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Ionic Liquids as an Ecological Flame-retardant Agent for Textile Fabrics

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Abstract

This study concerns the application of ionic liquids [A, PF_6] and [Py, PF_6] as non-toxic halogen-free flame retardants for textile materials. Ionic liquids were applied to cotton-polyester substrates via the coating process using Polyacrylic acid (PA). The process consists of the deposition of a polymer layer containing different ionic liquids as a flame-retardant agent onto the textile substrate to improve the water repellency of cotton/polyester blend fabrics. The optimal conditions used in the process of the functionalization of textile materials by ionic liquids have been studied using the Design Expert 11 software, with a quadratic model. The vertical combustion test according to ISO 6940: 2004 (F) and thermogravimetric analysis (TGA) on pre-treated fabric and coated fabrics have shown that ionic liquids combined with resins give the blend fabric a flame-retardant property and thermal stability for a percentage of 3% of ionic liquids. The scanning electron microscope (SEM) was used to study the morphology of fabrics. Mechanical properties and hydrophobic properties were also investigated according to ISO 13934-1: 2013 and AATCC 22-2005 standards, respectively.

Keywords

Ionic liquids, Flame-retardant agent, Textile fabrics, Polyacrylic acid

Introduction

Currently, equipping textile support with a technical property, in addition to its intrinsic properties, is of great interest in various fields [1]. Thus, functionalized textiles are used for different applications, such as comfort (Anti-odor and anti-stain,), the protection of individuals (protective clothing, professional clothing, etc.), and biomedical (prostheses, implants, and dressings) [2]. For the protection of individuals, for example, technical textiles manage to meet multiple functional criteria thanks to their barrier effects [3]. In the literature, properties of textile support have been studied and have been the subject of various patents which have in turn led to the marketing of functional textiles, among these textiles, we can mention: Anti-stain textiles; Antibacterial and antifungal textiles, and Flame-retardant textiles [4-6]. On the other hand, every year enormous fires are exposed to the world, and mainly in the textile industries, coming from the several damages. The combustion of textile materials introduces toxic greenhouse gases. Generally volatile organic compounds, which are released into the atmosphere, and they are transformed into tropospheric Ozone by photoreaction and into airborne particulate matter harmful to health. It is these pollutants that have a major effect on human health, causing thousands of premature deaths, hospitalizations, and visits to hospital emergency rooms each year.

Flame-retardant textiles can be obtained using retarders by different manufacturing and functionalization methods [7]. The flame retardants most used in the textile industries are based on free halogens [8], but these generate gases during combustion which impact the environment and the health of humans and animals [9]. For this, textile industries have recently been forced to eliminate toxic flame retardants and replace them with environmentally friendly flame retardants [10]. Environmental protection has become a socially critical point, so several toxic halogen flame retardant materials are prohibited [11]. So, researchers are dedicated to using environmentally friendly materials bearing flame-retardant or flame-retardant properties [12]. For this, textile industries have recently been forced to eliminate toxic flame retardants and replace them with environmentally friendly flame retardants [13].

The functionalization of textiles can be improved using several methods namely, dyeing, fiber treatments before weaving [14], printing, and coating method [4]. In this study, we treated textile materials by the method of knife coating. This coating method is used to cover a large area at high speed and consists of putting the polymer coating on the substrate in front of the knife; the movement of the latter ensures the deposition of the polymer on the surface of the substrate. Acrylic polymers are widely used in knife coating due to their wide range of properties. Coating formulations incorporating acrylic polymers provide good water resistance and do not age prematurely in direct sunlight [15].

In this context, we have developed blend fabrics of 70% polyester and 30% cotton with flame-retardant properties using novel ionic liquids as an ecological flame retardant Hexafluorophosphate N-Hexyl N, N, N tributyl ammonium [A, PF_6] and Hexafluorophosphate N-Hexylpyridinium [Py, PF_6], these flame retardants were deposited on the surface of textile materials by the direct coating method, by mixing them with PA. This method is used due to its low cost, the variety and availability of the polymers used, as well as the permanence of the properties that it can impart to the substrate, its stability in washing fastness, and its uniform spread on the surface of textile materials. Moreover, this method helps to improve the flame-retardant property due to the formation of the barrier layer on the surface of the coated fabrics. The percentage of ionic liquids used, and the thickness of the layer deposited on the surface of the tissues was chosen using the response surface methodology, processed by the Design Expert 11 software.

Materials and Method

Materials

A blended fabric of 30% cotton and 70% polyester was used after scouring and bleaching pretreatment. The fabric was functionalized by the knife coating method, using the following polymer:

PA with a density of 1.035. A cross-linking agent (KNITTEX CHN), a thickener HV30, from DICRYLAN, and 25% ammonia have been added to the polyacrylic acid. The materials used in the work are nanomaterials.

The ionic liquids [A, PF_6] and [Py, PF_6] were synthesized by Aicha BOUKHRISS.

A MATHIS-type SV manual coating machine equipped was used for the coating of textile materials.

Methods

To have a fabric with a flame-retardant property, different percentages of ionic liquids ([A, PF_6] and [Py, PF_6]) are dispersed in the coating polymer to prevent clumping. The dispersion is made by a sonicator for 30 min.

To obtain a PA paste, ammonia (25%) is added to adjust the pH to a value of 10, and the crosslinking agent was used to fix the pastes on the surface of the fabric during drying, the different ionic liquids were added to the mixture.

Characterization

Study of morphology

The morphology of the pristine and coated fabrics was analyzed by SEM type Hirox SH-4000M microscope.

Flame test

The vertical flame test was carried out according to standard NF EN ISO 6940:2004-08. A test piece of (80 mm x 80mm) is placed in contact with a 40 mm butane flame.

TGA analysis

The study of the thermal degradation of treated and untreated fabrics was carried out by TGA in a Versatherme HM machine. The analysis is carried out under an area with a temperature of 500 °C and a heating rate of 20 °C/min.

Drop test

The drop test method was carried out according to AATCC/ASTM Test Method TS-018 for untreated and treated fabrics. This test method is used to measure the water absorbency of textiles by measuring the time it takes a drop of water placed on the fabric surface (8 cm x 8 cm horizontal surface) to be completely absorbed into the fabric. The Absorbency Rating is calculated by obtaining five values and averaging the remaining three values. If the drop has not been absorbed in 10 min the test has to consider end, stop the timer, and record 10 min as the value.

Mechanical properties

The mechanical properties of uncoated and coated fabrics by ionic liquids were carried out by applying a preload of 10 N on three test pieces (50 mm x 300 mm) and studied according to NF EN ISO 13934-1: 2013 standard with H50KS/60 machine.

Optimization method

To study the optimum conditions for the process of functionalization of textile materials by ionic liquids to have a flame-retardant fabric, the response surface methodology was used. The Design Expert 11 software was used by varying different factors namely, the percentage of ionic liquids and thickness of the applied layer.

All these factors were varied to study the Flame time of the functionalized samples. Each variable has two levels coded as -1 for low level, and +1 for high level (Table 1). The matrix applied to this study consisted of 16 passages (Table 2).

Table 1: Variable levels for Design Expert 11 software.

Factor	Symbol	Levels	
		-1	+1
Percentage of ionic liquids (%)	A	1	5
The thickness of the paste (mm)	B	0.01	0.15

Table 2: Plan matrix used in the present study.

Run	Factor 1: A (%)	Factor 2: B (S)	Response: Flame time (s)
1	1	0,08	10
2	3	0,01	10
3	5	0,08	15
4	1	0,01	5
5	5	0,15	15
6	3	0,15	15
7	5	0,15	16
8	5	0,01	10
9	3	0,08	15
10	1	0,15	15
11	1	0,15	15
12	5	0,01	10
13	1	0,01	5
14	5	0,15	15

Results and Discussion

Optimization for the functionalization process

Analysis of variance (ANOVA)

The interaction factors influencing the flammability of tissues functionalized by ionic liquids were determined by performing the ANOVA (Table 3).

The **Model F-value** of 45,50 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.

P-values less than 0,0500 indicate model terms are significant. In this case, A, B, AB, A^2, and B^2 are significant model terms. The **Lack of Fit F-value** of 14,67 implies the Lack of Fit is significant. There is only a 0,65% chance that a Lack of Fit F-value this large could occur due to noise.

Fit statistics

To model statistics, the following parameters should be calculated:

- **Std Dev:** (Root MSE) Square root of the residual mean square.
- **Mean:** Overall average of all the response data.
- **C.V.:** Coefficient of Variation, the standard deviation expressed as a percentage of the mean.
- **R-squared:** A measure of the amount of variation around the mean explained by the model.
- **Adj R-squared:** A measure of the amount of variation around the mean explained by the model, adjusted for the number of terms in the model.

The results are presented in table 4.

The **Predicted R^2** of 0,8828 is in reasonable agreement with the **Adjusted R^2** of 0,9448. **Adeq Precision** measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 19,323 indicates an adequate signal. This model can be used to navigate the design space.

Table 4: Modeling statistics.

Std. Dev.	0,9038
Mean	12,21
C.V. %	7,40
R^2	0,9660
Adjusted R^2	0,9448
Predicted R^2	0,8828
Adeq Precision	19,3228

Model graphs

Figure 1 shows us the value of the factors studied that can be used to have an optimal flame time. Then the results confirm that for the textile material to be flame retardant, that is to say, that it does not burn at the 20 s, we can use a percentage of ionic liquid of 3% with a thickness of the layer deposited on the surface fabrics of 0.08 mm. The results presented below were based on these conditions.

Morphology study

To study the morphology of the surface of the pristine and coated fabric by 2% of different ionic liquids. A SEM was used. Figure 2 shows us the cross-sectional images taken by SEM for the treated and untreated tissues. For the first image of the pristine fabric, we observe the fibers of cotton/polyester blend fabric, and for the second we observe a thin film with a

Table 3: ANOVA for quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	185,82	5	37,16	45,50	< 0.0001	significant
A-A	26,63	1	26,63	32,61	0,0004	
B-B	137,28	1	137,28	168,08	< 0.0001	
AB	11,72	1	11,72	14,36	0,0053	
A^2	5,53	1	5,53	6,77	0,0315	
B^2	5,53	1	5,53	6,77	0,0315	
Residual	6,53	8	0,8168			
Lack of Fit	5,87	3	1,96	14,67	0,0065	significant
Pure Error	0,6667	5	0,1333			
Cor Total	192,36	13				

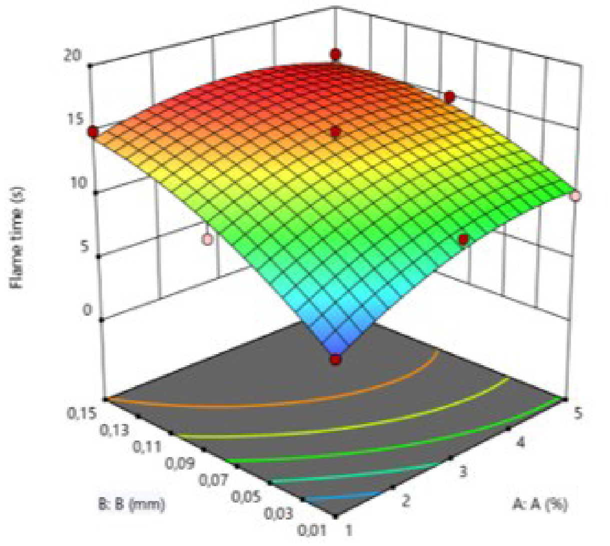

Figure 1: Optimized response.

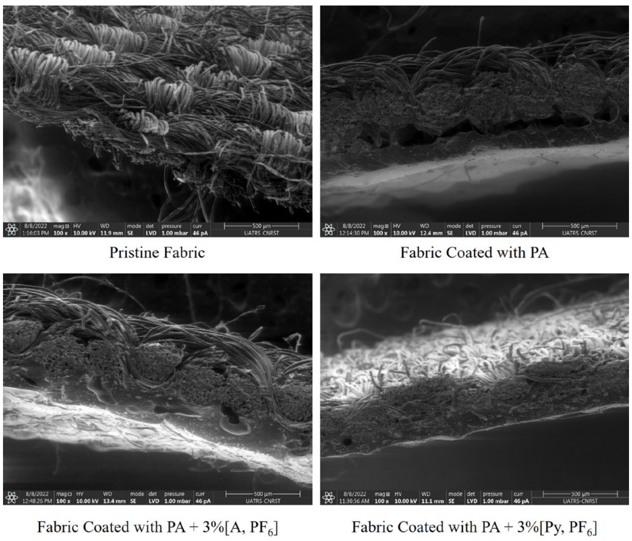

Figure 2: SEM images of pristine and coated fabrics.

soft surface that is due to the application of the PA polymer to the surface of the fabric. For the images of fabrics treated with 3% of [A, PF_6] and [Py, PF_6], we observe a thin film with some agglomerations, these agglomerations are due to the low dispersion of ionic liquids in the polymer.

Flame test

To study the flame-retardant property of samples treated with 3% ionic liquids, a vertical flame test was performed. The photos were taken after 20 s of contact with the flame. Figure 3 shows us the results of the flame test of the raw textile materials, and treated with the polymer PA, and PA + 3% ionic liquids. Untreated fabrics were burned after 5 s of contact with the butane flame. For the fabrics treated with the PA polymer, they were burned after 10 s of contact with the flame. On the other hand, the fabrics treated with the polymer mixed with 3% of ionic liquids were not burned even after 20 s of contact, in this case, we can confirm that the fabrics coated with PA + ionic liquids have a flame-retardant property.

The flame-retardant property of functionalized samples is

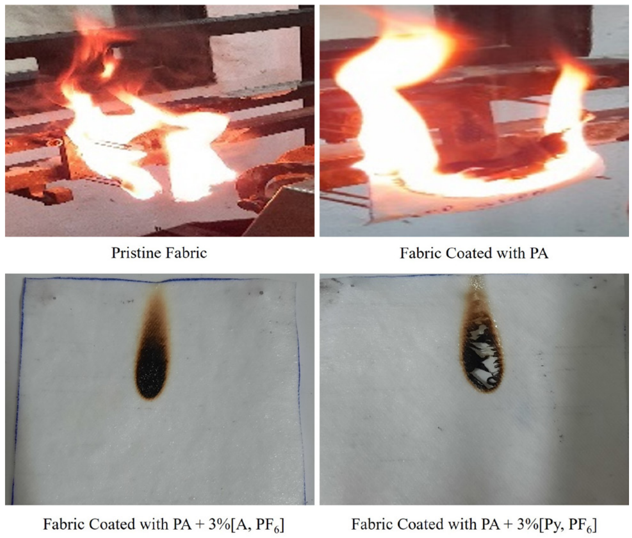

Figure 3: Flame test for coated and pristine fabrics.

due to the carbon layer formed on the surface of textile materials by ionic liquids, which can constitute an effective thermal barrier to protect fabrics from thermal irradiation [16].

TGA analysis

The data of thermal degradation of treated and untreated samples of cotton-polyester blend fabrics are summarized in figure 4. Figure 4 shows that the thermal stability of the fabrics coated with ionic liquids PF_6 - mixed with polymers was improved compared to the pristine fabric and fabrics coated with polymers. In the case of the pristine cotton-polyester blend, the decomposition takes place in three stages. The first stage of degradation is due to the decomposition of cotton-producing volatile products and aliphatic carbons. The second degradation step takes place between 341.8 °C and 391.2 °C due to the decomposition of the polyester which is a depolymerization step. The third stage of degradation is due to a carbonization reaction of cotton and polyester. On the other hand, the fabric residues coated with PA, with PA + 3% [Py, PF_6] and PA + 3% [A, PF_6] are respectively 8.03%, 11.95%, and 8.34%.

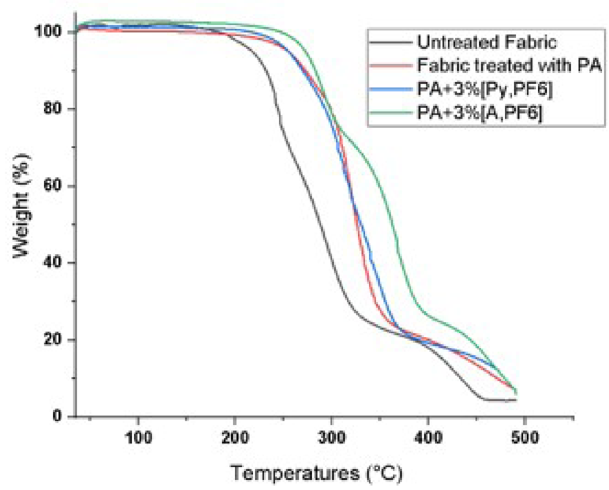

Figure 4: TGA analysis of pristine fabric, fabric coated with PA, fabric coated with PA + [A, PF_6], and fabric coated with fabric coated with PA + [P_y, PF_6].

The increment in thermal stability is attributed to the addition of the PF_6 - flame retardant additive which could catalyze the formation of a carbon layer and play a good role in thermal insulation and oxygen insulation in an early stage of fire development.

Drop test

The photos presented below were taken after 10 min of depositing the colored water droplets. Figure 5 shows us that the raw fabric has absorbed the drop of water deposited on its surface instantly, which confirms the hydrophilic property of cotton/polyester fabric, this property is due to the presence of abundant hydroxyl groups on its surface. For fabrics treated with the PA polymer, the drop of water begins to be absorbed by the sample after 2 min of deposition. On the other hand, the tissues treated with PA + 3% of ionic liquids did not propagate the drop for a period of more than 10 min. The spherical drops observed on the surface of samples treated with ionic liquids confirm that these new ionic liquids give hydrophobic properties to textile materials.

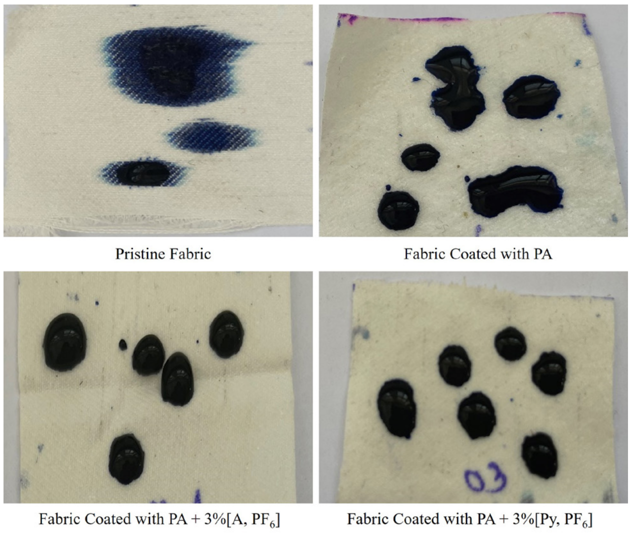

Figure 5: Results of drop test of coated and uncoated fabrics.

Mechanical properties

Tensile strength is the most important mechanical property for textile materials because it influences the performance of fabrics during use. For that, a mechanical test is carried out to study the tensile strength of treated and untreated fabrics. Figure 6 shows that the tensile strength of the fabrics coated with the polymers, or the fabrics coated with the ionic liquids mixed with the different polymers was not influenced. On the other hand, a slight improvement in the tensile strength between the raw fabric and the coated fabrics was observed. The increase in tensile strength and elongation is attributed to the polymeric film formed on the surface of the coated fabrics. The tensile strength results confirm that the ionic liquids do not affect the mechanical properties of the fabrics, they improve the flame-retardant property while maintaining the elasticity of the cotton/polyester blend fabrics, which affirm the purpose of our work.

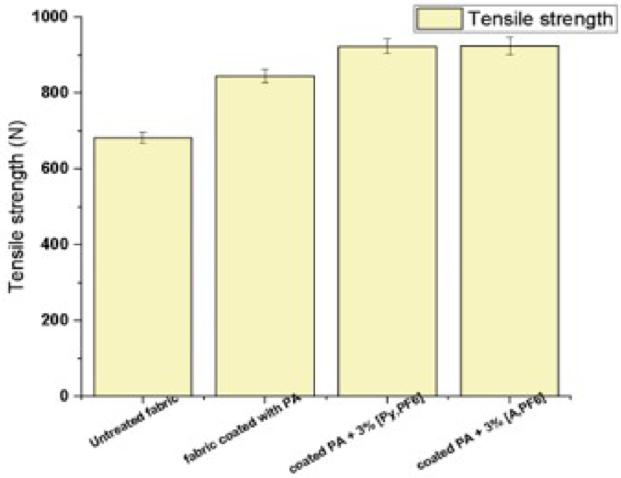

Figure 6: Mechanical properties of treated and untreated fabrics.

Conclusion

To enhance the fireproof properties of blended cotton/polyester fabrics, several compositions were used as fire retardants. Novel ionic liquids [Py, PF_6] and [A, PF_6] were considered environmentally respectful fire retardants since they don't produce toxic burns. Textile coatings with PA resins offer several properties such as abrasion resistance, resistance to water penetration, and also a leather aspect to the treated fabric. This type of coating is widely known for cotton or cotton-polyester blended fabrics. But these coatings have bad burning behavior. By applying the experimental plan using the Design Expert 11 software, the impact of the two independent parameters (percentage of ionic liquids and thickness of the applied layer) on the process of functionalization of textile materials to have flame-retardant fabrics were interpreted using the quadratic polynomial model. This study concerns the application of ionic liquids [A, PF_6] and [Py, PF_6] as non-toxic halogen-free flame retardants for textile materials. Ionic liquids were applied to cotton-polyester substrates via the coating process using PA. The process consists of the deposition of a polymer layer containing different ionic liquids as a flame-retardant agent onto the textile substrate to improve the water-repellency of cotton/polyester blend fabrics. Generally, the researchers find difficulty in the conservation of the mechanical properties of the textile materials after the functionalization, which is not the case in our work, the treatment with the polymers mixed with ionic liquids does not affect the mechanical properties. The treatment of fabrics with novel ionic liquids PF_6 - gave cotton/polyester blend fabrics excellent fire resistance These flame results are the best results found in the literature and they gave the hydrophilic fabric a satisfactory hydrophobic property.

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None.

Conflict of Interest

The authors declare that they have no competing interests.

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Not applicable.

Data Availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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