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Optimizing Organophosphorus Fire Resistant Finish for Cotton Fabric Using Box-Behnken Design

Sohail, Y.[1, 2, 3, *], Parag, B.[2], Nemeshwaree, B.[1], Giorgio, R.[2]

[1]ENSAIT-Ecole Nationale Supérieure des Arts et Industries Textiles, Roubaix, 59100, France
[2]Politecnico di Torino, Corso Giuseppe Pella, Biella 13900, Italy
[3]College of Textile and Clothing Engineering, Soochow University, Suzhou 215006, China

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ABSTRACT: N-methylol dimethyl phosphonopropionamide (MDPA) is one of the most utilized fire resistant (FR) finishes for cotton fabrics, utilized as part of a formulation with trimethylol melamine (TMM) to acquire better crosslinking and enhanced FR properties. The system parameters of the finishing treatment were upgraded for better FR properties and low mechanical loss to the fabric by the response surface methodology utilizing Box-Behnken statistical designed experimental strategy. The impacts of concentration on the cotton fabric€s properties (fire resistance and mechanical properties) were assessed with the regression equations. The optimum conditions by predicting the FR reagents focusing intact mechanical properties of the fabric were additionally studied. It was found that the parameters of crosslinking agents in the FR formulation have a prime role in the general FR properties of the cotton fabrics. The R-squared estimations of the considerable number of responses were above 92%, demonstrating the level of relationship between the predicted values by the Box-Behnken frameworks and the real test results.

Key words: Organophosphorus, Fire resistant, Cotton, Mechanical properties, Box-Behnken

INTRODUCTION

Fire resistant (FR) has been utilized for a long while to build the chances of survival against fire or flame by limiting its propagation. A part of types, FR textiles are utilized for diminishing their combustibility, in children attires, car seats and pushchairs, and so on. (Blum et al., 1978). Cotton fabrics being exceedingly combustible are treated with FRs. Among several chemical finishes being applied to impart FR properties to cotton fabrics, very few create finished fabrics that can withstand FR properties after being laundered several times. N-methylol dimethyl phosphonopropionamide (MDPA) is among the major FR materials utilized for the cotton fabrics (Ravichandrana et al., 2011). In FR finishes, crosslinking agents are added to enhance the fire resistance and durability by building up a phosphorus-nitrogen synergistic impact (Uddin, 2013). The crosslinking agents for cotton are typically formaldehyde based, for example, trimethylol melamine TMM and dimethylolurea (DMU) (Uddin, 2013). The TMM or DMU is used to increase the nitrogen content for the synergistic effect with the phosphorus group of the MDPA FR. The bonding of MDPA to the cellulosic fabrics with the help of TMM as a crosslinker in the presence of acidic conditions can be seen in Fig. 1. This FR treated cotton fabrics withstands an incredible number of launderings, dry cleanings or other cleaning methods (Van der Veen and de Boer, 2012). However, these FR finishes are linked with the formaldehyde release (Katovic et al. 2012).

In the present, formaldehyde reagents are used in commercially available FR finishes, as they are cost effective and extremely potent crosslinking agents for cellulosic fabrics. However, according to different legislations concerning the maximum formaldehyde level that can be released from textiles, has allowed textile industries to use it. For instance, the Oeko-Tex

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*Corresponding author E-mail: soh.yasin@gmail.com

Standard 100 and the American Apparel and Footwear Association (AAFA) have given the adequate limit of 75 ppm of formaldehyde release from the textiles such as, in apparels. In addition, Oeko-Tex Standard 100 recognized that textiles for babies up to two years old should release less than 20 mg/kg (Piccinini et al. 2007). These standards and legislations can control the formaldehyde release problem; however, it requires a long set of experiments to achieve the desired results with limited release information, particularly in formulations having numerous reagents or in the synergistic interactions with different fabric weight, the gram per square meter (GSM). Apart from the formaldehyde release, specific concentration of reagents is needed according to the cotton fabric€s GSM. A slight variation in the reagent concentrations can lead to higher formaldehyde release and significant loss to the mechanical properties of the fabric. Furthermore, there is a very limited research on the formulation and optimization of FR application processes, especially with statistically designed experiments.

In this study, a statistical experimental design system is used to optimize the performance of cotton fabrics treated with the organophosphorus FR by predicting an effective concentration of finishing reagents with a minimum loss to the mechanical properties. The prediction information was statistically obtained from the Box-Behnken design to compare with the experimental results. For a factorial design of four independent variables, 25 experiments were necessary to estimate. Optimization of the FR system for the textiles can be attained by statistically designed experiments with several reagents additives within the specific boundaries (Antia, 1982: Cullis, 1991).

MATERIALS & METHODS

MDPA FR (Aflammit KWB), the reagents including, formaldehyde crosslinking agents (Quecodur dm 70) and modified DHDMEU (Quecodur slf conc) were provided by Thor, France. The plain woven fabric (150 GSM) was utilized and were cut into 32 x 18 cm measurements. The FR was applied by pad-dry-cure process. The drying and curing temperature was kept at 100°C and 150°C for 4•5 minutes separately. To neutralize the treated cotton fabric, it was dipped into Na_2CO_3 bath to evacuate deposits and the impacts of acidic conditions utilized.

Fig. 1. Schematic illustration of MDPA bonding with cellulose and crosslinking agent TMM under acid conditions

The mechanical properties were carried out to check the fabric strength utilizing MTS (2/M) testing framework. The samples were cut into 30 x 5 cm. The tensile strength of every cotton test was carried out by repeating the test no less than 5 times as per French standard test system NF EN ISO 13934-1; 2013.

The FR classification to assess the fire resistance was done on cut samples (15 x 30 cm) as per French standard NF-G 07-113;1972. In which, a sample is clamped from both sides and at the center fire is introduced. Classification of the samples is calculated in the damaged area (cm^2) and classes are given accordingly (Table 1).

Response surface methodology is an empirical modelization technique utilized to find a relationship of controlled experimental factors and observed results (Annadurai & Sheeja, 1998). The strategy includes a model base knowledge achieved earlier by set of experiments, more information is formulated based on experimental or statistical outcomes. In this study, the organophosphorus FR finish was utilized, with the ingredients such as: Aflammit KWB, Quecodur slf conc, Quecodur dm 70 and the phosphoric acid agent were taken as substantial variables A, B, C and D (Table 2). The low, middle, and high levels of each variable were arranged as -1, 0, and +1 separately. The concentrations of FR finish used, were taken as the coefficients of experimental design of the said variables. The predicted yield (Y) is calculated from the equation of quadratic polynomial mathematical relationship of four independent variables A, B, C and D on the response system. The experimental design was adopted by Box-Behnken, considering three experimental results (damaged area, tensile strength and elongation) as the response parameters of the model.

RESULTS & DISCUSSION

There are a few parameters that can influence the fire resistance of the fabric, such as the type of FR used and the measure of reagents utilized in the finish. At first, a set of experiments was performed utilizing the organophosphorus FR, later a response surface experimental design was applied to decide the ideal or optimal concentrations of the finish by the empirical and observational conditions. The system variables, the physical properties such as, damaged area, tensile strength and elongation of the FR treated fabric at every stage are outlined in Table 2.

Table 3 demonstrates the empirical relationships between the FR (Aflammit KWB) A, Quecodur dm 70 B, Quecodur slc conc C and phosphoric acid D. The regression equation was acquired after the investigation of finish reagents utilized against the physical properties of the cotton fabric as a component of damaged area, tensile strength and elongation parameters.

Here Y1, Y2 and Y3 are the anticipated responses for the damaged area, tensile strength and elongation by the Box-Behnken experimental design. The critical level of the regression equations and square regressions of the considerable responses are given in Table. The R^2 is the coefficient of determination of the model, models with R^2 values above 60% is viewed as legitimate or a valid model. Though, the variety of probability (P) > F estimations of a model demonstrates the coefficient of significance and a relationship between the variables. Lower the P values, higher will be the significance of the relating coefficient (Cui et al. 2006).

Table 3 showed that the analysis of variance (F-test) for the experimental results, and the coefficient of determination (R^2) was shown above 92% in all the responses of finish reagents used. As the models conceded the minimum R^2 value (60%), which is the ratio of significance, indicates the precision and overall ability of the polynomial models to be accepted for further analysis. Whereas, the P-values in both models are up to the mark, it can be seen that the value of

Table 1. Flame retardant classifications according to French standard norm NF-G 07-113;1972

Classes	Surface of damaged area
A	Up to 10 cm^2
B	10-40 cm^2
C	40-100 cm^2 edge must not be reached
D	100-200 cm^2 or below 100 cm^2 if the edge has been reached
E	Above 200 cm^2

Table 2. The Box-Behnken experimental design for the organophosphorus FR reagents for cotton fabric

	Concentration of four independent variables				Physical properties taken in response		
Run	Aflammit KWB [g/l]	Quecodur dm 70 [g/l]	Quecodur slf conc [g/l]	Phosphoric acid [g/l]	Damaged area [cm^2]	Tensile strength [N]	Elongation [%]
1	200	10	45	22.5	16	350	9.2
2	200	40	45	22.5	15	348	9.2
3	200	25	10	22.5	17	345	9.3
4	200	25	45	20.0	14	339	9.1
5	200	25	45	25.0	14	338	9.1
6	200	25	80	22.5	13	337	9.0
7	350	25	45	22.5	12	334	8.9
8	350	25	80	25.0	11	330	8.8
9	350	10	45	25.0	12	331	8.7
10	350	40	45	25.0	10	330	8.8
11	350	40	80	22.5	10	329	8.5
12	350	25	10	25.0	12	330	8.7
13	350	25	80	20.0	9	328	8.5
14	350	40	10	22.5	10	329	8.8
15	350	10	80	22.5	11	327	8.6
16	350	25	10	20.0	10	330	8.7
17	350	10	45	20.0	11	329	8.8
18	350	40	45	20.0	9	328	8.4
19	350	10	10	22.5	12	326	8.8
20	500	40	45	22.5	6	317	7.9
21	500	25	10	22.5	9	320	8.1
22	500	25	80	22.5	7	319	7.8
23	500	25	45	20.0	6	318	7.9
24	500	10	45	22.5	7	317	7.8
25	500	25	45	25.0	6	316	7.7
	*0	0	0	0	Completely burnt	380	13

Here, the concentrations of Aflammit KWB (A), quecodur dm 70 (B), quecodur slf conc (C) and phosphoric acid (D) are taken as independent variables. Parameters of the damaged area (Y1), tensile strength (Y2) and elongation (Y3) are taken for predicting responses. *Untreated cotton fabric (not included in design run).

Table 3. Empirical design for the organophosphorus FR reagents for cotton fabric

Test responses	R-squared [%]	Adj R-squared [%]	F-value	P-value	Response equation
Damaged area (cm^2)	95.73	89.76	16.02	0.0001	$Y_1 = +12-4A-0.75B-0.75C+0.50D+AB+0.50AC+AD+0.25BC+BD+CD-0.46A^2-0.58B^2-0.33C^2-1.21D^2$
Tensile strength (N)	92.78	82.68	9.19	0.0006	$Y_2 = +334-12.50A+0.083B-0.83C+0.25D+0.50AB+1.75AC-0.25AD-0.25BC+BD+0.50CD-1.12A^2-1.50B^2-2.88C^2-3.25D^2$
Elongation (%)	97.86	94.86	32.67	0.0001	$Y_3 = +8.90-0.64A-0.025B-0.10C+0.033D+0.025AB+AC-0.050AD-0.025BC+0.13BD+0.075CD-0.28A^2-0.10B^2-0.092C^2-0.14D^2$

„probability (P) > F€€ is less than 0.0500 in all the responses, suggesting the model is highly significant. The response equations for predicting yield Y, shows the reliability of the process over the assorted experimental conditions of both formulations with a degree of accuracy.

For a general view, the combustibility of FR cotton fabric treated with the most reduced reagents of the organophosphorus FR finish (Run 3 • Table 2) has been diminished to 6.8% from 100%. While, finish with the highest reagents (Run 22 • Table 2) of the organophosphorus FR treated cotton fabric loses mechanical properties to 40% and 16.05% in elongation and tensile strength. This radical change in the mechanical properties can be controlled by achieving the optimal finishing reagents statistically. Previously stated, the model is satisfactory and the surface plots can be utilized for evaluating the estimations of surface response for ideal or optimal finishing reagents for the yield response parameters with the decreased damage area and enhanced mechanical properties of the FR cotton fabrics.

The three-dimensional (3D) response surface plots are utilized for better examination and finish impacts of four variables on physical properties of the cotton fabric. As found in Fig. 2, the individual impact of the parameters, for example, crosslinking reagents (Quecodur dm 70 and Quecodur slc conc) has a less critical impact on the combustibility of the organophosphorus FR for the cotton fabric. However, the consolidated impact of the FR and crosslinking reagents has a potent impact on the combustibility, as the damaged area is diminished with the increased crosslinking reagents utilized as a part of the finish. Indeed, formaldehyde as a crosslinking agent build a strong bonding among the MDPA and cellulose (Wu et al., 2005). Besides, it can be seen that the concentration of phosphoric acid likewise has less individual impact on the combustibility of the fabric, as seen in Fig. 2C, yet the aggregate impact with FR finish has an average effect on the fabric. The cellulosic fabrics respond effectively with MDPA in acidic catalyzed conditions, utilizing phosphoric acid (Yang et al., 2006). In addition, clearly the organophosphorus FR finishing has a notable control over combustibility of the fabric, when the amount of reagents is right. In any case, the general effectiveness of the organophosphorus FR finish indicated less damaged area of the cotton fabric, as seen in Fig. 2, which is because of a synergistic impact of nitrogen conveyed from formaldehyde sources in the occurrence of phosphorous (Edward et al., 2008).

The anticipating yield from the empirical equation for the damaged area (Y1) for the organophosphorus FR finishing reagents for cotton fabric, recommends that for the combustibility consider; A, B and C are the significant parameters of the model (see Table 3).

Fig. 3 and Fig. 4, demonstrates the impacts of FR finishing reagents on the cotton fabric,s mechanical properties. It can be seen, that the tensile strength and elongation indicated reduced, yet stable properties with the organophosphorus FR finish. In the mean time, as the concentration of phosphoric acid increased, the elongation and tensile strength was reduced, as seen in Fig. 3C and Fig. 4C, which is obvious that the

Table 4. Optimized formulations for the organophosphorus FR reagents for cotton fabric

For individual parameters	Aflammit KWB [g/l]	Quecodur dm 70 [g/l]	Quecodur slf conc [g/l]	Phosphoric acid [g/l]	Predicted Values	Actual values
Damaged area (cm^2)	499.97	34.62	19.26	20.00	5.68(cm^2)	6 (cm^2)
Elongation (%)	200.00	23.32	28.06	22.80	9.29(%)	9.15(%)
Tensile strength (N)	200.00	23.48	29.60	22.61	345.97(N)	345(N)
For combined parameters						
Optimised damaged area, elongation and tensile strength	295.89	40.00	55.99	25.00	11.35(cm^2), 8.98(%) and 333.27(N)	12 (cm^2), 8.8 (%) and 331 (N)

Fig. 2. Response surface 3D plots showing the influence of (A) Quecodur dm 70, (B) Quecodur slf conc (C) phosphoric acid on the cotton fabric€s damaged area with the organophosphorus FR formulation

Fig. 3. Response surface 3D plots showing the influence of (A) Quecodur dm 70, (B) Quecodur slf conc (C) phosphoric acid on the cotton fabric€s tensile strength with the organophosphorus FR formulation

phosphoric acid has adverse effects on the cotton fibers. From the empirical perspective, for the tensile strength (Y2) predicting yield, parameter A and for the elongation (Y3) predicting yield, A C, BD and A2 are the significant parameters (see Table 3).

The optimal concentrations for the organophosphorus FR finish was investigated from the numerical optimization approach with the assistance of software Design-Expert form 7.0.0 (StatEase, trial version) and is shown in Table 4. As the aim of this study was to get the optimal or ideal finish concentration for the organophosphorus FR cotton fabric having certain GMS with least combustibility and maximum mechanical properties. Finally, a test was carried at the optimal concentrations with anticipated results taken from the model can be found in the Table 4. It was observed that in the organophosphorus FR with concentrations of Aflammit KWB [296g/l], quecodur dm 70 [40g/l], quecodur slf [56g/l] and phosphoric corrosive [25g/l] will give the optimal results, dependent to wanted parameters. It is interesting to see that the optimal concentrations focusing singular parameters are not the same as each other, which is clear for a reason that for better combustibility the fabric needs more FR and crosslinking reagents. While, lower concentrations of FR and crosslinking reagents gives better mechanical properties of the cotton fabric.

The related experimental and predicted values were analysed and the percentage errors were calculated to be 5.41% for damaged area, 2.04% for elongation and 0.68% for tensile strength, in the organophosphorus FR finish. The negligible difference between the anticipated and actual results are within the permissible limits indicating the finish concentration obtained by the response surface methodology were practical.

CONCLUSIONS

In this work, a response surface methodology was employed to study the effects of reagent concentrations on the finishing process and optimization of the parameters to attain the optimal formulation using Box-Behnken design. The R-squared values of the responses were above 92%, confirming model is significant. Nevertheless, the synergistic impact of each reagent utilized have immediate or peculiar importance on combustibility or the mechanical properties. The experimental estimations of the ideal or optimal conditions chosen, were comparably similar to the predicted values in the formulation indicates the adequacy of the model.

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