyphosphate (APP) and room temperature vulcanizing (RTV) silicon rubber. RTV dispersed in petroleum ether was mixed with different amounts of APP. Each composite of RTV-APP was then pad-dry-cured onto the electroconductive Cot-Ni blend fabrics under ambient conditions. The average size of the generated RTV-APP particles was monitored at the micro-scale in the range of 200–300 nm as demonstrated by transmission electron microscopic images (TEM) shown in Fig. 2. The RTV-APP microparticles were isolated from the coated fabric (RTV-APP-4) by stirring in distilled water for two hours followed with exposure to ultrasonic at 25 kHz for additional two hours. The fabric was then removed from the liquor, from which one drop was poured onto copper grid for TEM analysis. This research can be dedicated to render flame-retardant and superhydrophobic properties to electricoconductive Cot-Ni blend fabrics utilizing composites consisting of silicon rubber and ammonium polyphosphate.

3.2. Morphological properties

The morphological characterization of RTV-APP coated Cot-Ni blend fabrics was studied by scan electron microscopic images (SEM), energy-dispersive X-ray spectra (EDX) and Fourier-transform infrared spectroscopy (FT-IR). Figure 3 displays SEM images of RTV-APP film deposited onto fibers of Cot-Ni blend fabric at different total contents of APP (zero, 25, 50, 75, 100, 125 and 150 g/L), while the total content of RTV was held constant at 15 g/L. The blank Cot-Ni blend fabric (RTV-APP-0) showed a smooth surface as depicted in Figs. 3a-c. At low total contents of APP (RTV-APP-1, RTV-APP-2, RTV-APP-3 and RTV-APP-4), the coated surfaces displayed moderate roughness in comparison to the surface of RTV-APP-0 as displayed in Figs. 3d-f assigned for RTV-APP-1. In the cases of lower concentrations, the fibrous surfaces were covered with a thin layer of RTV-APP. Upon increasing the total content of APP (RTV-APP-5 and RTV-APP-6), the surface was highly coated with the RTV-APP composite to the degree that the pores among those fibers were also filled by RTV-APP leading to decreasing the surface roughness of the coated Cot-Ni blend fabric as shown in Figs. 3g-i assigned for RTV-APP-6. Thus, the surface roughness of the pad-dry-cured fabrics was decreased at higher total contents of RTV-APP as a result of increasing the thickness of the RTV-APP film. From these results, we can conclude that the optimal total content of the applied functional composite was at RTV-APP-4. In the case of RTV-APP-4 sample, the entire fibrous surface was fairly coated with the superhydrophobic composite particles, whilst the pores among the fibers were maintained empty. The elemental contents of the Cot-Ni blend fabrics at different total contents of RTV-APP were reported at two different surface positions of each fabric as summarized in Table 1. The energy-dispersive X-ray spectra were also explored as demonstrated in Fig. 4. The elemental content at the two inspected positions on the pad-dry-cured Cot-Ni blend fabrics was quite similar for the same sample. This verified a homogeneous distribution of the RTV-APP composite particles on the surface of Cot-Ni fabrics.

Table 1

Chemical composition in weight% of RTV-APP-0 and RTV-APP-4 at two different surface spots; a fixed total content of RTV (15 g/L) was applied.

RTV-APP		C	O	Ni	Si	P	N
RTV-APP-0		24.07	66.66	9.27	0	0	0
RTV-APP-4	area 1	21.67	65.39	8.28	3.61	0.58	0.47
	area 2	21.86	65.05	8.31	3.78	0.46	0.54

FT-IR spectra were utilized to inspect the functional groups of the RTV-APP coated Cot-Ni blend fabrics as shown in Fig. 5. Only small increments were detected in the intensities of the absorption peaks at 2911 and 1079 cm^{-1} assigned to aliphatic CH stretching and bending, respectively. This was associated with a small decrease in the absorption peak at 3325 cm^{-1} assigned to the cellulosic hydroxylic substituents. The characteristic absorbance bands of RTV-APP-0 were monitored at 3325 cm^{-1} due to hydroxyl

stretching, 2911 cm^{-1} assigned to aliphatic CH stretching, 1179 cm^{-1} attributed to aliphatic CH bending, and 1079 cm^{-1} due to ether group stretching. Both stretching and bending vibrations of the ammonium group from the ammonium polyphosphate were monitored at 3098 , 2990 and 1464 cm^{-1} , while the vibration modes of P-OH, P-O and P-O-P were monitored at 1708 , 1251 and 864 cm^{-1} , respectively. An absorption band was observed at 808 cm^{-1} assigned to the bending vibration of Si-O. No considerable shifts were monitored for the absorption peaks. These results confirmed a complete and efficient pad-dry-curing to generate a very thin film of RTV-APP onto the Cot-Ni blend fabrics.

3.3. Contact angle measurements

A surface roughness was generated through the pad-dry-curing process of the RTV-APP composites applied on the RTV-APP coated Cot-Ni blend fabrics. We were capable to generate Cot-Ni surfaces coated with RTV-APP composites to result static water contact angles (Table 2) in the range of 149.8 - 160.7° for the pad-dry-cured Cot-Ni blend fabrics from RTV-APP-1 to RTV-APP-6. There are various methods were described in literature to achieve the formation of a superhydrophobic surface utilizing expensive materials, which are applied by means of complicated procedures and instrumentation as well as time-consuming processes [23–29]. Therefore, the current procedure can be considered as an efficient, simple and low cost method to generate a superhydrophobic surface without the need for any sophisticated equipments. Moreover, the current easy method can be utilized for large-scale production of water-repellent merchandise, such as electrically conductive, superhydrophobic and flame-retardant tents. The contact angle of RTV-SAO-0 was recorded at 88.6° , while the slide angle was monitored at 15° . On the other hand, the Cot-Ni blend fabrics coated with microparticles of RTV-APP displayed much higher water contact and slide angles as shown in Table 2. When increasing the amount of APP, the contact angle was moderately increased from 149.8° for RTV-APP-1 to 160.7° for RTV-APP-4. Nonetheless, the contact angle was decreased from 160.7° to 155.2° with the increase of APP amount from RTV-APP-4 to RTV-APP-6, respectively. This could be ascribed to the improved roughness with the increase of APP amount. However, the higher amounts of APP results in filling the voids and spaces between fibers, which adversely decreased the surface roughness leading to a decreased contact angle. The slide angle was also measured to evaluate the efficiency of the superhydrophobic effect on the Cot-Ni blend fabrics. The wetting behavior changes due to decreasing the sliding angle with increasing the amount of APP. Hence, the slide angles were similarly, in agreement with the contact angles, moderately decreased from 12° for RTV-APP-1 to 9° for RTV-APP-4 with increasing the total content of APP, and then increased from 9° to 11° with the increase of APP amount from RTV-APP-4 to RTV-APP-6, respectively.

Table 2
Screening results of slide and static water contact angles.

Sample	Contact angle (°)	Slide angle (°)
RTV-APP-0	88.6	15
RTV-APP-1	149.8	12
RTV-APP-2	153.1	12
RTV-APP-3	156.8	11
RTV-APP-4	160.7	9
RTV-APP-5	158.9	10
RTV-APP-6	155.2	11

3.4. Electrical conductivity

The conductivities of RTV-APP-0 as well as the pad-dry-cured Cot-Ni blend fabrics are summarized in Table 3. It was monitored that RTV-APP-0 displayed an electrical conductivity at 0.9582 S/cm as a result of the incorporated nickel strips twisted with cotton core yarns, and woven with other pure cotton yarns. The conductivities of the pad-dry-cured Cot-Ni blend fabrics were found to slightly decrease with increasing the amount of APP. This could be ascribed to the isolation effect of the coated RTV-APP film as the RTV-SAO composite microparticles relatively fill the voids between fibers. The conductivities were in the range of 0.9105 – 0.8801 S/cm.

Table 3
Conductivity of Cot-Ni blend fabrics coated with RTV-APP composites at different total contents of APP and fixed total content of RTV (15 g/L).

Fabric	Conductivity (S cm ⁻¹)
RTV-APP-0	0.9582
RTV-APP-1	0.9105
RTV-APP-2	0.9038
RTV-APP-3	0.9095
RTV-APP-4	0.8953
RTV-APP-5	0.8837
RTV-APP-6	0.8801

3.5. Mechanical properties

The main reason of using a pad-dry-curing was to acquire a flame retardant and superhydrophobic layer with lowest optimized surface roughness onto an electrically conductive cotton fabric without affecting the blend breathability and flexibility. The flexibility of Cot-Ni blend fabrics was determined by studying the bend length in both warp and weft directions. It was monitored that the pad-dry-curing process did not considerably affect on the bend length of the treated fabrics; however, a slight increase in the cotton rigidity was detected in both warp and weft direction with increasing the total content of APP. Similarly, only slight decrease was monitored in air permeability of the treated fabrics with increasing the total content of APP. Thus, the pad-dry-curing procedure of RTV-APP composites onto Cot-Ni blends showed softness to touch almost similar to that of blank fabric. Both bend length and air permeability of the coated and uncoated Cot-Ni blends are depicted in Table 4.

Table 4
Effects of pad-dry-curing RTV-APP onto Cot-Ni blends on air permeability and stiffness at different total contents of APP (total content of RTV is 15 g/L).

Cot-Ni blend fabric	Air permeability (cm ³ cm ⁻² s ⁻¹)	Bend length (cm)	
		weft	warp
RTV-APP-0	57.07	3.12	4.00
RTV-APP-1	55.32	3.71	4.66
RTV-APP-2	55.76	3.86	4.82
RTV-APP-3	55.95	3.99	5.07
RTV-APP-4	54.00	4.22	5.32
RTV-APP-5	54.34	4.51	5.61
RTV-APP-6	53.88	4.86	5.85

3.6. Colorimetric evaluation

In order to evaluate the colorimetric variations owing to the treatment of the Cot-Ni blend fabrics with RTV-APP, both colorimetric strength (*K/S*) and three dimensional CIE Lab coordinates were measured and summarized in Table 5. As anticipated, no major colorimetric differences were monitored due to the coating process. This was verified with the close values of CIE Lab and colorimetric strength previous and following to the pad-dry-curing Cot-Ni blends with RTV-APP composites. In comparison to RTV-APP-0, the pad-dry-cured Cot-Ni blends displayed negligible changes in L* with increasing the total content of APP in

the prepared composites. On the other hand, little changes were observed in a^* and b^* with increasing the total content. These results prove the formation of translucent composite films on the Cot-Ni blend surface. In general, the superhydrophobic and flame-retardant properties created on the electricoconductive Cot-Ni blends have had no considerable adverse effects on their inherent physico-mechanical characteristics. The absorbance spectra of Cot-Ni blend fabrics before and after treatment with the RTV-APP composite as shown in Fig. 6. The maximum absorbance wavelength at 372 nm of RTV-APP-0 was not changed upon coating.

Table 5
Colorimetric changes of blank and coated Cot-Ni blends at different total contents of APP (total content of RTV is 15 g/L).

Cot-Ni fabric	L^*	a^*	b^*	K/S
RTV-APP-0	76.10	1.02	0.88	1.09
RTV-APP-1	74.65	1.30	1.73	2.15
RTV-APP-2	74.21	1.66	2.58	2.74
RTV-APP-3	73.84	1.82	2.90	3.07
RTV-APP-4	73.35	1.97	3.13	3.28
RTV-APP-5	73.17	2.18	3.49	3.70
RTV-APP-6	72.83	2.73	3.85	3.91

3.7. Flammability and durability

There have been two main flame-retardant finishing methods known as Pyrovatex and Proban treatment procedures, which exhibit industrial significance in the manufacture of the flame-retardant finishing on cellulose substrates. Proban method utilizes an organophosphorus-containing compound, tetrakis(hydroxymethyl)phosphonium chloride, with the hydroxymethyl groups exposed to urea via condensation to exchange the phosphonium group to phosphine oxide concurrently with the release of formaldehyde. After padding, the partly wetted fabric is then exposed to dry gaseous ammonia followed by oxidation utilizing hydrogen peroxide. Therefore, insoluble high molecular weight phosphorus-containing polymers are generated between fibrous gaps and voids of the cotton yarns. No actual chemical bonding was generated between those phosphorus-containing polymers and cotton surface; nonetheless, those water-insoluble polymers are held physically inside the fibrous gaps and voids of the cellulosic material. Thus, Proban-based flame-retardants usually impart harsh handle; and accordingly, the utilization of a softening agent, such as TURPEX ACN NEW, is required. Hydrogen peroxide has been also preferred as an oxidizing agent due to its ability to decrease the quantity of the released toxic formaldehyde. A wetting agent, such as INVADINE® PBN, is usually applied in the Proban procedure to

allow better immobilization of the flame-retardant material deeply inside the fabric matrix. Pyrovatex has been almost with same procedure; however, treatment with ammonia gas is no required.

Table 6
Effect of APP total content on the flammability of the treated Cot-Ni blend fabrics (total content of RTV is 15 g/L).

Cot-Ni fabric	Damaged char length (mm)	Maximum char width (mm)
RTV-APP-0	Completely burnt	
RTV-APP-1	71	17
RTV-APP-2	66	17
RTV-APP-3	55	19
RTV-APP-4	44	17
RTV-APP-5	42	19
RTV-APP-6	41	17

As shown in Table 6, the uncoated Cot-Ni blend fabric (RTV-APP-0) failed to pass the flammability test and was completely burnt to indicate poor flame-retardancy. On the other side, the treatment of Cot-Ni blend fabric with RTV-APP composite resulted in high-quality flame-retardancy as the burning process of the Cot-Ni blend samples was found to stop instantaneously after removing the flame source. The Cot-Ni blend fabrics coated with RTV-APP composite at different total contents of APP (zero, 25, 50, 75, 100, 125 and 150 g/L), and a fixed total content of RTV (15 g/L) displayed char lengths of 71, 66, 55, 44, 42 and 41 mm, respectively. To enhance the efficiency of the fire-retardant, silicone rubber was utilized as a crosslinking agent for APP. Pad-dry-curing of Cot-Ni blend fabric with RTV in the absence of APP led to a complete burning of Cot-Ni blend fabric during flammability exam. Therefore, it is apparent that silicone rubber on its own cannot establish any fire-retardant property to Cot-Ni blend. Nonetheless, a composite of silicone rubber and APP in petroleum ether accomplished a high-quality enhancement in the flame-retardant activity of Cot-Ni blend fabric. The damaged char length of the Cot-Ni blend fabrics treated with RTV-APP was found to decrease from 71 to 44 mm with increasing the total content of APP from 25 to 100 g/L, respectively. On the other side, the damaged char length continued to be almost stable from 44 to 41 mm with increasing the total content of APP from 100 to 150 g/L, respectively. This could be attributed to reaching the equilibrium of APP uptake. This could be beneficial to decrease the quantity of the expensive and less eco-friendly commercial Pyrovatex fire-retardant as well as decreasing the released toxic formaldehyde byproduct during the treatment process. Pyrovatex can be replaced with the more eco-friendly and cheap RTV-APP composite. A total content of APP upto 100 g/L as an optimized quantity demonstrated a considerable efficiency on decreasing the char length, while maintaining the high-quality performance of the flame-retardant textile product.

To examine the durability of the coated Cot-Ni blend fabric, we explored the effect of the washing cycles on the fabric flammability. In addition to introduce a superhydrophobic character to the Cot-Ni blend fabric, the major reason of using RTV as a cross-linking agent was to enhance the wash durability of the fire-retardant finish at the lowest total content of APP. The washing durability was reported by measuring the char length of the coated Cot-Ni blend fabric after different washing rounds as shown in Fig. 7. No considerable effects were monitored in the durability of the flame-retardant finishing after ten washing cycles. This could be ascribed to the increased number of binding sites among APP and Cot-Ni blend fabric through the cross-linking agent RTV. However, the char length considerably increased after 15 washing cycles. RTV can function as cross-linker with both APP from one side and cotton fibers from the other side. Therefore, the presence of silicone rubber in the fire-retardant composite will allow the fire-retardant composite to be more effective and durable to wash.

4. Conclusion

Facile production of multifunctional cotton-nickel (Cot-Ni) blend fabric was developed via pad-dry-cure procedure under ambient conditions using a composite film (RTV-APP) consisted of ammonium polyphosphate (APP) to introduce flame-retardant activity and silicon rubber (RTV) to establish a superhydrophobic surface. The RTV-APP composite was integrated into the electrically conductive Cot-Ni blend fabric to afford flame-retardant activity with maintaining the inherent physico-mechanical characteristics of the blank Cot-Ni sample such as stiffness, appearance and air-permeability. The generated water-repellent and flame-retardant surface showed a relatively thick smart coating with the lowest total content of APP using RTV as cross-linking agent. The flame-retardant properties were monitored and found to be highly dependent upon the total content of APP. The electroconductive properties of both blank and coated Cot-Ni blend samples showed approximately no changes after coating. The measured electrical conductivity of the blank Cot-Ni fabric was 0.9582 S cm^{-1} , whereas the electrical conductivities of pad-dry-cured samples were in the range of $0.9105 - 0.8801 \text{ S cm}^{-1}$. TEM data disclosed that the isolated RTV-APP composite has an average size of 200–350 nm. The damaged char length decreased from 71 to 44 mm upon increasing the total content of APP from 25 to 100 g/L, respectively. After that, the char length remained almost stable from 44 to 41 mm with increasing the total content of APP from 100 to 150 g/L, respectively. The eco-friendly RTV was applied to establish a water-repellent character. The surface morphologies of the coated Cot-Ni blend fabrics were studied by SEM, FT-IR and EDX. With increasing the amount of APP, the water contact angles increased from 88.6° to 160.7° , whereas the slide angles were decreased from 15° to 9° . The comfort characteristics of Cot-Ni blend fabrics coated with RTV-APP composite microparticles were investigated and showed satisfactory air-permeability and stiffness. The current reported procedure is distinguished with a simple bath, stability to washing, easy to handle procedure, low-cost and no requirement for softening or wetting agents. It introduces a good opportunity for large scale manufacture of electrically conductive, flame-retardant and water-repellent textiles that can be utilized in various environmental and protection applications.

Declarations

Acknowledgement

The authors extend their appreciation to the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project number-RDI-KSU-10.

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Figures

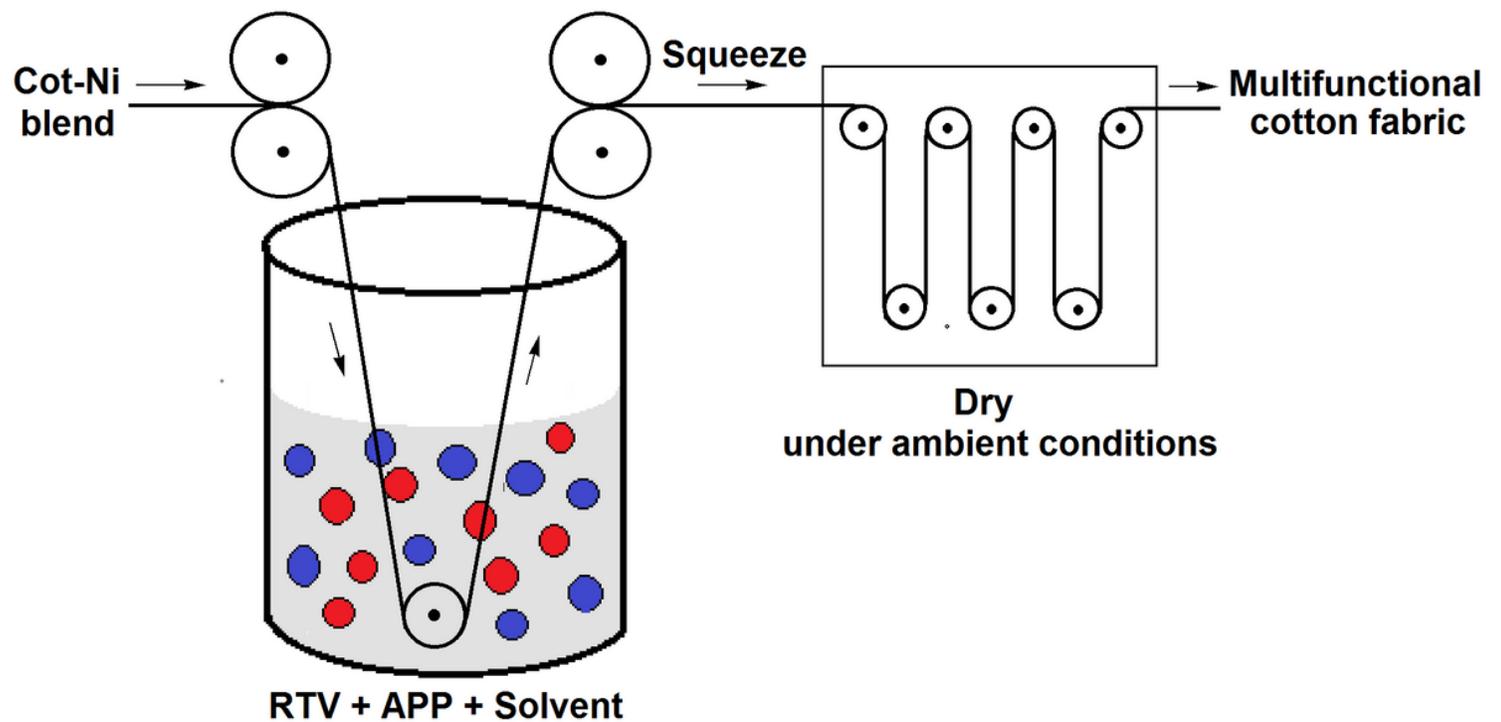


Figure 1

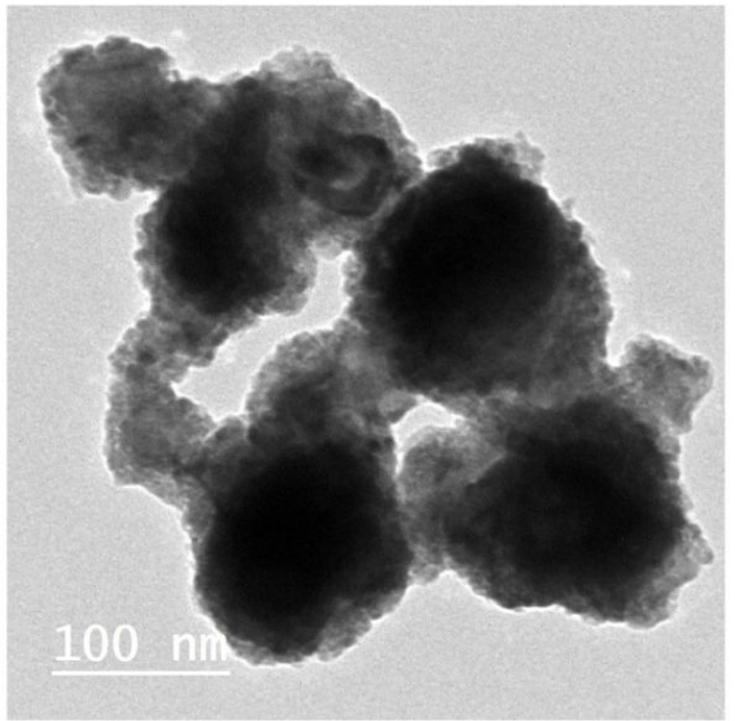
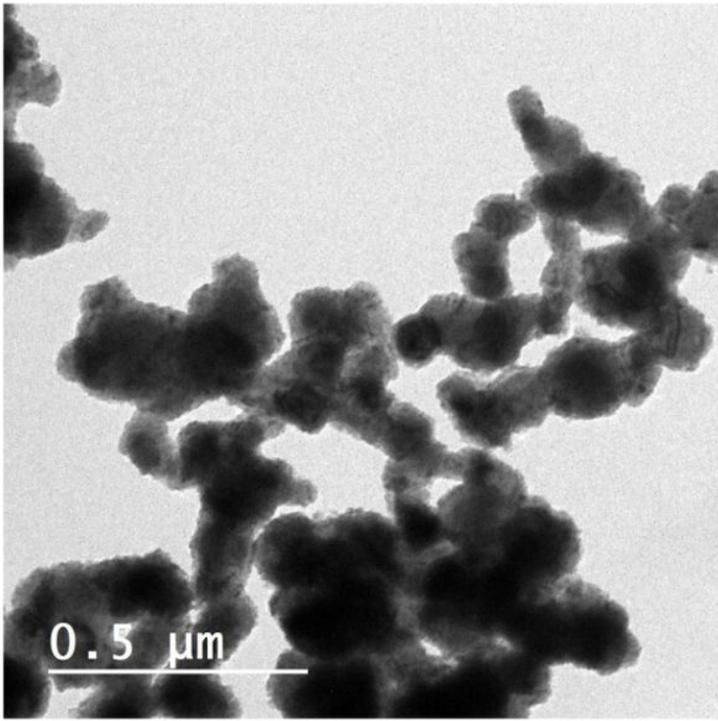


Figure 2

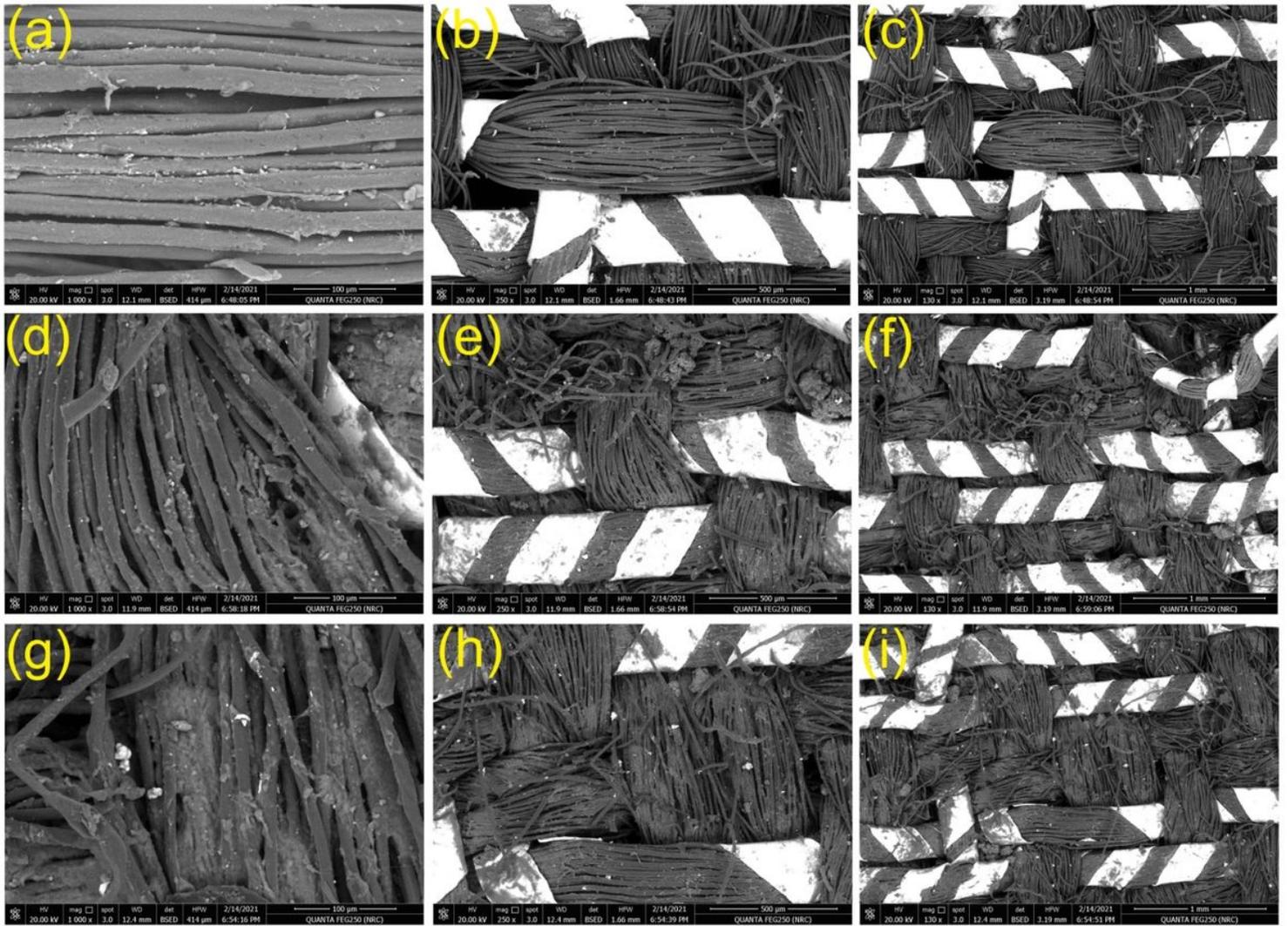
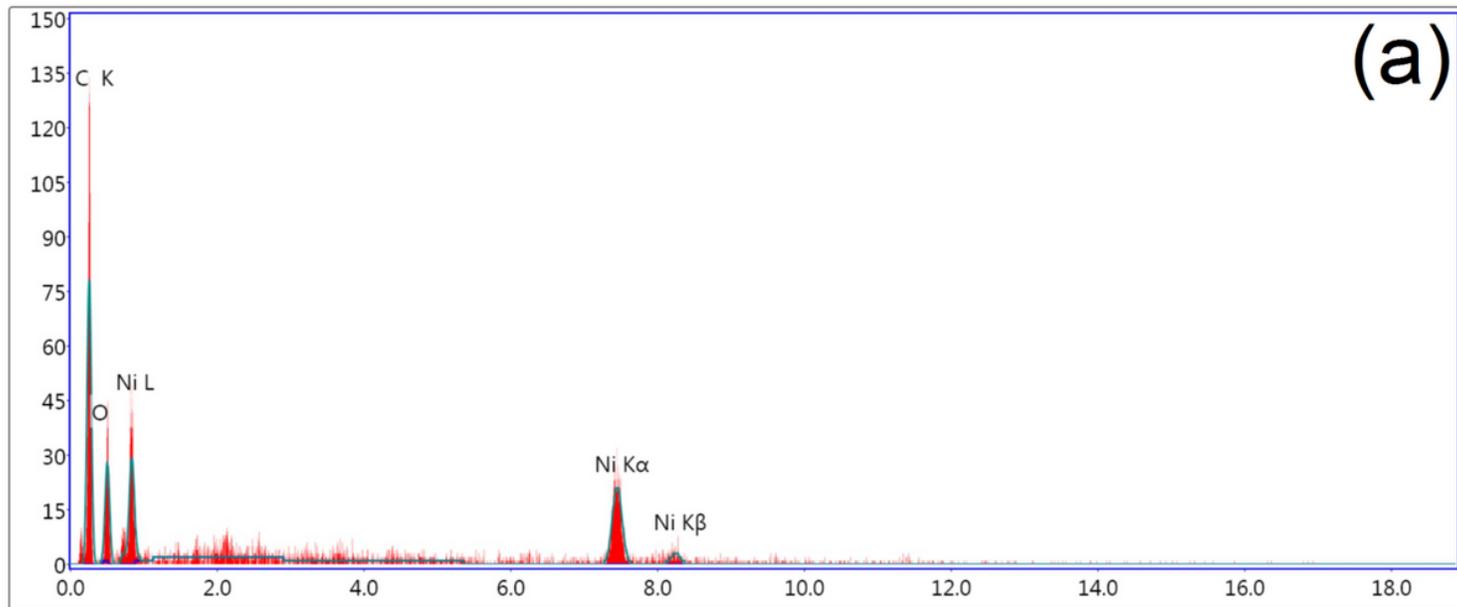
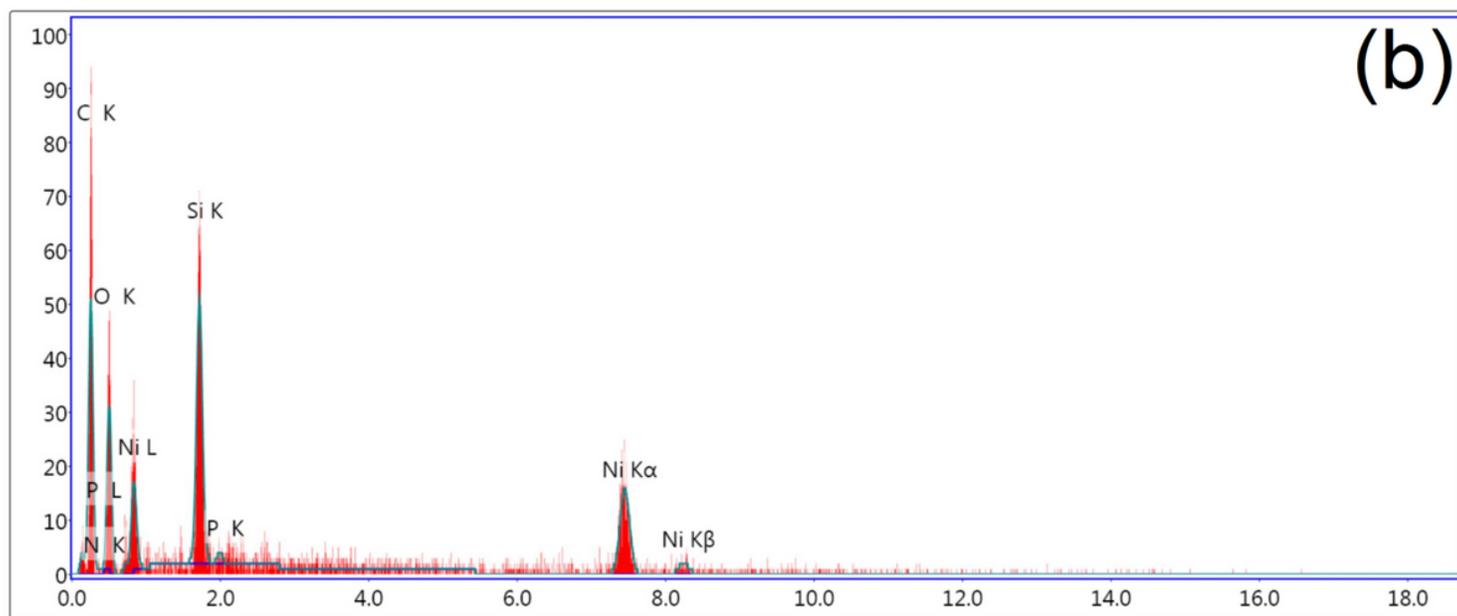


Figure 3



Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Pro Det Reso



Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Pro Det Reso

Figure 4

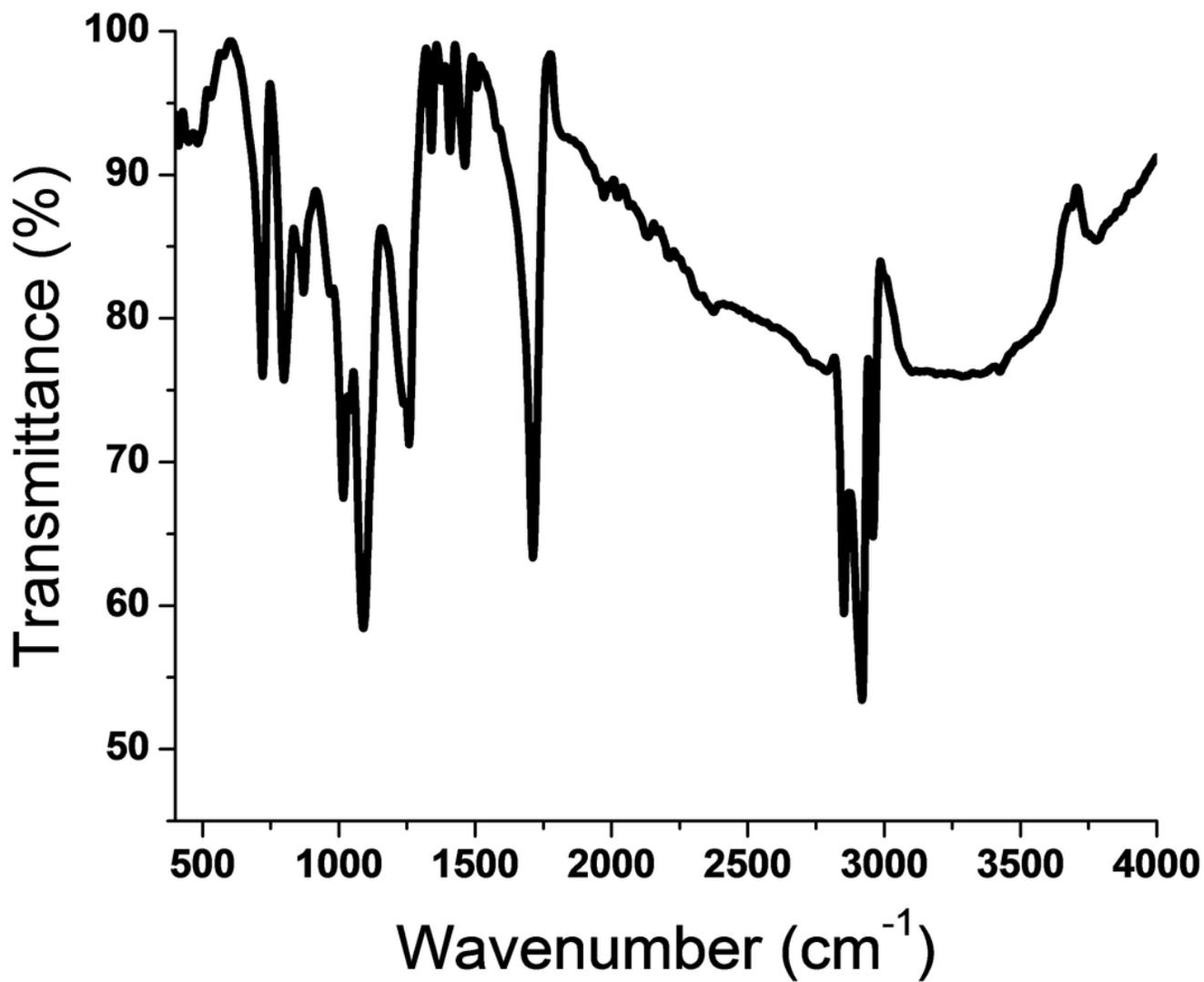


Figure 5

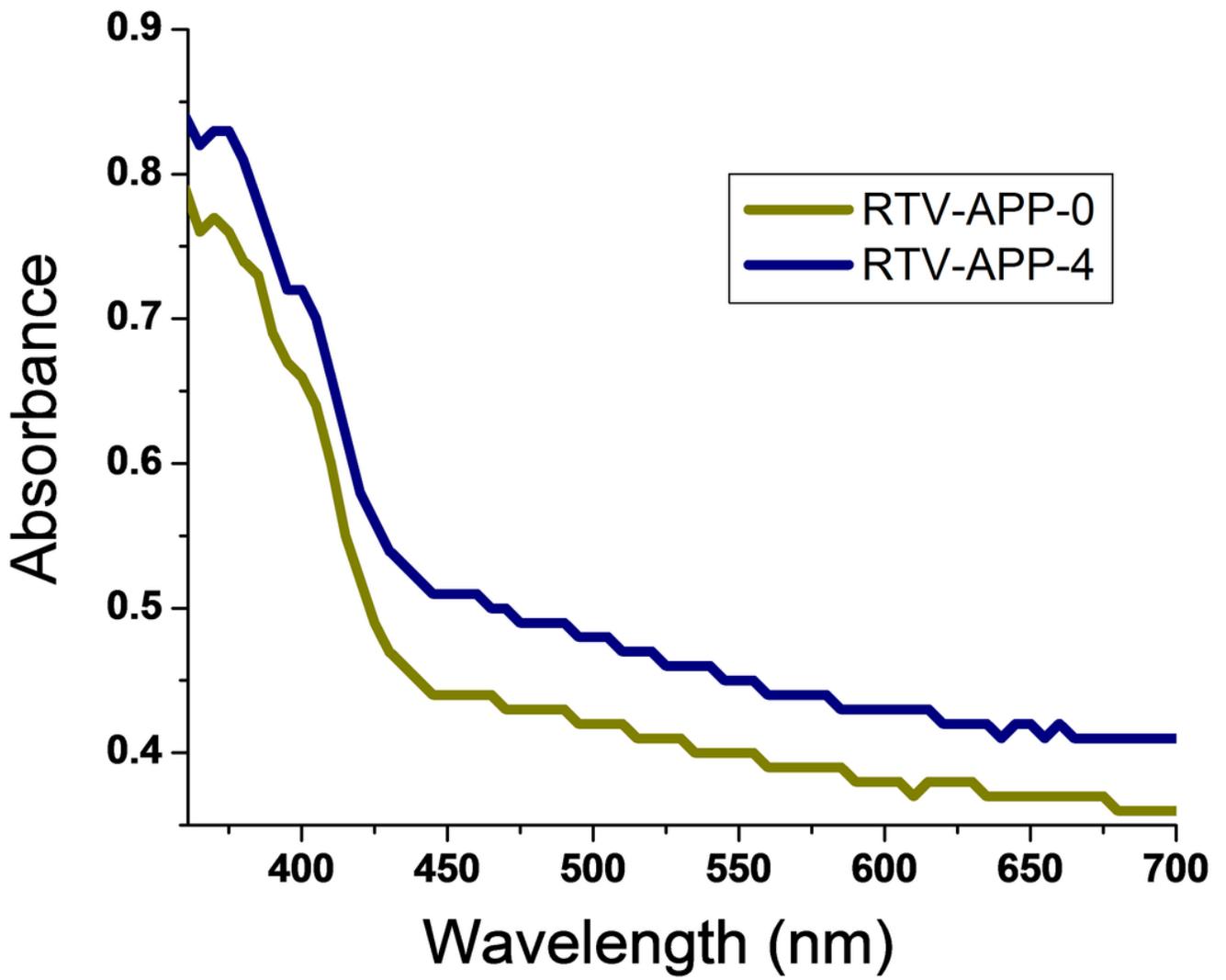


Figure 6

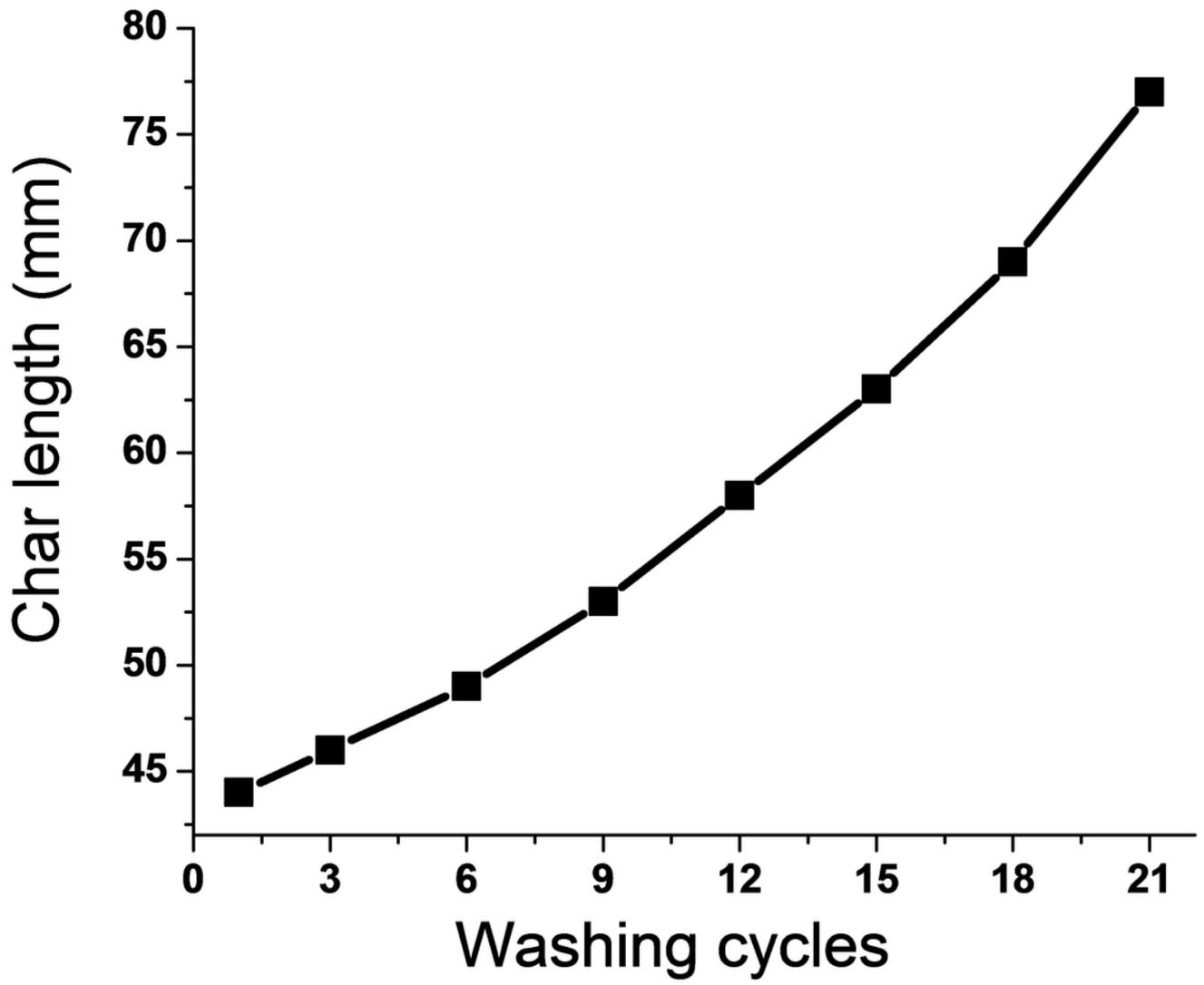


Figure 7