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Optimizing Synergistic Silica–Zinc Oxide Coating for Enhanced Flammability Resistance in Cotton Protective Clothing

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Abstract: This study reports process optimization studies of silica and zinc oxide-based flame-retardant (FR) coatings on cotton fabric for protective clothing and enhanced flammability properties. The experiments were designed by central composite design (CCD) using response surface methodology (RSM) to assess the synergistic protective effects of silica and zinc oxide FR coating. These prepared sols were coated on cotton fabrics by a simple dip dry cure process. The resulting FR-finished fabrics were characterized by SEM, mechanical properties, flame retardancy, and air permeability. SEM results confirmed the homogenous spreading of particles on cotton fabrics. From TGA results, it was noticed that the incorporation of silica and ZnO in the prepared nano-sols results in improved thermal stability of the FR-finished fabrics. These sol–gel-treated FR cotton fabrics showed excellent comfort properties, which shows their suitability for fire-retardant protective clothing. RSM analysis proved that the predicted values are in good agreement with the experimental values since R^2 values for time to ignite, flame spread time, and air permeability were greater than 0.90. The optimized concentration of silica and ZnO in FR-finished fabrics was found to be 0.302% and 0.353%, respectively, which was further confirmed by confirmatory experiments. The optimization analysis successfully optimized the process for synergistic coating of silica and zinc oxide nanoparticles for enhanced flammability properties of FR cotton fabric for protective clothing.

Keywords: CCD; coating; comfort properties; flame-retardant; protective clothing; RSM; silica; zinc oxide

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1. Introduction

Industrialization introduced human beings to several safety risks that became an important issue to be addressed. A growing segment of protective textile products was introduced in recent years that is involved in the development of new fibers, fabrics, and advanced finishes. Protective textiles are a class of textile products that mainly provides protection to the user against adverse and severe working conditions. According to a market survey, the global market share of protective textiles was estimated to be around USD 4.8 billion in 2019 and is expected to grow at a rate of 3.4% annually from 2020 until 2027. Flame-retardant (FR) clothing is one of the important classes of textile products that not only protects the wearer from fire hazards but also ensures the comfort properties of the garment, such as air permeability and water content [1]. To develop FR products, different specialized coating methods are used such as sol–gel, dip-dry, or layer-by-layer techniques, and various types of procedures like plasma treatment and surface functionalization are

employed. However, a major challenge to manufacture these FR products is the adoption of environmentally friendly and non-toxic processes to guarantee sustainability.

FR materials are generally classified into various types depending upon their essential elements such as halogen-based, nitrogen-based, phosphorous-based, and metal-based FR materials. Among all these FR materials, halogen-based finishes are the most practical, but the toxic nature of byproducts after combustion makes it an undesired option [2]. To overcome this problem, metal-based nanoparticles like ZnO and silica are considered safe and efficient alternatives. When applied in combination, their synergistic effect significantly enhances the FR properties. ZnO nanoparticles exhibit many distinguished features like flame retardancy, UV shielding, and antibacterial properties [3]. On the other hand, silica nanoparticles impart mechanical strength, flame resistance, thermal stability, and breathability [4].

Throughout history, cotton has been a prime source as a raw material for textile products such as clothing, upholstery, and home furnishing due to its good moisture management and comfort properties. Although cotton has superior wettability and air permeability, its flammable nature makes it a poor choice for FR applications [2]. To attain FR properties in cotton fabric, several chemical finishes are applied utilizing nanoparticles of ZnO and SiO_2.

Several techniques have been used for the application of FR finishes in fabrics. These techniques include layer-by-layer (LBL) deposition [1], plasma treatment [5], chemical grafting [6] and sol–gel coating [7] methods. In the LBL method, multiple layers of a substance are deposited on a charged substrate by immersing it in a positively and negatively charged species, to create a protective barrier [8]. Plasma treatment increases the surface reactivity of the substrate by exposing it to low-pressure plasma, thereby allowing the reduction in the amount of FR finish required [9]. On the other hand, in chemical grafting, FR-finish molecules are attached to the surface of the substrate by the covalent bonding mechanism [10]. Lastly, the sol–gel process applies a thin film of FR-finish material through hydrolysis and condensation of a colloidal solution on the substrate [11]. Among these methods, the sol–gel method has been considered the most attractive method due to its unique characteristics and advantages over other FR finish methods. Among other advantages, its ability to use the existing finishing equipment in the textile industry for different textile substrates makes it a versatile approach because no extra setup is required for FR-finish application [12,13]. Furthermore, considering the irregular surface topography of textile substrates, this technique is very suitable as it covalently binds FR chemicals to the high number of hydroxyl functionalities on the fabric surface, ensuring long-lasting FR properties. Additionally, the coating is thermally stable, and its thickness can be precisely controlled, thus making this coating method useful for a variety of applications [14].

Response surface methodology (RSM) is a valuable statistical analysis tool which is widely used to model and optimize different processes for enhancing system performance and process efficiency [15]. It offers the freedom to evaluate and correlate the effect of multiple inputs or process factors on the outputs or process responses of a system simultaneously. One of the commonly used designs in RSM is central composite design (CCD) [16]. CCD allows the construction of a design of experiment (DoE) that combines factorial, axial, and center points, enabling the establishment of a comprehensive correlation between the independent variables (such as the concentration of two types of nanoparticles) and the response variables [17]. Karim-nejad et al., (2015) used RSM and the CCD approach to design experiments for flame-retardant properties of mercerized cotton. They treated cotton fabric with citric acid and ZnO nanoparticles and optimized their concentration by DoE [18]. Similarly, Forouharshad et al., (2011) also optimized flame-retardant properties of wool with zirconium oxychloride using RSM and the CCD approach. They considered four variables for their design, which were zirconium oxychloride content (%), temperature (°C), citric acid (%), and HCl (%), and optimized their values against a single response, i.e., char length [19].

The current work is a continuation of our previous work on silica-and-ZnO-based flame-retardant finishes for cotton fabric [20]. In the previous work, we evaluated the wash durability of flame-retardant finishes along with mechanical and permeable properties. Herein, we evaluated and optimized the synergistic effect of these two FR finishes on flammability and comfort parameters through the response surface method using CCD in the Design Expert® software package (version 13, Stat-Ease Inc., Minneapolis, MN, USA). To the best of our knowledge, no systematic study is available in the literature on optimization of synergistic effects of silica-and-ZnO-based flame-retardant finishes for cotton fabric using RSM. Moreover, we investigated comfort properties in the present work at a slightly higher loading range of silica and ZnO content. The two flame-retardant materials were applied through the sol–gel method using tetramethoxysilane (TMOS) as a binder. The resulting FR-finished fabrics were characterized by SEM, mechanical properties, flame retardancy, and air permeability. This approach will enable us to generate a statistical model that accurately predicts the FR behavior, providing valuable insights for the development of efficient and cost-effective FR finishes.

2. Materials and Methods

2.1. Materials

Pure 100% cotton with a weight of 155 g/m^2 and quality of (22 × 22/76 × 68) was provided by Lucky Textile Mills, Karachi, Pakistan. Silica nanoparticles (SiO_2: <12 nm), zinc oxide (ZnO: <100 nm), tetramethoxysilane (TMOS) 99%, ethanol 95%, and hydrochloric acid (HCl) 37% were purchased from Sigma Aldrich, Karachi, Pakistan. All reagents and chemicals were used directly as purchased.

2.2. Preparation and Coating of Sol–Gel

The preparation of sol–gel was carried out by hydrolysis of tetramethoxysilane (TMOS), which was achieved using ethanol (45 mL) as a solvent. HCl (24 mL) was incorporated in the same quantity as a catalyst in all sol solutions. Zinc oxide was separately mixed in 20 mL water, and this mixture was placed for 30 min in an ultrasonic bath for homogenization. Furthermore, silica nanoparticles, TMOS, HCl (0.01 N), ethanol, and the prepared ZnO solution were mixed under constant stirring at 5 °C for 30 min. These prepared sols were applied on cotton fabrics by a simple dip dry cure process.

2.3. Characterization

The surface morphology of pure and treated FR cotton samples was analyzed by scanning electron microscopy (SEM, JEOL-6380 LV). As cotton is non-conductive, gold sputter coating was applied on all samples before testing.

The ASTM D1230 standard [21] was used to examine the time to ignite and spreading time of flame using a flame-retardant tester at 45° angle.

Thermal gravimetric analysis was used to analyze the thermal degradation behavior of pure and treated FR finish samples at a heating rate of 10 °C/min within the temperature range of 30–600 °C under nitrogen supply. A SDTQ600 thermogravimetric analyzer was used for this test.

The vertical wicking test was performed using the AATCC 197 standard [22]. In this test, the pure and treated samples of cotton fabrics were cut into a length of 250 mm and a width of 25 mm, and suspended vertically with the lower end of 5 mm being immersed in water to examine the capillary rise of liquid in a specific time. A stopwatch was used to record the time in seconds. This test helps to identify the wicking rate (wicking per second).

The permeability of fabric with respect to air is the key comfort property. The air permeability test was conducted using air a MS012 permeability tester (Uster, Shanghai, China). The air permeability test was performed at a pressure of 100 Pa following the ASTM D737 method [23]. The BS 5636 standard was used to examine the air permeability of pure and treated samples [20].

Coating enhances the tensile properties of treated samples. Titan 3 was used to evaluate the tensile strength of pure and treated samples using ASTM Standard D5035 [24].

Water content (%) of pure and treated samples were also examined to explore the comfort properties. The samples are prepared according to the combinations reported in Table 1. The fabric thickness, weave structure, and add on (%) of treated and untreated cotton are also shown in Table 1. A slight change in fabric thickness was observed in sol–gel treated cotton samples. Similarly, as the concentration of silica and ZnO nanoparticles was increased, the add on (%) also increased.

Table 1. Combinations of silica and zinc oxide in nano sol-gels.

No.	Samples	Silica (%)	Zinc Oxide (%)	Thickness (mm)	Fabric Structure	Add on (%)
1	Pure Cotton	0	0	0.20 ± 0.03	Plain weave	-
2	CSZ 1	0.25	0	0.24 ± 0.02		1.51
3	CSZ 2	0	0.25	0.25 ± 0.05		1.54
4	CSZ 3	0.25	0.25	0.27 ± 0.02		1.66
5	CSZ 4	0.5	0.5	0.30 ± 0.04		1.98

2.4. Central Composite Design (CCD) for Coating Process

The interactions between silica content and ZnO content and their effect on the responses of the sol–gel coating process were analyzed by response surface methodology. For this purpose, a design matrix was constructed using Design Expert® (v.13.0) software by selecting the central composite design (CCD) approach. The software generated a set of randomized experimental conditions to cover the full range of selected parameters and optimize the process. Table 2 summarizes the details of the design by enlisting design factors, their levels, responses, and number of experimental runs. Silica and ZnO content were selected as the design factors, whereas time to ignite, flame spread timing, and air permeability were selected as the responses to evaluate the synergistic effect of silica and ZnO on flammability and comfort properties of FR cotton fabrics. A total of 13 experimental runs were performed, as shown in the design matrix in Table 3. The corresponding experimental values of each response for the sol–gel coating process are also given in Table 3. These data were further analyzed by Design Expert® to fit them against the developed model equations and estimate regression coefficients. The significance of the developed regression models and regression coefficients was further analyzed using analysis of variance (ANOVA). The comparison between actual vs. predicted responses was evaluated by coefficient of determination (R^2) values. Three-dimensional response surface plots were also constructed to analyze the effect of process factors on individual process responses. Finally, the process optimization studies were performed by desirability analysis and the confirmatory experiments were performed against the recommended optimum conditions to confirm the robustness of the developed models and the adopted RSM approach.

Table 2. Summary of design.

Design	Design Model	Factors		Code-Level			Responses	No of Runs
		Actual	Coded	$-\alpha$	0	$+\alpha$		
Central composite design (CCD)	Quadratic	Silica Content (%)	A	0	0.25	0.50	Response 1: Time to Ignite (s) Response 2: Flame Spread Timing (s) Response 3: Air Permeability (mL/s)	13
		ZnO Content (%)	B	0	0.25	0.50		

Table 3. The design matrix.

Run	Factor 1 A: Silica Content (%)	Factor 2 B: ZnO Content (%)	Response 1 Time to Ignite (s)	Response 2 Flame Spread Timing (s)	Response 3: Air Permeability (mL/s)
1	0	0.50	3	16	225
2	0.50	0.25	5	19	221.5
3	0	0	2	11	235
4	0.25	0.25	4	16	225.3
5	0.50	0.50	6	20	220
6	0.25	0.25	4.6	16	224.8
7	0.50	0	3	16	223
8	0	0.25	3	15	229
9	0.25	0.25	4.2	17	225.1
10	0.25	0.50	5	18	222
11	0.25	0.25	4	17	224.9
12	0.25	0.25	4.5	16	225.2
13	0.25	0	3	15	228

3. Results and Discussion

3.1. Surface Morphology of FR-Finished Cotton Samples

The surface morphology of pure and modified cotton samples was analyzed using SEM. Figure 1 shows the micrographs of pure and modified cotton samples at 1.200× magnification using 5 KV. The morphology of silica (Aerosil 200) and ZnO nanoparticles observed in our treated samples represents a typical structure of these nanoparticles as reported in the literature [25]. It is depicted that pure cotton possesses a smooth surface. On the other hand, silica-and-ZnO-coated fibers had nanoparticles deposits on the fiber surface, which increased the roughness of the fiber. A similar behavior of nylon fabric is reported in the literature after sol–gel coating of silica nanoparticles [26]. The silica and zinc nanoparticles were evenly distributed on the outer layer of FR-finished fibers, as shown in Figure S1 in the Supplementary Materials at higher magnification. At higher loading of silica and zinc nanoparticles, excessive nanoparticles are visible on the fiber surface, which shows successful coating of nanoparticles on the cotton fiber. This homogenous spreading of particles results in improved flame-retardant properties and consequently delays cotton fabric combustion, as further explained below regarding flammability testing.

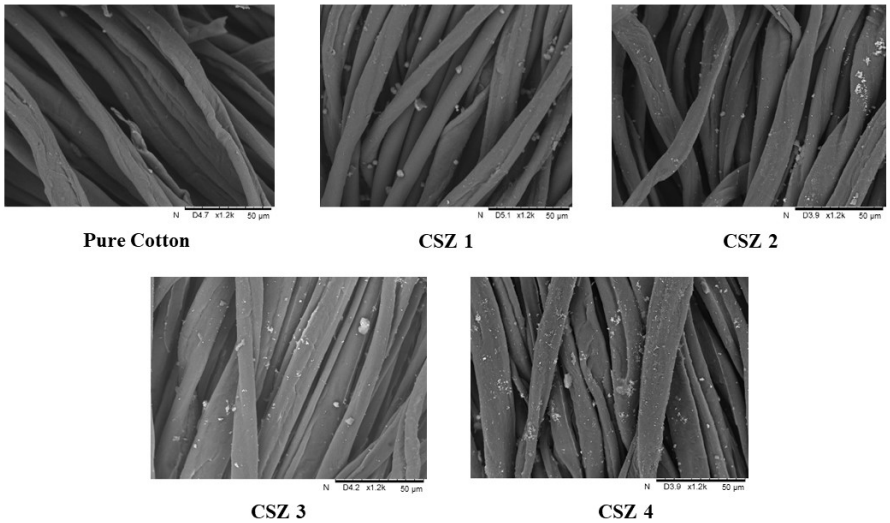
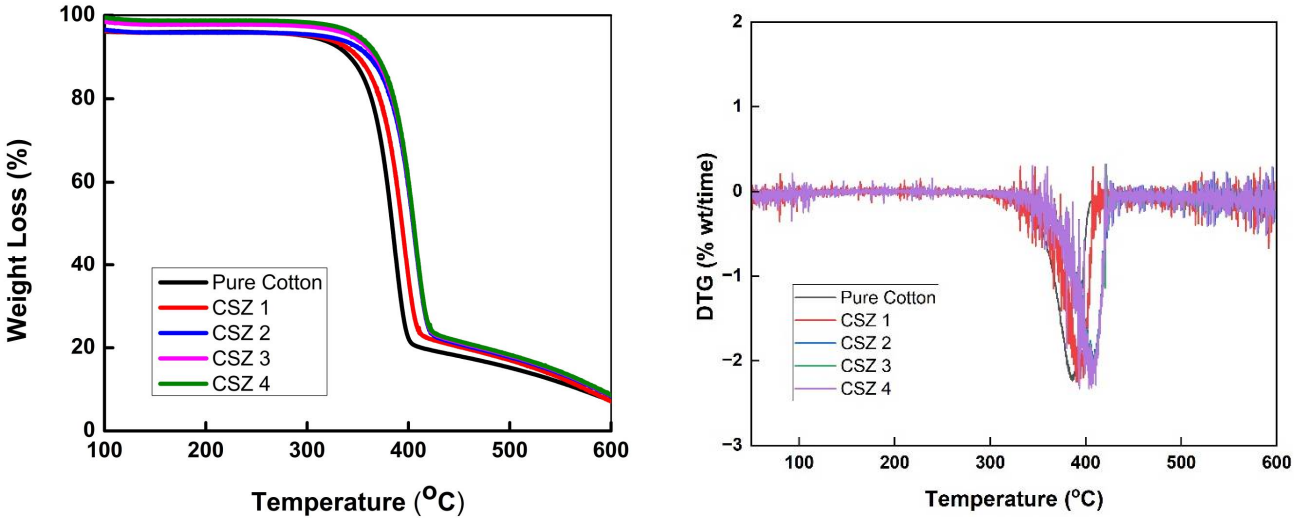


Figure 1. SEM images of pure and treated FR-finished cotton samples.

3.2. Thermal Properties

To further explore the thermal properties of FR-finished samples, coated and uncoated samples were examined by thermogravimetric analysis, and the corresponding results are shown in Figure 2a. All the samples show a similar trend of thermal degradation and completely degrade at 600 °C under nitrogen supply. Mostly, cotton fabrics tend to degrade in three phases. The first phase covers volatilization of cotton by converting it into volatile products. In the second phase, the main degradation of cotton samples takes place, leading to the third phase of carbonization [27]. The degradation of pure and FR-finished coated samples takes place between 350 °C to 450 °C, as shown in Figure 2b. It was noticed that the existence of SiO_2 and ZnO in the prepared nano-sols results in improved thermal degradation. The pure cotton degraded earlier as compared to CSZ1, CSZ2, CSZ3, and CSZ4. Thus, SiO_2 and ZnO coatings via sol–gel provide a protective layer on cotton, acting as a barrier against heat and oxygen. As a result, treated FR-finished samples show better thermal resistance as compared to pure cotton.



(**a**) (**b**)

Figure 2. (**a**) TGA and (**b**) DTGA of pure and treated FR-finished cotton fabrics.

3.3. Comfort Properties

Considering the importance of flame-retardant textiles in protective clothing, water content and wicking measurements are important aspects to be considered along with tensile and air permeability. Comfort properties of treated and untreated samples are given in Table 4. The cotton textiles treated with silica or zinc oxide through sol–gel coatings result in low water uptake. The water content of pure cotton is 72%, which was decreased from 60% to 53%. This is because of two main reasons: firstly, the increase in the hydrophobicity of cotton due to the presence of silica and zinc nanoparticles [20,28]; and secondly, due to the rough surface of cotton after finishing, which was observed in SEM analysis [29,30]. Similarly, the wicking length of pure cotton was 60 mm, which was decreased to 32 mm, showing that these coatings restrict the path for liquor or dye to travel vertically throughout the length of fabric. These outcomes indicate that coating via sol–gel can exhibit less absorbency.

Table 4. Comfort properties of pure and FR-finished cotton fabrics.

No.	Samples	Water Content (%)	Wicking Length (mm)	Bending Length (mm)	Air Permeability (mL/s)	Tensile Strength (N)
1	Pure Cotton	72	60	11	235	432.9
2	CSZ 1	60.6	35	11.6	230	522.7
3	CSZ 2	58.8	45	11.2	229	555.4
4	CSZ 3	54.2	38	11.8	225	555.5
5	CSZ 4	53.7	32	12.6	220	580.2

The bending length of fabrics represents the stiffness of fabric. The stiffness of any object can be defined as the extent to which it resists deforming in response to applied force. It is directly proportional to bending length, which means it increases with an increase in bending length. This can be measured by using the cantilever principle. Thus, the length of fabric that may bend under its own weight is considered the bending length [31,32]. The lower the bending length of fabric, the lower the stiffness of the fabric. The bending length of fabric is also considered one of the components of drape. Here, in this work, the bending length of pure cotton was 11 mm and increased up to 12.6 mm. Although this increase is not too high, it is again due to the presence of cross-linkers and nanoparticles in sols. However, as these sols are converted to gel after curing, the fiber retains its flexibility and bending after treatments [33].

Table 4 also shows that the treated cotton fabric showed slightly less air permeability compared to pure cotton fabric. This is because the particle size of silica and zinc oxide is in the range of the nanoscale. Among all treated samples, CSZ 1 showed the lowest change in air permeability in treated samples, while CSZ 4 showed the maximum change in air permeability. These results show that the concentration of nanoparticles in nano-sols also affects the overall comfort properties of the protective clothing, and an optimum concentration of nanoparticles should be used for better comfort properties. Additionally, it can also be observed from Table 4 that these coatings with different combinations of nanoparticles result in increased tensile strength. This is because of the crosslinking effect of sol–gels due to the presence of TMOS crosslinker. These results are supported by various studies reported in the literature [20,29,34].

3.4. Analysis of Central Composite Design and RSM Modeling

3.4.1. Statistical Analysis and RSM Modeling

The data reported in Table 3 were used to develop the model Equations (1)–(3) using response surface methodology with a central composite design. These models were developed to estimate the effect of process parameters, i.e., silica and ZnO content, on process responses, viz., time to ignite, flame spread timing, and air permeability. By this statistical analysis, dominating, influential, significant, and non-significant factors can be determined for the optimization of the sol–gel coating process. The following equations can be used to predict and estimate time to ignite (Equation (1)), flame spread time (Equation (2)), and air permeability (Equation (3)) against silica and ZnO content for the development of cotton protective clothing:

$$\text{Time to Ignite} = 4.29 + A + B + 0.5AB - 0.38A^2 - 0.38B^2 \quad (1)$$

$$\text{Flame Spread Time} = 16.31 + 2.17A + 2B \quad (2)$$

$$\text{Air Permeability} = 225 - 4.08A - 3.17B + 1.75AB + 0.46A^2 + 0.21B^2 \quad (3)$$

Equations (1)–(3) are reported in terms of coded factors, i.e., silica content (A) and ZnO content (B), for process responses, viz., time to ignite, flame spread time, and air permeability. The process responses at any given level of factors can be assessed using these equations. Analysis of variance (ANOVA) for time to ignite, flame spread time, and air permeability was also carried out as shown in Tables 5–7. ANOVA results show that all

model terms are significant, since *p*-values are less than 0.0500 for the developed regression models [18]. The F-values for time to ignite, flame spread time, and air permeability are 56.76, 56.67, and 301.80, respectively, which also shows the accuracy of the models. A greater F-value shows the significance of the model [35]. Finally, the coefficient of determination, i.e., R^2 value, can be used to test the fitness of the models. The R^2 and adjusted R^2 values for time to ignite, flame spread time, and air permeability are in the range of 0.90–0.99, as shown in Tables 5–7. This shows a good fit between the experimental and model data [36]. Finally, the lack of fit is not significant for all models, which shows that the predicted data fit well against the experimental data. The comparison between actual vs. predicted values for time to ignite, flame spread time, and air permeability for pure and treated cotton samples is shown in Figure 3. The graphs show a good distribution of data points along the diagonal line, which shows the suitability of the developed regression models for silica and ZnO coating process using the sol–gel method.

Table 5. Analysis of variance for Response 1: Time to Ignite.

Source	Sum of Squares	Df	Mean Square	F-Value	*p*-Value	
Model	14.26	5	2.85	56.76	<0.0001	Significant
A-Silica Content	6.00	1	6.00	119.41	<0.0001	
B-ZnO Content	6.00	1	6.00	119.41	<0.0001	
AB	1.00	1	1.00	19.90	0.0029	
A^2	0.3902	1	0.3902	7.77	0.0270	
B^2	0.3902	1	0.3902	7.77	0.0270	
Lack of Fit	0.0397	3	0.0132	0.1698	0.9115	not significant
R^2	0.9759					
Adjusted R^2	0.9587					

Table 6. Analysis of variance for Response 2: Flame Spread Time.

Source	Sum of Squares	Df	Mean Square	F-Value	*p*-Value	
Model	52.17	2	26.08	56.67	<0.0001	significant
A-Silica Content	28.17	1	28.17	61.20	<0.0001	
B-ZnO Content	24.00	1	24.00	52.14	<0.0001	
Lack of Fit	3.40	6	0.5671	1.89	0.2799	not significant
R^2	0.9189					
Adjusted R^2	0.9027					

Table 7. Analysis of variance for Response 3: Air Permeability.

Source	Sum of Squares	Df	Mean Square	F-Value	*p*-Value	
Model	173.53	5	34.70	301.80	<0.0001	significant
A-Silica Content	100.04	1	100.04	870	<0.0001	
B-ZnO Content	60.17	1	60.17	523.23	<0.0001	
AB	12.25	1	12.25	106.53	<0.0001	
A^2	0.58	1	0.58	5.10	0.0587	
B^2	0.12	1	0.12	1.06	0.3369	
Lack of Fit	0.69	3	0.21	4.91	0.0792	not significant
R^2	0.9954					
Adjusted R^2	0.9921					

The residual plots versus the experimental runs are shown in Figure 4. From all residual plots, it is evident that the data are randomly distributed along the estimated regression line at zero (0). There is no regular or unusual pattern in the residuals, which shows the effectiveness of the randomization process in the design matrix and suitability of the models [36].

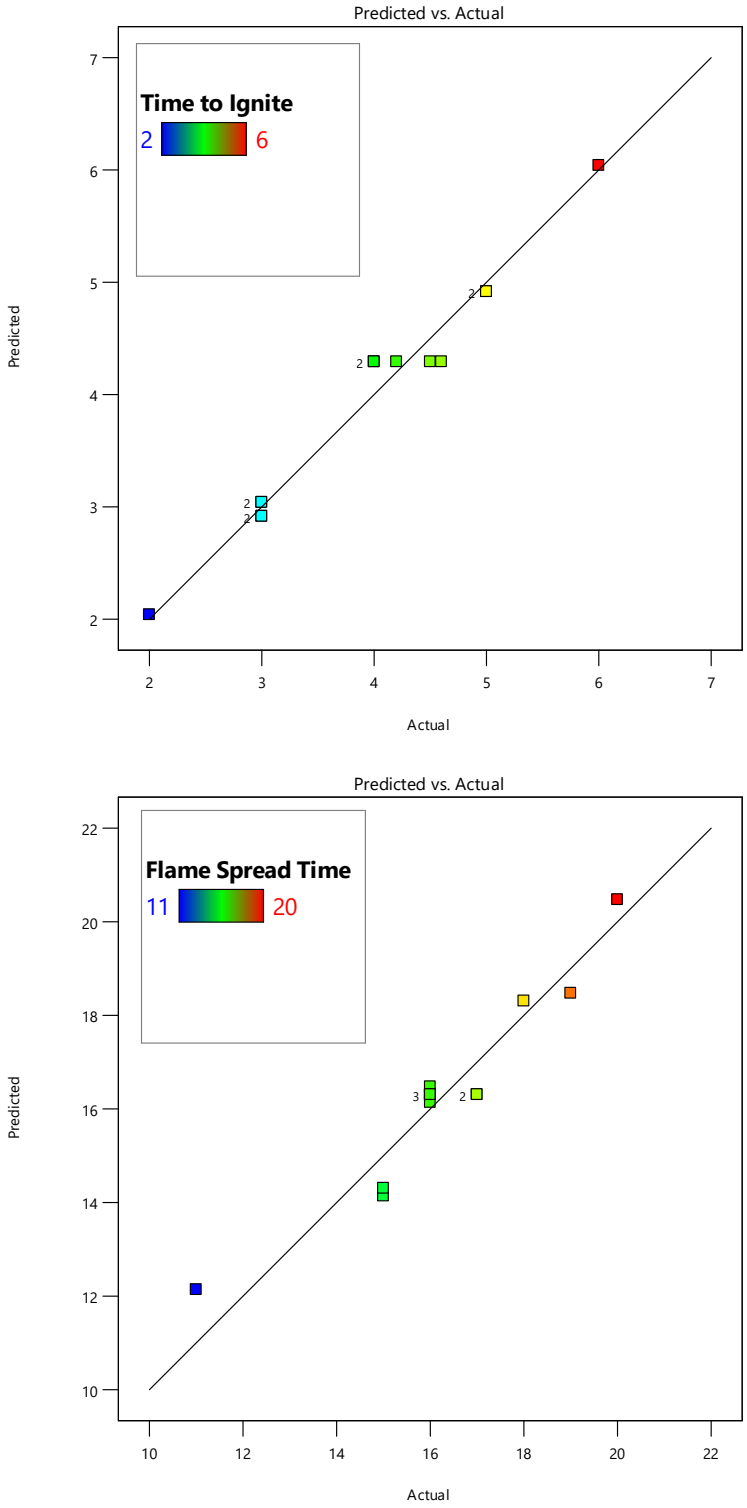


Figure 3. *Cont.*

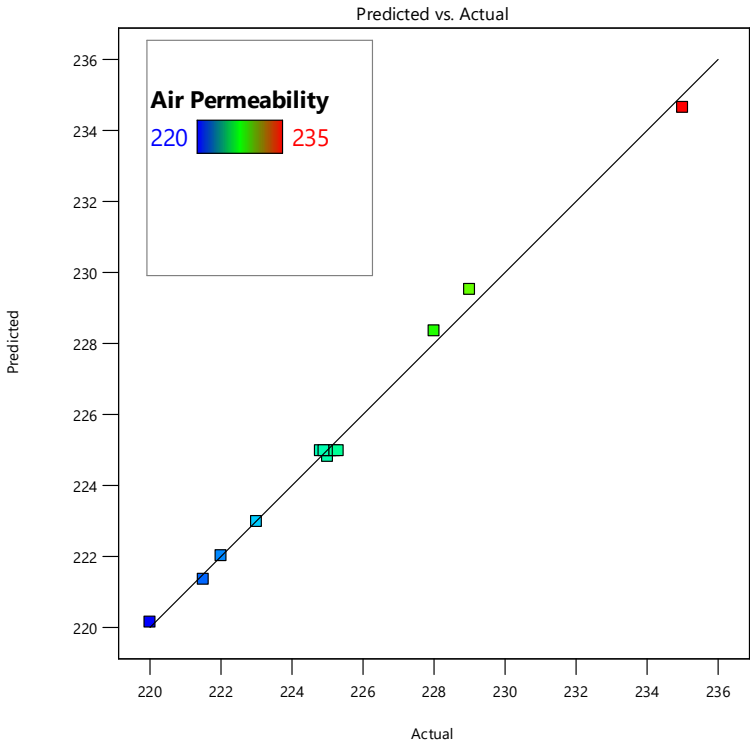
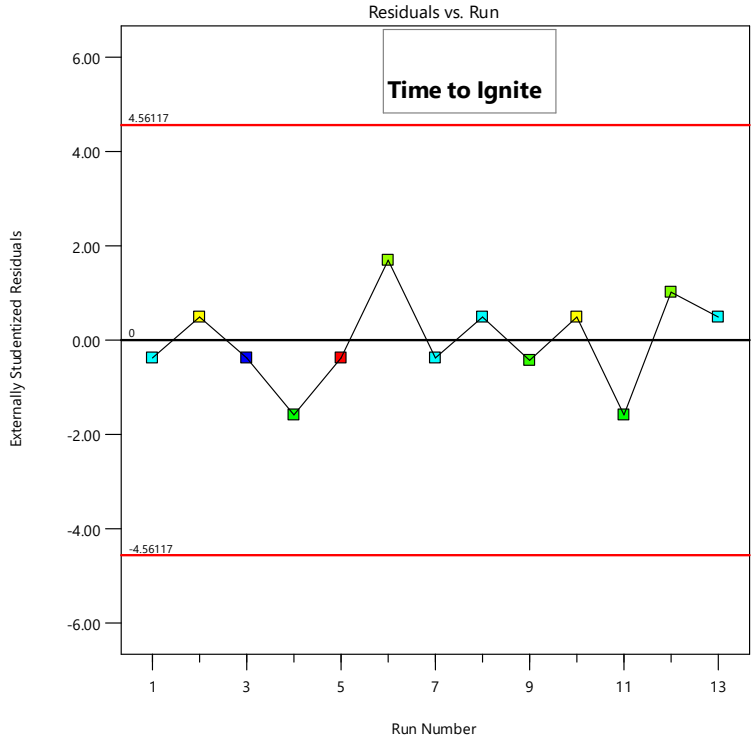


Figure 3. Predicted vs. actual response for process responses.



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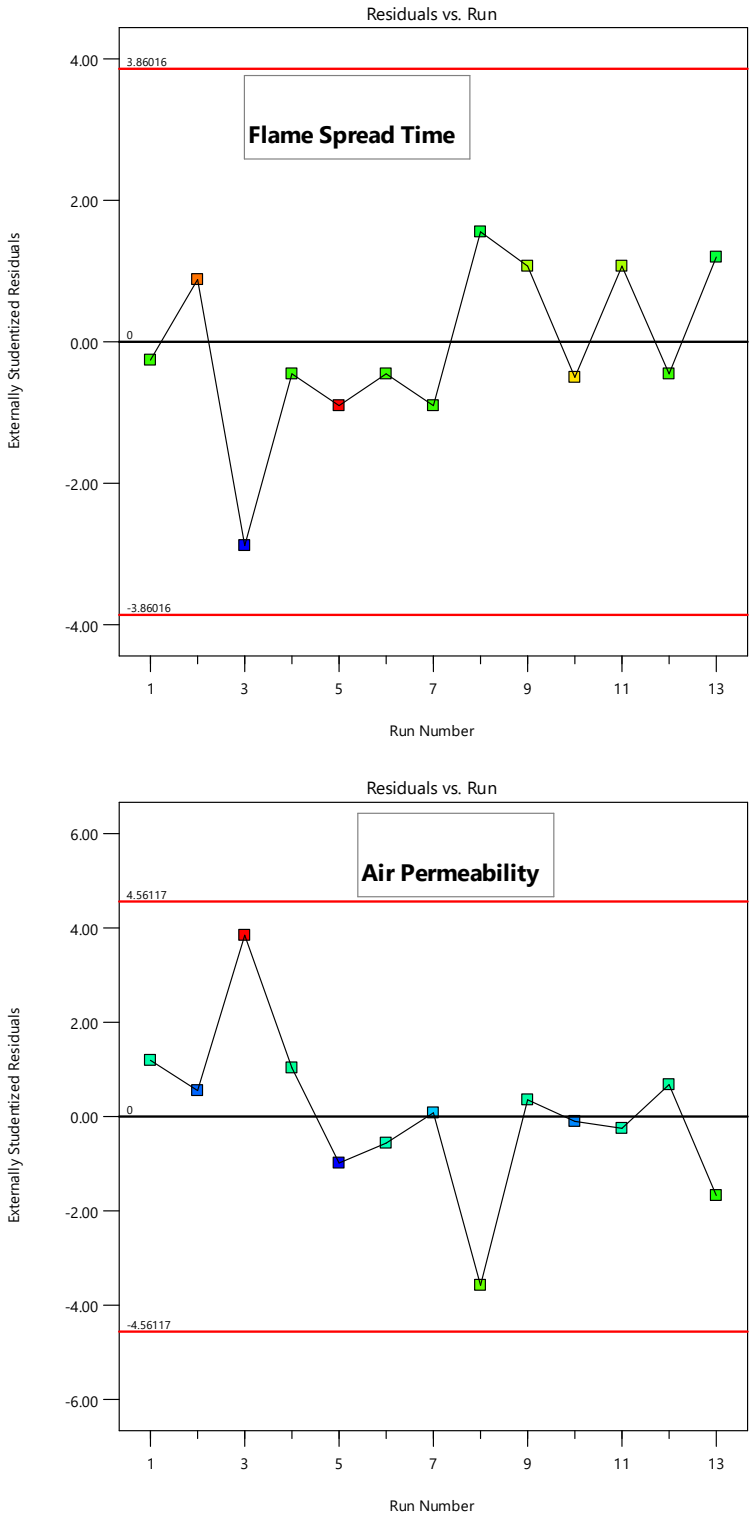

Figure 4. Residual plots for central composite design.

3.4.2. Effect of Process Parameters on Process Responses

The effect of silica and ZnO sol–gel coating on time to ignite, flame spread time, and air permeability of treated cotton samples was evaluated, as shown in Figure 5a–c. With the increase in silica and ZnO coating, time to ignite increased as depicted in Figure 5a, which shows the delayed ignition of treated cotton samples. The 3D plot corresponds to the quadratic model (Equation (1)). The maximum time to ignite was noted at for 0.50% coating

of silica and ZnO. A comparison of flammability properties with the previous literature is given in Table S1 in the Supplementary Materials. A similar trend was observed for flame spread speed, as shown in Figure 5b. However, in this case, a linear relation was observed in the 3D plot, which is also represented by a linear model (Equation (2)). Contrary to this, a decrease in air permeability was noticed for FR-treated samples because of the presence of silica and ZnO nanoparticles on the fiber. The nanoparticles hindered the air permeability by reducing the available transport sites in the fiber [37,38].

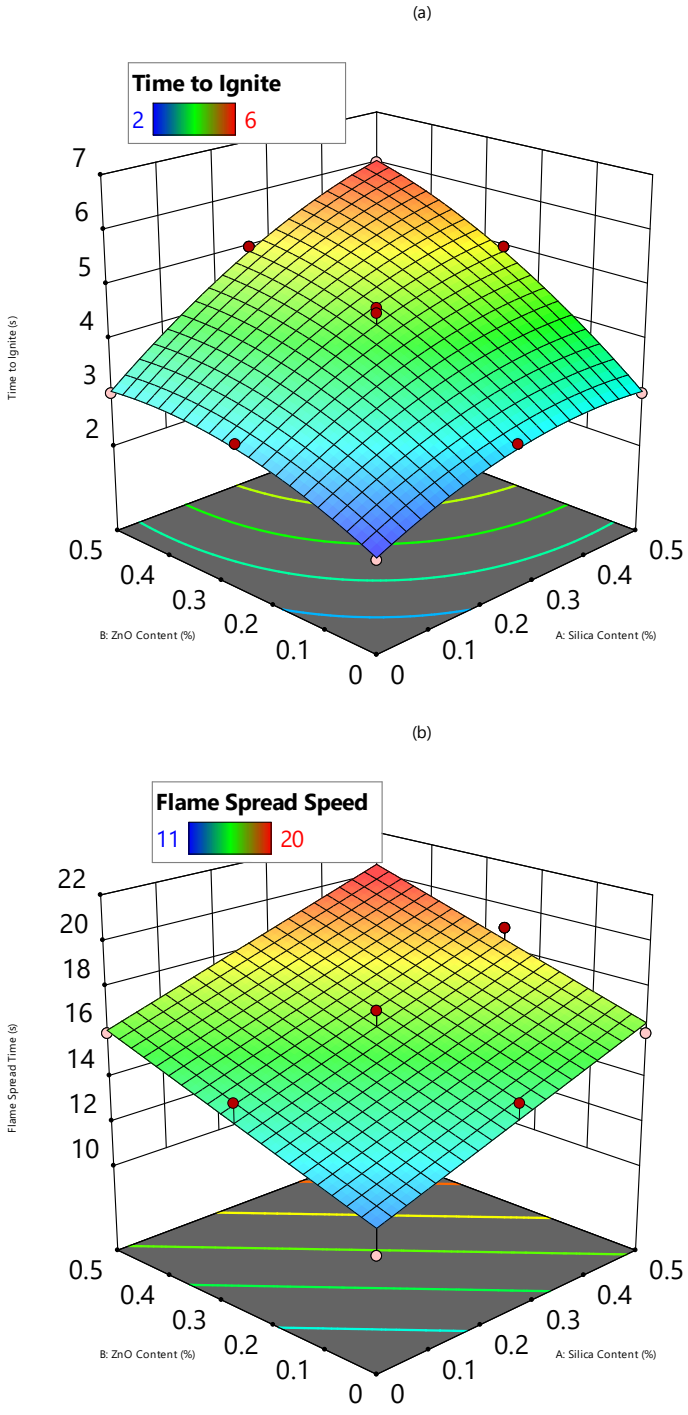

Figure 5. *Cont.*

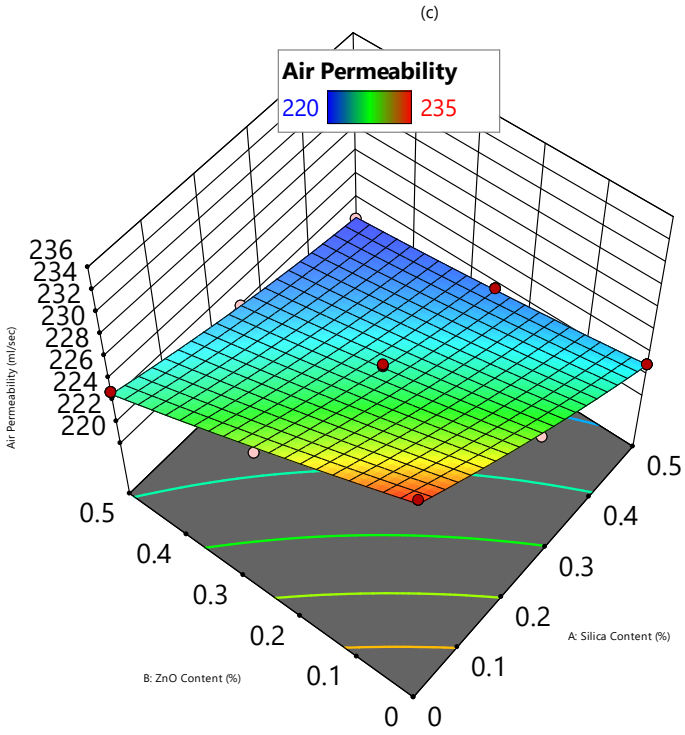

Figure 5. Three-dimensional plots showing the effect of silica and ZnO coating on (**a**) time to ignite, (**b**) flame spread time, and (**c**) air permeability.

3.4.3. Optimization Analysis

The process optimization of the coating process of FR cotton samples for protective clothing applications was evaluated by RSM models. From the effect of process parameters, it was observed that time to ignite and flame spread time have a direct relation with silica and ZnO concentration. On the other hand, air permeability has an inverse relationship with silica and ZnO concentration. Therefore, determining an optimum concentration of silica and ZnO nanoparticles or an 'optimum design point' is essential for the optimized protective properties. For the optimization analysis, 'the-larger-the-better' approach was adopted to determine the ideal cutting conditions by Design Expert® software (version 13, Stat-Ease Inc., Minneapolis, MN, USA) [39]. This criterion was selected because delayed time to ignite and extended flame spread time are preferred for FR protective clothing. Similarly, enhanced air permeability is required for better comfort properties. Under these constraints, the software proposed only one optimum solution or optimum design point, which is shown in Table 8. It was noticed that the maximum desirability was exhibited by flame spread speed, which was 0.731 for the overall optimization criteria, compared to other flammability and comfort properties, as shown in Figure 6. The air permeability showed the lowest desirability (0.20), which shows the complexity of the optimization problem. Therefore, the overall desirability value of the coating process under these constraints was 0.527. The ramp function graph shown in Figure 7 represents the suggested optimization results for process factors and process responses. The dot on the ramp shows the optimum level of each process factor and process response under the employed optimization constraints.

Table 8. Process optimization results.

No.	Silica Content	ZnO Content	Time to Ignite (s)	Flame Spread Time (s)	Air Permeability (mL/s)	Desirability
1	0.302	0.353	4.876	17.582	223.035	0.527

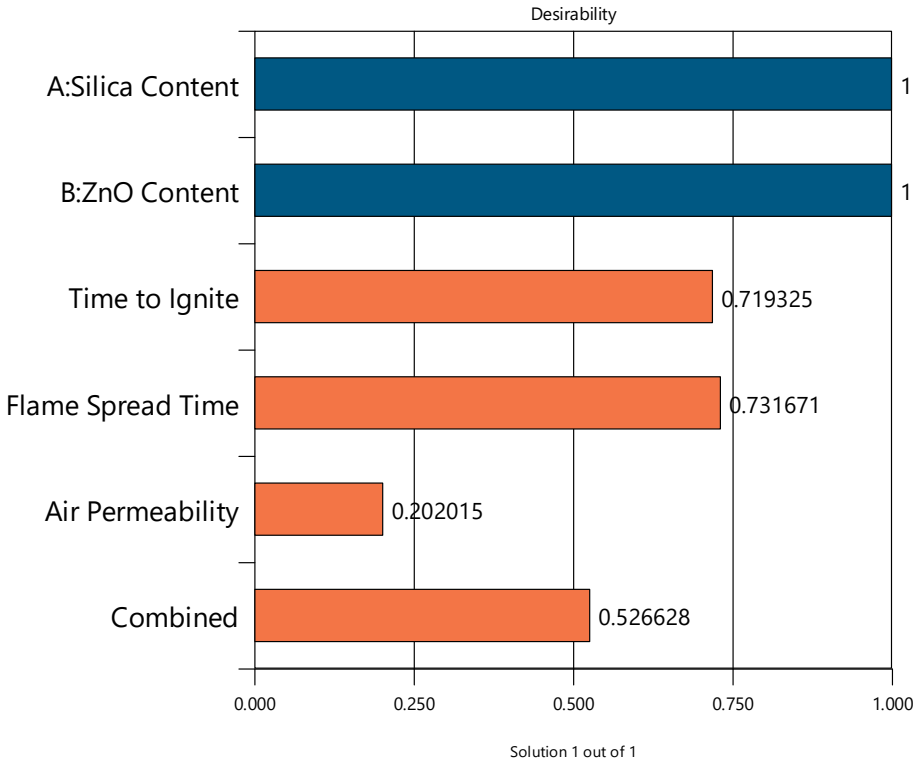

Figure 6. Desirability bar chart for process optimization of coating process.

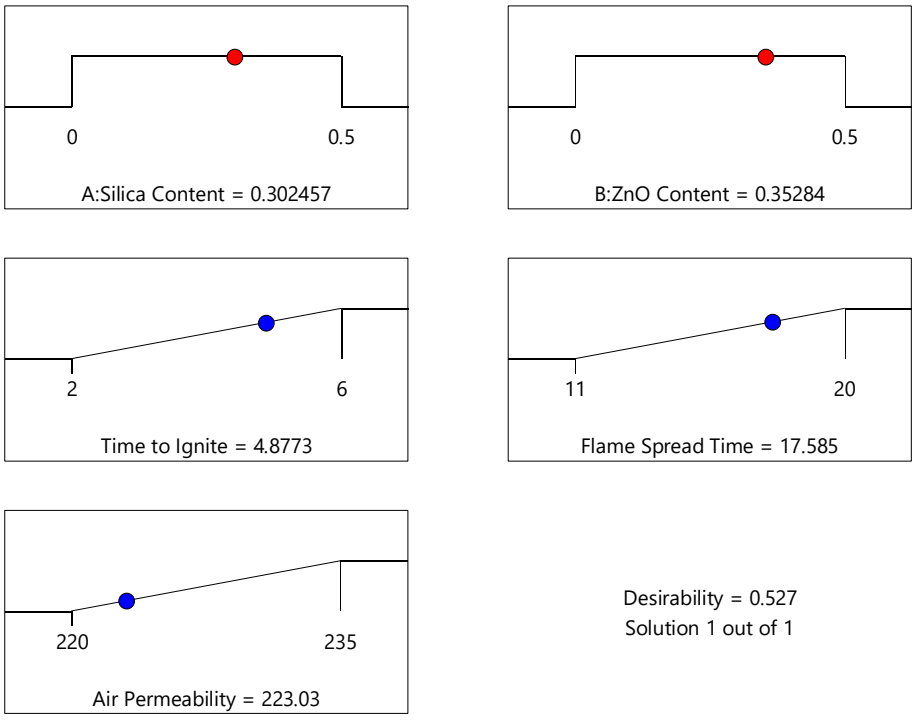

Figure 7. Ramp function graph of the selected optimized solution.

The confirmatory experiments were completed under the optimum conditions reported in Table 8. Table 9 shows the experimental values of confirmatory runs using the optimized solution. For this purpose, three independent samples with optimized silica and ZnO content were fabricated and tested. The corresponding statistical analysis of these experimental runs is given in Table 10. An excellent agreement was observed between the values predicted by optimization analysis reported in Table 8 and the experimental values

reported in Table 9. Hence, it was concluded that a silica concentration of 0.302% and a ZnO concentration of 0.353% yielded the best protective properties among the studied FR cotton samples.

Table 9. Experimental values of confirmatory runs at the optimized solution.

No.	Time to Ignite (s)	Flame Spread Time (s)	Air Permeability (mL/s)
1	4.84	17.49	223.53
2	4.77	17.33	221.87
3	4.81	17.41	224.63

Table 10. Summary of confirmation runs at the optimized solution.

Analysis	Actual Mean	Actual Median	Std Dev	N	SE Pred	95% PI low	Data Mean	95% PI High
Time to Ignite (s)	4.78402	4.78402	0.224157	3	0.159072	4.40787	4.80667	5.16016
Flame Spread Time (s)	17.3617	17.3617	0.678422	3	0.445898	16.3682	17.41	18.3552
Air Permeability (mL/s)	223.317	223.317	0.339104	3	0.240645	222.748	223.343	223.886

4. Conclusions

In conclusion, this study reports a comprehensive investigation into the synergistic coating effect of silica and zinc oxide on fire-retardant-finished cotton fabric designed for protective clothing applications. The optimization of the sol–gel coating process on FR cotton fabrics was successfully accomplished by the utilization of central composite design (CCD) and response surface methodology (RSM). The prepared silica and zinc oxide sol–gel FR coatings exhibited homogenous particle dispersion on the cotton fabric surface, as confirmed by SEM analysis. The thermal stability of the treated FR cotton fabrics was remarkably improved with the incorporation of silica and zinc oxide nanoparticles, as demonstrated by thermogravimetric analysis results. The treated FR cotton fabrics exhibited enhanced flame retardancy while maintaining excellent comfort properties, highlighting their suitability for protective clothing applications. Noticeably, lower water uptake and decreased wicking showed the lower absorbency of the treated cotton fabrics while maintaining their flexibility and bending after sol–gel treatment. Moreover, the optimized concentrations of silica and zinc oxide were found to be 0.302% and 0.353%, respectively, through confirmatory experiments, indicating the effectiveness of the optimization process. Remarkably, the results of the RSM analysis showed a high level of agreement between predicted and experimental values for flammability and comfort parameters such as time to ignite, flame spread time, and air permeability, with R^2 values exceeding 0.90. Overall, this study highlights the effectiveness of synergistically coating silica and zinc oxide nanoparticles onto cotton fabric using the sol–gel process to enhance its flammability resistance, thereby contributing to the advancement of materials for protective clothing in high-risk environments.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fib12050044/s1, Figure S1: SEM images of Pure and Treated Cotton at Higher Magnification; Table S1: Comparison of flammability properties of FR finished materials via Sol-gel [7,40–44].

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