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AN OPTIMIZATION STUDY ON THE SOL–GEL PROCESS TO OBTAIN MULTIFUNCTIONAL DENIM FABRICS

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Abstract:

This study introduces the results of an optimization study on sol–gel application conditions applied to obtain multifunctional (water repellent/flame retardant) denim fabrics using the Design Expert software and a step-by-step approach. The study started by obtaining the proper drying/condensation parameters and water-repellent additive amount, followed by determining the proper co-precursor and flame-retardant additive amount, and finally covering the mechanical tests of the samples to determine if the results would be applicable for industrial purposes. The results indicate that it is possible to approach the optimum process conditions applicable to industrial-scale working conditions to produce denim fabrics with high levels of water repellency and flame retardant performance.

Keywords:

Sol–gel, denim fabric, water repellent, flame retardant

1. Introduction

Denim fabric is mainly characterized by certain physical properties like high abrasion, high weight, tensile and tear resistance compared to frequently used cotton fabrics such as gabardine or poplin produced from cotton yarn [1]. It is also a popular choice in the clothing industry because of its breathable structure with a good level of thermal comfort owing to its hydrophilic nature, and it has been produced for casual wear for many years.

In recent years, various processes (coating/lamination, ozone fading, laser finishing, sandblasting, and resin finishing) have been applied to denim products to provide a new look and/or functionalities. There is an important market demand in the denim industry for functional properties, especially for liquid repellence and flame retardancy, especially when considering the use of denim for work clothes [2]. Combining these functionalities and producing multifunctional textiles has a large market share. In the textile sector, sol–gel application is expected to lead to the production of multifunctional fabrics because it is easy to perform and does not require special conditions or high temperatures. The sol–gel process is simply defined as the formation of a homogeneous solution with a precursor that, through hydrolysis and condensation reactions, originates a colloidal solution denominated by sol. By condensation, the sol is transformed into an integrated and often nanostructured solid network with a liquid phase (including solvent, acid, or alkali as catalysts and additives for various functionalities) in the interstices, which is called a gel. It generally includes a pad-dry-cure process line, which consists of impregnation of the fabric by a sol bath followed by drying and curing under the appropriate conditions [3,4]. The sol–gel technique gained interest since it has diverse applications suitable for bulk products, and the sol–gel matrix can be chemically modified by using various precursors, co-precursors, and additives [5]. There are various studies on sol–gel applications over textile surfaces exploring the modification of sol–gel coatings with specific additives, i.e. for antimicrobial activity [6–8], photochromic activity [9], controlled drug delivery [10,11], insect-repellent property [12], phase change performance [13], and UV protection [7]. Various studies have also pointed to the high contribution of drying and condensation, which would be accepted as the most critical parameters on the final product performance by largely controlling the thickness, density, porosity, mechanical properties, and adhesion of xerogel to the fiber surface [14–18].

This study aimed to optimize the drying and condensation parameters and finalize the application recipe of a sol–gel bath to produce a water-repellent and flame-retardant multifunctional denim fabric using additives in determined amounts. The Design Expert software and a step-by-step approach were used for the optimization of sol–gel process conditions.

2. Materials and methods

2.1. Materials

The properties of the denim fabric used in this study are listed in Table 1. The fabric was supplied after caustic soda scouring by Çalık Denim/Turkiye. The chemicals used in this study are tetraethylorthosilicate (TEOS), hexadecyltrimethoxysilane (HDMS), trimethoxyphenylsilane (TEFS), 3-(triethoxysilyl)propylamine (TSP), dodecyltrimethoxysilane (DTMS), glycidoxypropyltrimethoxysilane (GPTMS), ethanol (analytical purity), 0.01 N HCl solution, urea, Tween 20 (surfactant), non-fluorinated commercial water repellent (Bodo Möller Chemie/Germany),

Table 1. Properties of the denim sample

Fiber composition	Woven type	Warp × weft density (ends and picks/cm)	Warp yarn number (Ne)	Weft yarn number (Ne)	Weight (g/m^2)
97%:3%, cotton: elastane	3/1 Z	21 × 18	14/1	18/1	275

Table 2. Input variables used in the sol–gel bath in the first step

Input variables	Levels		
	−1	0	+1
Drying temperature (°C)	90	100	110
Drying time (min)	5	10	15
Condensation temperature (°C)	130	150	170
Condensation time (min)	1.5	5	20
Amount of water-repellent additive (mL)	0	10	50

and diammonium phosphate (DAP). TEOS was employed as the precursor, HDMS, TEFS, TSP, and DTMS were used as co-precursors, and GPTMS was used as an organic modifier, all of which have alkoxysilane chemistry for the synthesis of hydrophobic sol, urea as cross-linkers, and HCl for acidic hydrolysis, as suggested previously [19–22]. Commercially available water-repellent agents and DAP were selected as additives to improve hydrophobicity and flame-retardant performance. The flame-retardant activity of DAP is based on a decrease in the temperature of combustion, leading to the formation of large amounts of chars [23], where non-fluorinated water repellents are expected to enhance the hydrophobic behaviour of xerogels.

2.2. Methods

The step-by-step approach used in this study consisted of four steps: the first step was to optimize the drying/condensation conditions and amount of water-repellent chemicals as additives; the second step for the selection of the co-precursor;

Table 3. First suggested trial conditions in the first step

Trial number	Drying temperature (°C)	Drying time (min)	Condensation temperature (°C)	Condensation time (min)	Commercial water-repellent chemical (mL/100 mL bath)
1	94.05	15.00	138.11	10	3.99
2	90.00	15.00	150.00	5	2.50
3	94.05	15.00	161.89	2.5	3.99
4	105.95	7.00	138.11	10	37.50
5	100.00	10.00	130.00	20	2.50
6	105.95	7.00	161.89	2.5	25.00
7	100.00	10.00	150.00	5	2.50
8	105.95	7.00	138.11	10	25.00
9	100.00	10.00	150.00	5	0.00
10	94.05	15.00	138.11	10	50.00
11	110.00	5.00	150.00	5	2.50
12	100.00	10.00	150.00	5	2.50
13	100.00	5.00	150.00	5	2.50
14	105.95	7.00	161.89	2.5	37.50
15	100.00	10.00	150.00	5	5.00
16	100.00	10.00	170.00	1.25	2.50
17	100.00	10.00	150.00	5	2.50
18	100.00	10.00	150.00	5	50.00
19	100.00	10.00	150.00	5	2.50
20	94.05	15.00	161.89	2.5	37.50

Table 4. Final suggested trial conditions in the first step

Trial number	Drying temperature (°C)	Drying time (min)	Condensation temperature (°C)	Condensation time (min)	Commercial water-repellent chemical (mL)
1	95.00	15.00	140.00	10	4.00
2	90.00	15.00	150.00	5	2.50
3	95.00	15.00	160.00	2.5	4.00
4	105.00	7.00	140.00	10	37.50
5	100.00	10.00	130.00	20	2.50
6	105.00	7.00	160.00	2.5	25.00
7	100.00	10.00	150.00	5	2.50
8	105.00	7.00	140.00	10	25.00
9	100.00	10.00	150.00	5	0.00
10	95.00	15.00	140.00	10	50.00
11	110.00	5.00	150.00	5	2.50
12	100.00	5.00	150.00	5	2.50
13	105.00	7.00	160.00	2.5	37.50
14	100.00	10.00	150.00	5	50.00
15	100.00	10.00	170.00	1.25	2.50
16	95.00	15.00	160.00	2.5	37.50

the third step for determining the amount of DAP to finalize the sol–gel bath process, and the fourth step was to assess the mechanical properties of the treated samples.

For the experimental plan, which was determined by the Design Expert software (Stat-Ease/USA), the input variables were introduced as drying/condensation (temperature and duration) and the commercially available water-repellent chemical additive amount in mL for 100 mL of the sol–gel bath. The Design Expert software used response surface methodology, which is a set of systematic tools to investigate the effect of a wide range of variables and their levels. The software then models an experimental design with a minimum number of trials and selected variable parameters, as well as the effect of input variables on any output data, using polynomial equations by another tool. In this study, Design Expert software was used in two ways. The levels of the input variables were determined based on the knowledge obtained from the preliminary experience of the authors and are shown in Table 2.

The sol–gel bath to be applied in the first step was prepared as follows: TEOS was dissolved in ethanol, and then distilled water was added to the solution. GPTMS was then dropped, and the solution was stirred using a magnetic stirrer for 60 min until a transparent solution was obtained. The pH was adjusted to 4.5 by HCl solution; urea, Tween 20, and water repellent were added while stirring. The volume-to-volume ratios of TEOS, GPTMS, urea, Tween 20, and the solution bath were 1:10, 1.25:10, 0.25:10, and 0.25:10, respectively.

Table 5. Output data of the first step

Trial number	Contact angle* (°)
0 (nontreated sample)	94.40
1	138.37
2	138.96
3	121.83
4	131.72
5	140.65
6	143.64
7	134.05
8	140.99
9	123.90
10	143.23
11	143.17
12	143.17
13	136.88
14	143.84
15	130.25
16	140.12

*Average of ten measurements.

Table 6. Optimized input and output data set using the Design Expert in the first step

Drying temperature (°C)	Drying time (min)	Condensation temperature (°C)	Condensation time (min)	Commercial water-repellent chemical (mL/100 mL)	Expected contact angle (°)
99.97	7.44	148.34	4.99	37.17	146.347
105.05	7.02	139.62	9.78	41.66	140.030
101.03	9.41	139.24	15.19	21.35	141.311
98.88	11.16	162.41	4.41	38.84	148.846
98.18	11.59	152.15	15.82	19.59	119.289
100.89	9.68	154.44	7.19	16.22	135.697
100.22	9.97	156.69	11.56	36.52	148.288
102.29	8.55	149.28	11.66	17.80	119.716
98.18	11.88	156.12	5.11	34.98	147.601
99.92	10.58	136.94	11.02	41.72	131.113

Table 7. Test results of repeated trials in the first step

Trial number	Contact angle* (°)
5	138.61
8	141.17
10	142.03

*Average of ten measurements.

In the second step, HDMS, TEFS, TSP, and DTMS were applied in separate baths with a volume-to-volume ratio of 0.5:10. After selecting the precursor, DAP was applied in varying amounts (6 and 12 g) to 100 mL of the solution. The denim samples were then tested for contact angle and limit oxygen index (LOI) measurements according to ASTM D5946 and ASTM D 2863 as output data for water-repellent and flame-retardant performance assessments. Contact angles were measured with a contact angle measurement system (KSV Cam200/Finland) at room temperature (23°C) using distilled water with a droplet volume of 10 µL.

When the sol–gel bath was finalized (after the third step), the treated denim samples were also subjected to weight (ASTM D3776), abrading fastness (AATCC 8), elasticity (ASTM 3107), breaking (ASTM D 5034), and tearing strength (ASTM D 1424) measurements to evaluate the final performance of fabrics (the fourth step)

Table 8. Test results of the second step

Recipe in the second step	Contact angle* (°)
With HDMS	151.91
With TEFS	160.56
With TSP	156.25
With DTMS	158.24

*Average of ten measurements.

3. Results and discussion

The Design Expert software proposed a trial matrix (the minimum number of trials) with the suggested input variable parameters, as shown in Table 3. However, when some of the model-supported input data were rounded up, and duplicate trials were deleted, the final application plan was obtained for use in the first step, as shown in Table 4. When the trial setup was ready, the denim samples were dipped into a sol–gel bath and squeezed using a lab-scale foulard with 75% pick-up. The samples were dried and cured under the conditions listed in Table 4. All the applications were repeated three times. The output data were contact angle, and Table 5 shows the output data obtained.

A positive correlation was found between the water-repellent chemical amount and water-repellent performance. However, it was possible to obtain a satisfactory contact angle value with a lower amount of chemicals because of the effect of drying and condensation conditions. Then, the Design Expert software was run again between the minimum and maximum limits of the obtained outputs and ten new suggested application conditions with the expected output (contact angle value) were derived, as given in Table 6. Table 6 shows that when the lowest suggested amount of water-repellent chemical was 16.22 mL, a contact angle of >135° would be obtained. Therefore, a new application set was prepared where the commercial water-repellent chemical was 16 mL for 100 mL of the bath, and drying and condensation conditions were as used in trial numbers 5, 8, and 10 (which applied low, medium, and high amounts of the suggested

Table 9. Test results of the third step

Recipe in the third step	Contact angle* (°)	LOI (%)
6 g DAP	133.62	24.7
12 g DAP	130.61	39.8
Untreated sample	94.40	19.0

*Average of ten measurements.

Table 10. Test results in the fourth step

Recipe in the third step	Weight (g/m^2)	Abrading fastness		Elasticity (%)	Breaking strength in the warp direction (kgf)	Tearing strength in the warp direction (kgf)
		Dry	Wet			
12 g DAP	355	3/4	1/2	49	80	4,967
Untreated sample	275	4	1/2	50	92	5,219

water-repellent chemicals), as shown in Table 4. These applications were completed by a foulard with three repeats, and the contact angle measurements were repeated. The results in Table 7 show that sol–gel application, with selected drying/condensation conditions and water-repellent amounts, resulted in very good water-repellency performance (contact angle values of between 138 and 142°). Because Experiment 8 applied lower drying and condensation times, it was selected for use in the following steps of the study.

In the second step, four new sol–gel baths were prepared, as described above, differing from the dropping of the co-precursor. All of them included 16 mL of commercial water-repellent chemicals (the final bath was adjusted to 100 mL). These applications were completed in the same manner as in the first step, with drying and condensation conditions of trial number 8. The contact angle measurement results of the second step are shown in Table 8.

Table 8 shows that all selected precursors positively affected the water-repellent performance of the denim samples; TEFS gave the best performance. In the third step, new sol–gel baths with TEFS and 16 mL of water-repellent chemicals were prepared with different DAP amounts. The application, drying, and condensation conditions were the same as in the second step, and the samples were later subjected to contact angle and LOI measurements. The results are shown in Table 9.

A contact angle of water droplet >130° on cotton fabrics is regarded as advanced hydrophobicity [24] and obtainable with fluorochemicals [25], and an LOI of >25% as flame-retardant [26]. Thus, Table 9 shows that denim fabric treated with the sol–gel bath, including h 6 and 12 g of DAP, would give a multifunctional (water-repellent and flame-retardant) performance; however, considering the higher LOI value, the sol–gel bath with 12 g of DAP, was chosen for the finalized sol–gel application.

Table 10 lists the mechanical properties of the samples measured in the fourth and last steps of the study. The results revealed that the finalized sol–gel bath decreased elasticity, abrasion fastness, breaking, and strength values of denim samples due to acidic hydrolysis and increased the weight due to coating; however, the final performance was found to be within the quality control acceptance limit of the industrial partner of the study (Çalık Denim/Turkiye).

4. Conclusion

This optimization study was performed to obtain the final application details of a sol–gel bath to produce multifunctional denim fabrics. Design Expert software and a step-by-step approach were used. It has been shown that by defining proper chemicals and drying/condensation parameters, a contact angle of around 130°C and an LOI value of 39% can be obtained in the denim fabric. The fabric sample also exhibited acceptable mechanical performance; thus, the findings of this study were successfully applied to industrial-scale denim fabric production.

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