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Surface Functionalization of Cotton and PC Fabrics Using SiO_2 and ZnO Nanoparticles for Durable Flame Retardant Properties

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Abstract: In recent years, the use of functional textiles has attained attention due to their advantageous health and safety issues. Therefore, this study investigated the flame retardancy on cotton (COT) and polyester-cotton (PC) fabrics treated with different concentrations of silica and zinc nanoparticles through a sol-gel finishing technique. FTIR, SEM, and TGA were conducted for the characterization of coated fabric samples. The FTIR and SEM of Pristine and Treated Cotton and PC fabrics illustrated that the SiO_2 (silica dioxide) and ZnO (Zinc oxide) nanoparticles were homogeneously attached to the fiber surface, which contributed to the enhancement of the thermal stability. The starting thermal degradation improved from 320 to 350 °C and maximum degradation was observed from 400 to 428 °C for the COT-2 cotton substrate. However, the initial thermal degradation improved from 310 to 319 °C and the highest degradation from 500 to 524 °C for the PC substrate PC-2. The outcomes revealed that the silica has a greater influence on the thermal properties of COT and PC fabric samples. Additionally, the tensile strength and flexural rigidity of the treated samples were improved with an insignificant decrease in air permeability.

Keywords: flame retardant; sol-gel coating; silica and zinc oxide nanoparticles; cotton; PC; fabric

1. Introduction

Textiles are the most popular materials for the protection and comfort of humans of all ages [1], particularly, due to health and safety issues in recent years [2]. Therefore, diversification and performance optimization of textile materials is continuously in demand, for example, for functional textiles (heat and flame resistant clothing, fire-protective clothing, radiant heat protective clothing, protective clothing for coal miners, protective clothing for racing drivers, protective clothing for astronauts, protective clothing for armed forces, and antimicrobial protective clothing) [3–5]. As a result, scientists have focused on fabricating novel applications including sensors and effective development of textile polymeric materials that may also have environmental impact [6–9].

Since textile materials are readily combustible, their thermal stability and flame retardant behavior have many complexities and are therefore a challenging topic [10]. However, with advancements in technologies, researchers have developed new and innovative merchandises in textiles because these could be transformed into highly protective flame retardant [11]. Flame retardant materials can react physically and chemically in the gas phase (halogens), liquid phase (phosphorus), and solid phase (borate) depending upon their nature and characteristics [12]. Halogen derivatives and phosphorus compounds have a severe effect on the environment due to the generation of toxic corrosive gases, smoke, and formaldehyde [13,14]. However, boron and silicon are non-toxic and formaldehyde-free flame retardants and have thus drawn much attention in the field of textiles given their eco-friendly characteristics [15].

Many techniques, including nanotechnology, have been applied to textile fabrics for flame retardant functionalization [16,17]. Nanoscale particles have been used to increase the effects in properties of textile fibers and fabrics through either assimilation or surface treatment on the surface during the finishing process [18]. Similarly, graft polymerization, chemical modification, the layer by layer assembly method (LLAM), physical vapor deposition (PVD), chemical vapor deposition (CVD), laser vaporization, electroplating or electroless plating, plasma deposition, pad-dry-cure and sol-gel processes have also been used for textile modifications [19–22]. The sol-gel process, introduced by Textor, has been considered the most effective and simplest surface modification for textile fabrics and is coated with a high degree of homogenous nanoparticles [23]. This approach has demonstrated exceptional potential for eco-friendly association by reducing harmful effects [15].

The sol-gel process has been extensively studied in recent years for flame-retardants [24–27]. Synthesis is based on two-step reactions, i.e., hydrolysis (converted to unstable hydroxides) and condensation (formation of covalent bonds) of a metal-organic precursor such as an alkoxide, tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), and titanium tetraisopropoxide (TTIPO) [28,29]. Alongi et al. examined the synergistic influence of silica sol doping with aluminum phosphinate [30]. NeclaYaman et al. used silica and phosphoric acid with PAN fibers via a sol-gel process to produce flame retardant fabric [31]. Qianghua Zhang et al. applied the boron-doped silica to wool fabric through the sol-gel process for fire retardant treatment [32]. Zhiang-hua Zhang et al. fabricated silk fabric via boron hybrid silica through the sol-gel method using TEOS and boric acid (H_3BO_3) [33]. They achieved fire retardancy; however, the tensile strength and handle-ability of the treated samples were reduced. In the review of literature data, a lot of studies have also described layer-by-layer techniques [34–36], green synthesis methods, and natural approaches [9] for thermal stability and FR performances; however, due to the involvement of high cost of technology and loss of deposited minerals during repeated washings, the FRs predicament has yet to be resolved [37]. Recently, organosilicon derivatives (silanes and polysiloxanes) have been applied to cotton fabrics for high FR efficiencies and protection coatings [38]. They exhibit high reactivity and cross-linking for siloxane functionalization to enhance high washing durability and thermal stability [39]. Thus, in this respect, these properties are attributed to the most suitable, easy, and promising fixation of FR elements into the molecular structure of treated fabrics [40].

The goals of this investigation are to examine the synergistic effects of silica (SiO_2) and zinc oxide (ZnO) on the flame retardant properties of cotton and polyester-cotton (PC) fabrics through the sol-gel process, since inorganic metallic ions (silica, zinc oxide, alumina, and zirconia) have more stability than organic metals that also incorporate readily with cellulosic fibers and their blends (like PC) [41]. SiO_2 has the highest water content and therefore reduces burning kinetics and smoke production [42], while ZnO (a photocatalyst) promotes the formation of a char layer to enhance the flame retardant action [43]. Many attributes, such as UV resistance, antibacterial activity, and outstanding hydrophobicity, have been investigated; however, fire-retardant properties through silica and zinc oxide nanoparticles are still very limited. To our knowledge, there have been no investigations into the synergistic effect of silica and zinc oxide coating via sol-gel technique on fire-retardant properties. Therefore, in this research, the flame retardancy on COT and PC fabrics treated with different concentrations of silica and

zinc nanoparticles through the sol-gel finishing technique (acts as barrier to heat and oxygen transfer through substrate) [34] have been investigated and evaluated for thermal stability.

2. Materials and Methods

2.1. Materials

First, 100% cotton (COT) fabric and polyester-cotton (PC) blended fabric both with weights of 155 g/m^2 were obtained from Lucky Textile Mills, Karachi, Pakistan. Table 1 shows the detailed specifications of the fabric samples. Moreover, zinc oxide (ZnO: <100 nm), silica nanoparticles (SiO_2: <12 nm), 95% ethanol and 37% hydrochloric acid (HCl) were purchased from Sigma Aldrich Company, Karachi, Pakistan. All chemicals and reagents were of analytical grade and applied directly to the fabric samples through a sol-gel process.

Table 1. Fabric construction and surface wettability of fabric samples.

Fabric Samples	Blend Fabric Ratio %	Warp Count (Tex)	Weft Count (Tex)	Ends/Inch	Picks/Inch	Weight g/m^2	Thickness mm	Structure	Surface Wettability
Cotton fabric (COT)	100	22	22	76	68	155	0.20	Plain weave	Highly absorbent
Polyester-cotton fabric (PC)	50/50	22	22	76	68	155	0.20	Plain weave	Highly absorbent

2.2. Sol-Gel Process and Preparation

The sol-gel process was carried out in two stages, hydrolysis of tetraethoxysilane (TEOS) and the formation of a thin layer of an inorganic coating of zinc oxides and silica dioxide nanoparticles prepared in different percent combinations of TEOS. Since TEOS is insoluble in water, solvent ethanol (45 mL) and catalyst HCl (24 mL) were used in similar concentrations in all sol solutions. Table 2 shows different combinations of zinc oxide and silica nanoparticles. These were applied to COT fabric samples and PC blended fabric samples. Zinc oxide was dissolved in 20 mL of water and placed in an ultrasonicator for 30 min for emulsification. Silica nanoparticles, TEOS, ethanol, and HCl (0.01N) were added to the solution and stirred for 30 min at 5 °C. Finally, the solution was applied to both fabrics through a pad-dry-cure-method. The fabrics were dried at room temperature and then cured for 2 h at 100 °C in a curing chamber (Rapid R-3). These nanoparticles were attached with cotton through crosslinking during curing. The chemical reaction occurred in both fibers separately on PC as it was blended of cotton and polyester (shown in Figure 1). Figure 1 demonstrates that the silica dioxide and zinc oxide nanoparticles were cross-linked with hydroxyl groups of cotton and polyester with the support of the TEOS cross-linker [29].

Table 2. Sol-gel preparations.

Samples	Silica dioxide Wt.%	Zinc oxide Wt.%	Water	TEOS	Ethanol	HCl (0.01N)	Add-On (%)
COT			Pure cotton				
COT-1	0.25%	0.25%	20 mL	20 mL	45 mL	24 mL	1.66
COT-2	0.5%	0.25%	20 mL	20 mL	45 mL	24 mL	1.91
COT-3	0.25%	0.5%	20 mL	20 mL	45 mL	24 mL	1.91
PC			Pure PC				
PC-1	0.25%	0.25%	20 mL	20 mL	45 mL	24 mL	1.66
PC-2	0.5%	0.25%	20 mL	20 mL	45 mL	24 mL	1.91
PC-3	0.25%	0.5%	20 mL	20 mL	45 mL	24 mL	1.91

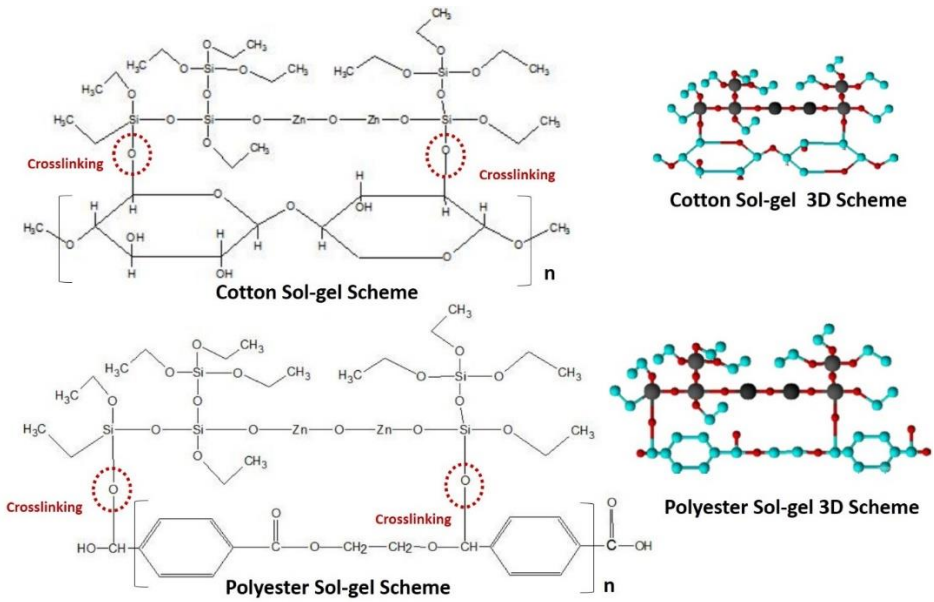

Figure 1. Reactions scheme of cotton and polyester.

2.3. Characterization

2.3.1. FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) spectra of all fourteen samples, COT, PC, before and after wash samples of COT-1, COT-2, COT-3, PC-1, PC-2, PC-3, were captured through IR Prestige-21 (Shimadzu) using an attenuated total reflectance (ATR) accessory equipped with a zinc selenite (ZnSe) crystal. The frequency ranged from 4000–400 cm^{-1}.

2.3.2. Morphological Structures

The morphology of all samples was determined by scanning electron microscopy (SEM, JEOL-6380 LV). All samples were pre-coated with gold before testing.

2.3.3. Thermal Analysis

Thermal resistance was evaluated by thermogravimetric analyzer SDTQ600 (CHNOS elemental analyzers, Germany) at a heating rate of 10 °C/min and the temperature was maintained at 30–600 °C. Nitrogen was supplied at a rate of 20 mL/min to inhibit the corrosive gases involved in the degradation.

2.3.4. Flammability Analysis

Before the fire-retardant test, treated fabrics were conditioned according to ASTM D1776-98 [30,31]. The ignition time and flame spread time were evaluated using a fire retardancy test at a 45° flame angle according to the ASTM D1230 standard.

2.4. Physical Properties

2.4.1. Air Permeability Analysis

The air permeability of the treated fabrics was measured by a MS012 air permeability tester (Utstesters, China) according to the BS 5636 standard [44,45]. The test was conducted under specific conditions, i.e., 100 Pa air pressure and a 20 cm^2 circular test area. Air permeability is defined as the volume of air passing in 1 s through 100 mm^2 of a fabric sample at a pressure variance of 100 Pa.

2.4.2. Flexural Analysis

For the stiffness of treated fabrics, the bending length was measured by a Shirley Stiffness Tester according to ASTM D 1388 [46].

2.4.3. Tensile Strength Analysis

The tensile strength and elongation percentage of treated fabrics were calculated by Titan 3 according to the US standard of ASTM D5035 [47].

2.5. Durability Analysis

The fabrics were washed according to AATCC 61 for the examination of the durability of treated samples. According to this standard, 1 industrial wash equals 5 home washes.

3. Results and Discussion

3.1. FTIR Results

Figure 2a shows the FTIR (ATR) outcomes of COT, COT-1 (B.W (Before Wash) and A.W (After Wash)), (B.W and A.W), COT-2 (B.W and A.W), and COT-3 (B.W and A.W). The bands at 3550–3050 cm^{-1} confirmed the presence of OH stretching for cellulose. Regarding the modified samples, i.e., COT-1, COT-2 and COT-3 (B. W and A. W), peak shifting was observed at 3650–3250 cm^{-1}, which proves the presence of silica in the cotton fabric, i.e., Si-OH.

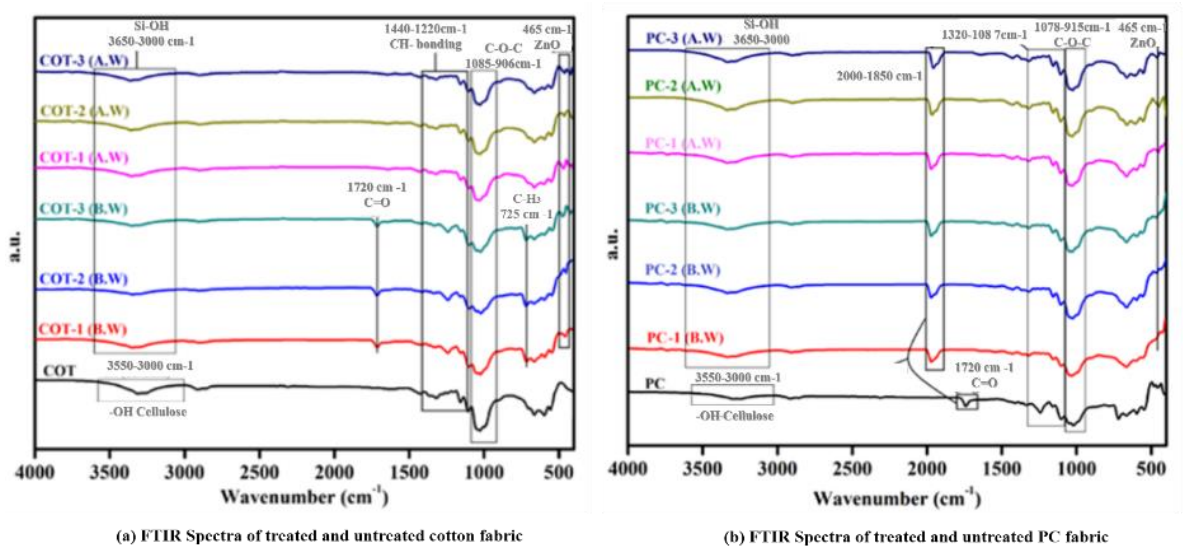

Figure 2. Spectra of treated and untreated (**a**) cotton and (**b**) polyester-cotton (PC) fabric samples.

Similarly, a new peak at 1720 cm^{-1} was observed due to C=O group as reported in previous literature [48]. This effect was not observed with the COT, COT-1 (A.W), COT-2 (A.W), or COT-3 (A.W) samples. The band at 1440–1220 cm^{-1} indicates $–CH_3$ bending. Another region at 1085–906 cm^{-1} indicates C–O–C. A new peak at 725 cm^{-1} indicates the COT after wash (A.W) samples and is due to the –Cl since HCl was used as a catalyst with ethanol that was drained after wash samples. The peak of ZnO was perceived at 456 cm^{-1} in the FTIR spectra. Thus, SiO_2 and ZnO have increased the flame retardancy [49,50].

Figure 2b has shown the FTIR (ATR) results of PC, PC-1 (B.W and A.W), PC-2 (B.W and A.W), and PC-3 (B.W and A.W). These fabrics were modified with SiO_2 and ZnO. The shifting of the peak for –OH was similar to Figure 3a. The band was at 3650–3000 cm^{-1} for Si-OH while it varied from 3550–3000 cm^{-1} for –OH (cellulose). Moreover, in this group, a new peak of polyester fabric

appeared at 1730 cm^{-1} due to C=O and in the modified samples, a peak shift was observed at 2000–1850 cm^{-1}. The band at 1320–1087 cm^{-1} represents the C-O for esters. At 1078–915 cm^{-1}, a peak of C-O-C for saccharides appeared [51]. The peak at 456 cm^{-1} was for ZnO, similar to Figure 3a. FTIR characterization of the samples resulted in identification and confirmation of chemical species, which resulted improved flame retardancy.

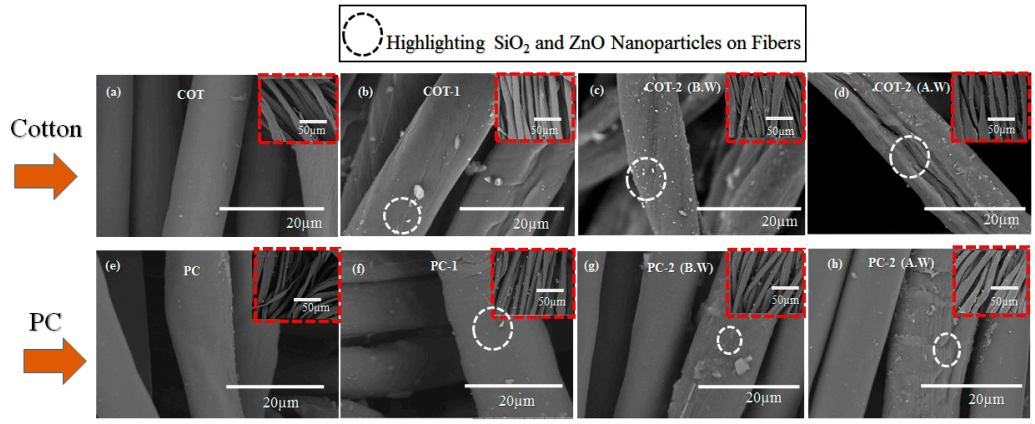

Figure 3. Surface morphology of the treated and untreated samples.

3.2. Morphological Structure

The surface morphology of untreated (COT, PC) and treated samples (COT-1, COT-2, COT-3, PC-1, PC-2, PC-3) was studied using SEM. In Figure 3, the COT fabric samples showed a smooth surface using 4000× magnification at 5KV. The zinc and silica nanoparticles were homogeneously dispersed on the fibers as displayed in Figure 3c,g.

Figure 4a,e shows the surfaces of COT and PC fabrics before coating, and Figure 4b,f reveals the effect of silica dioxide (SiO_2) and zinc oxide (ZnO) on COT and PC fabrics after coating forming a rough surface [10]. These well-dispersed particles were responsible for the flame retardant properties and resisted the combustion behavior of fibers as shown in Figure 3c,g, respectively, for COT and PC fabric. Figure 3b,c is the before wash samples of cotton and Figure 3f,g is the before wash samples of PC. Figure 3d,h demonstrates the zinc and silica remained on the fibers after five industrial washes, indicating the coating durability [33]. SEM analysis confirmed the surface morphological changes involved behind the flame retardancy.

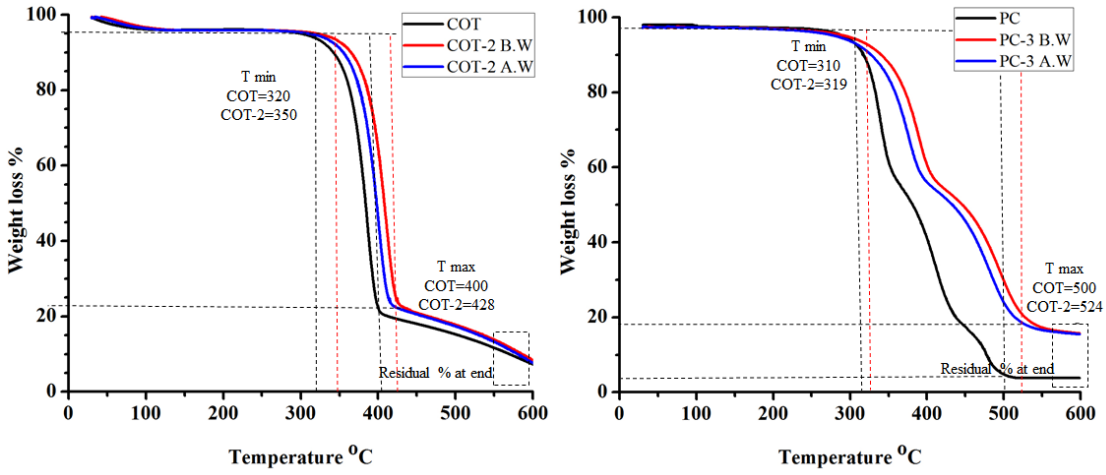

Figure 4. Thermogravimetric analysis of (**a**) untreated (COT, PC) and (**b**) treated fabric samples (COT 2 and PC 2).

3.3. Thermal Analysis

The thermal stability of different nanosols was investigated by thermogravimetric analysis (TGA) and flame retardancy at 45°. The TG analyses of the pure and treated samples were performed in a nitrogen supply of 20 mL/l. The obtained data is expressed in Table 3. Moreover, Figure 4 explains the thermogravimetric analysis results of untreated samples (COT and PC) and treated samples (COT-2 and PC-2) B.W and A.W.

Table 3. Stability of untreated and treated cotton (COT) and PC blend fabric.

Substrate Type	T_{min} (°C)		T_{max} (°C)		Weight Loss at T_{max} (%)		Residue at End (%)		Time to Ignite (s)		Flame Spread Time (s)	
	B.W	A.W	B.W	A.W	B.W	A.W	B.W	A.W	B.W	A.W	B.W	A.W
COT	320		400		92.91		7.1		2		8	
COT -1	330	333	410	413	91.1	92.4	8.9	7.6	4	3	17	15
COT-2	350	341	428	418	91.5	92.1	8.5	7.9	5	4	21	19
COT-3	340	336	420	415	91.4	92.2	8.6	7.8	5	4	14	13
PC	310		500		96.2		3.8		2		8	
PC-1	315	311	514	511	86.2	87.3	13.8	12.7	4	3	17	17
PC-2	319	314	524	520	85.5	87.9	14.5	12.1	6	5	22	20
PC-3	317	313	521	519	86.9	87.7	13.1	12.3	6	5	18	17

3.3.1. Thermal Degradation

In Figure 4a, the trend line of all curves was similar; however, COT-2 (B.W) had weight loss at a higher temperature [47]. Untreated COT was completely degraded at 600 °C in a nitrogen supply. Generally, COT decomposes in three stages: volatilization, main degradation, and carbonization [48]. The first stage started (300–400 °C) involves the conversion of COT into aliphatic char and volatile products. The second stage (400–600 °C) simultaneously resolves into two phases, i.e., carbonization and char oxidation, by converting the aliphatic char into aromatic form. The oxidation occurred at 600 °C by liberating CO and CO_2 [12]. The presence of SiO_2 and ZnO in nanosols enhanced the thermal degradation of COT samples. Silica dioxide and zinc oxide (acting as a physical barrier) protected cotton from the heat and oxygen and favored the formation of a carbonaceous residue. As a result, silica was more effective with the combination of silica and zinc for degradation. COT-2 demonstrated maximum thermal stability on cotton fabrics.

Similar to Figure 4b, the black, red, and blue lines represent the PC sample, PC-2 (B.W) sample, and PC-2 (A.-W) sample. Thus, the PC-2 sample (red line) showed weight loss at higher temperature than the other samples. Untreated fiber started rapid thermal degradation at 310 °C and lost about 96.2% of the weight at 500 °C. A significant residue was observed for the PC substrate impregnated with silica dioxide and zinc oxide at higher temperatures up to 524 °C. After the combustion of all organic parts of the SiO_2 and ZnO coated fibers, the residual amount (14.5% by weight) corresponds to SiO_2 and ZnO nanoparticles. Based on this result, the thermogravimetric analysis technique in nitrogen allows for the evaluation of the presence of ZnO covering the cotton and PC fibers. Conversely, for the PC, the degradation mechanism differed from the COT in all sol-gel recipes, which enhanced the thermal oxidative stability of the treated fabrics. PC was decomposed in nitrogen in two stages, breakdown of the main chain at 280 °C and the carbonization reactions at (440 °C). PC was entirely degraded at 600 °C. These values are less than pure polyester given the cotton involvement in PC decomposition. Silica and zinc nanoparticles, applied to PC fabric through the sol-gel method, improved the thermal stability of the polymers since both acted as a barrier and prevented the thermal decomposition of the main chain. Similarly, for COT, SiO_2 was more effective for protection than ZnO on PC blend fabrics.

3.3.2. Flammability at 45°

The ignition time and flame spread time for COT and PC blended fabrics are depicted in Table 3 while images of flammability behavior for COT and PC blend fabrics BW and AW for 10 s are shown

in Figure 5. The flame spread time and ignition time of the untreated samples were much less than the treated samples. COT and PC fabric samples demonstrated resistance to a flame when treated with nanosols of SiO_2 and ZnO nanoparticles. The total burning time increased significantly along with the ignition time.

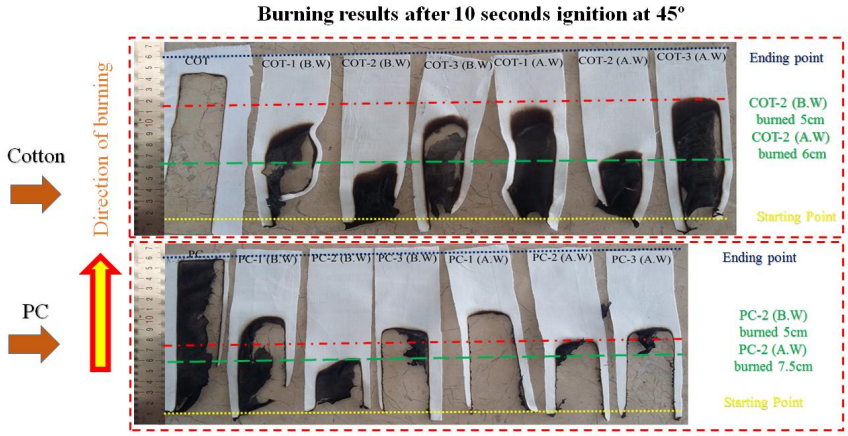

Figure 5. Flammability test for COT and PC blend fabrics BW and AW for 10 s.

Furthermore, the performances of COT-1, COT-2, and COT-3 effectively resisted the flame and took 17, 21, and 14 s to burns out completely. However, the entire time for pure cotton burn out was 8 s. A similar effect was observed in the PC fabric samples as well; all nanosol-treated substrates showed good resistance to the flame with improved ignition time, and PC-2 delivered better results than the other combinations.

3.4. Assessment of the Physical Properties

Untreated and sol-gel treated substrates were tested to elucidate the effect of the sol-gel coating on air permeability, flexural rigidity, and tensile strength. An insignificant decrease in air permeability was observed in the treated samples as shown in Figure 6a. This was due to the presence of SiO_2 and ZnO nanoparticles in fabric samples in which their very small size results in minor changes in resistance, i.e., 250 mL/s to 242 mL/s for pristine and treated cotton. The after-wash samples lost small amounts of finish due to washing; however, compared to untreated samples, they showed good durability. Although the GSM of cotton and PC fabric was the same, the PC blended fabric showed lower passage of air due to the entanglement of fibers from blending; similar insignificant change in the air permeability was also observed in the PC fabric as revealed in Figure 6a. The error bar is applied to illustrate the potential standard deviation from the mean value, which depicted no significant deviation from the mean.

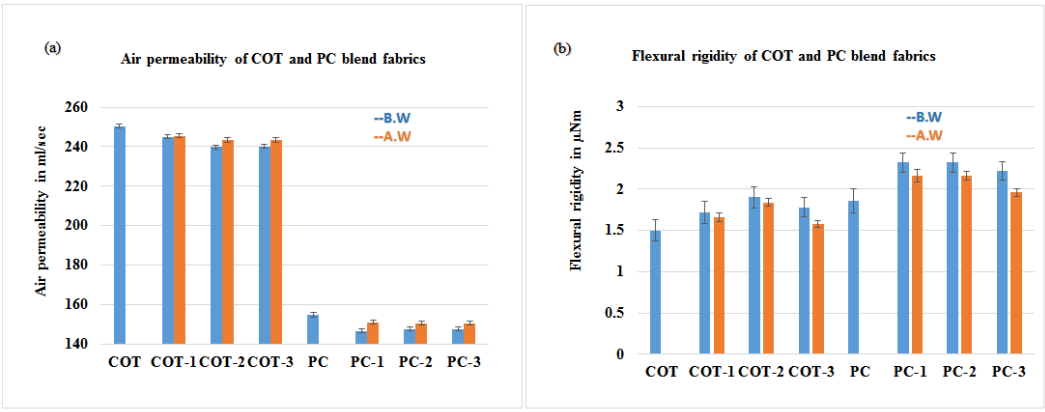

Figure 6. (**a**) Air permeability and (**b**) flexural rigidity of COT and PC fabrics.

The flexural rigidity mostly depends upon the type of precursor used for the sol formulation and the amount of nanoparticles in the recipes. The silica and ethanol formed a thin layer on the treated fabric, which improved the flexural rigidity. Minor changes were observed in treated COT and PC fabrics. The error bar illustrated in Figure 6b, revealed the overall distribution of data with a minor deviation of individual measurement from the mean value.

Application of sols with ethanol and nanoparticles also enriched the tensile properties of COT and PC fabrics. In total, 432.9 N force was required to break the untreated COT, whereas the force was much higher for COT-1 COT-2 and COT-3, i.e., 504.4 N, 518.4 N and 519.0, respectively. COT-2 and COT-3 have nearly equal amounts of nanoparticles, therefore, a slight improvement in strength was observed as shown in Figure 7a. A similar trend was observed for the PC blend fabrics. Additionally, a reduction in extension on both the COT and PC treated fabrics was observed due to the homogenous coating that helped in crosslinking the fibers in the yarns. Laundering affected the thin layers of coatings and increased the extension in the COT-1 case of treated substrates, as described in Figure 7b, whereas COT-2 and COT-3 showed negligible changes after laundries. In the case of PC treated, PC-1, PC-2, and PC-3 (B.W and A.W) indicated similar results, but due to crosslinking, these results were less than pristine PC fabric. An error bar was applied to the graph to check the distribution of data and precision, which revealed that there was perfect precision in the measurement.

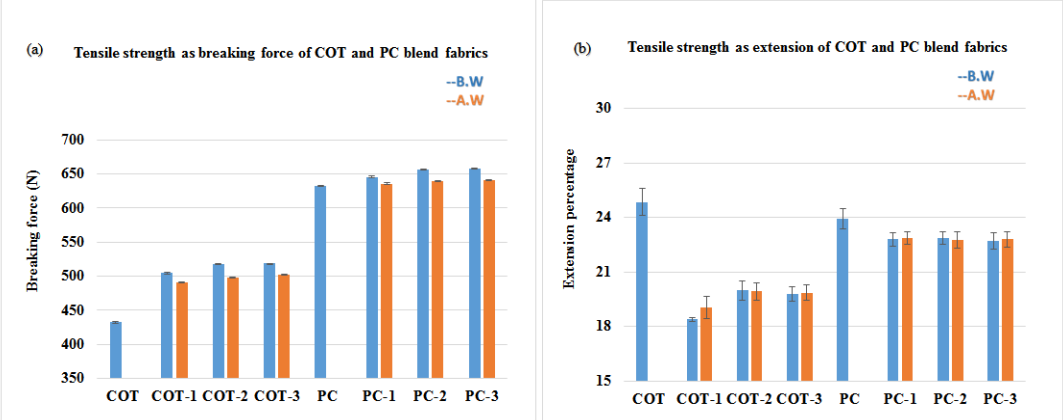

Figure 7. (**a**) Breaking force and (**b**) extension test for COT and PC fabrics.

4. Conclusions

In this research, the flame retardant intensity of cotton (COT) and polyester/cotton (PC) blend fabrics was investigated and improved using the nanoparticles of SiO_2 and ZnO via a sol-gel finishing method. FTIR, SEM, thermal, and physical analysis were conducted for the characterization of the coated fabric samples. The important results of the study are summarized as follows:

- The flame retardancy was more improved with the addition of silica nanoparticles than zinc oxide in both COT samples and PC samples.
- The blending of SiO_2 with ZnO showed more impact than their separate usage on both COT and PC samples.
- The flame retardancy was more improved on PC fabric samples than the COT fabric samples. FTIR and SEM revealed that these coatings were durable and showed an insignificant decrease after five industrial washes.
- The physical properties, i.e., strength and flexural rigidity of treated fabrics, also increased due to the crosslinking of nanoparticles, which results in decreased tensile force at extension.
- The air permeability was insignificantly decreased since the nanoparticles also resist the passage of air through them.

Thus, the fibers can be considered an effective choice for more technical advancements to assist functional textile manufacturers and ultimately people's health and safety.

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