Studies of Effects of Fireproofing and Anti-creasing Simultaneous Technology on Cellulose Materials

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The purpose of this study is to obtain multiple effects on cellulose materials treated with a compound resulted after the interaction between a flame retardant agent (Aflammit KWB), a melamine derivate selected as modifier and a natural polymer, chitosan, using H_3PO_4 as catalyst. The resulted compound was applied to the fabric by pad-dry-cure technology. We studied the influence of chitosan concentration, as anti-creasing agent, and Tubifix MF100 concentration, a flame retardant synergic system, on the behaviour of the system based on Aflammit KWB as agent, with known flame retardant characteristics. The experimental data used in this study were determined using the qualitative method (FT-IR) and quantitative methods.

Keywords: *cellulose material, cotton, chitosan, anti-creasing, fireproofing, pad-dry-cure technology*

The cotton is a very inflammable fibre. Fireproofing is an important feature involved in using cotton; it can be accomplished using chemical finishing technologies. Nowadays phosphorus and nitrogen compounds are highly used in order to reduce to minimum the combustion time [1-2].

The number of flame retardant substances used to fireproof fabric cellulose are more and more investigated, the number of systems involved are increasing. Another very serious effect is the flue gas poisoning, so the substances we use must generate minimum toxicity residues following the combustion [3-4].

From this point of view, the problem of combustion residues toxicity from flame retardants, and reducing the burn made by the combustion of flame-retardants is a major concern in the research-development-innovation issues of these systems.

The modern manufacturing technologies of flame retardant substances, is focusing on increasing the fabrics fireproofing, the extinction and reduction of smoke.

Lately, the global demand asks for slowing down the fire rate to 4-5% [6-8].

The fireproofed fabrics are used to manufacture different products requiring this characteristic. These products are very important, because of the wide application in several areas (clothes, pyjamas, linens, blankets, matrix, furniture coverings, carpets, curtains etc.) at offices, public buildings, transport, work (protection garments in industry, firemen) [9]. The difference between a flame retardant agent and a flame resistant one is that the first is used to reduce the combustion speed and flame spreading, whereas the second one protects against the heat and the flame penetration into substances [10-11].

In this paper we present the study of effects on fabric cellulose, like cotton, treated with two flame-retardant agents (Aflammit KWB and Tubifix MF100) and an anti-creasing agent based on chitosan, using pad-dry-cure technology. The influence of chitosan and Tubifix MF100% concentration was studied on system behaviour with Aflammit KWB ,as agent with known fireproofing characteristics. The experimental data used in this study were determined using the qualitative method (FT-IR) and quantitative methods.

Experimental part

Samples preparation

The samples of fabric cellulose (cotton) were treated by coating with flame-retardancy and anti-creasing using *pad-dry-cure* process. Choosing the chemical agents for fireproofing and anti-creasing was difficult due to the great number and their structural-functional diversity, the usage toxicity, the thermal deterioration residues, and providing high resistance for repeated washings [12]. So, Aflammit KWB is a phosphorus retardant agent often used for textiles, Tubifix MF 100 (a nitrogen melamine derivate), their mixture improves the capacity of the fire retardant due to P-N (phosphorus-nitrogen) synergy [1]. Another agent, chitosan is used as an anti-creaser, in the presence or absence of oxygenated water. It is known that Aflammit KWB as well as Tubifix MF 100 are non toxic products for skin contact [13-14].

Chitosan, used as an anti-crease agent, consists of β-(1-4)-2-acetamido-2-deoxy-β-D-glucopyranose (N-acetylglucosamine) and 2-amino-2-deoxy-β-D-glucopyranose (D-glucosamine) units (fig. 1), it is also non toxic, and it is a natural product often used to preserve the organic materials by coating. The use of chitosan is preferred when the nitrogen concentration is higher than 7% of the weight or the degree of deacetylation is over 60%. The main aspect of chitosan is the NH_2 group that explains the successful use in chemical completion of fabrics [15, 16].

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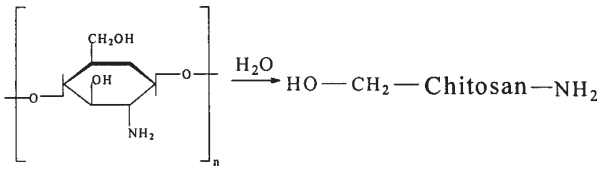


Fig. 1. Chitosan chemical structure

The fabric sample (cotton) studied, was prepared using an alkaline boiling treatment with cleaning purpose (degreasing), from which some vials were prepared, by impregnation in two solutions: Chitosan + Aflammit KWB + TubifixMF100 (Ch+A+T) and Chitosan + H_2O_2 + Aflammit KWB + TubifixMF100 (Ch+H+A+T), for 5 min, at room temperature, according to the two recipes presented next.

Recipe I. In the first stage, in the impregnation system Ch+A+T, being a aqueous solution containing: 20-80g/L chitosan, 20-80g/L Tubifix MF 100, 4mL CH_3COOH conc., in 50mL H_2O, was added by slightly stirring 0.25mL H_3PO_4 conc., 200g/L Aflammit KWB, until it became homogeneous; then the fabric cellulose sample was immerged at a hydromodule (Hm) of 1:10. At the next stage, the sample was removed and squeezed until a squeezing degree of (G.S.) of 80%, then dried to 120° C for 2 min, after wards the coating was fixed by polycondensation at 160° C for another 2 min, in the end the coated samples were washed with a aqueous solution slightly alkaline of Na_2CO_3, 1.0g/L, at 20°C, for 10 min and dried in a minitherm device, of ERNST BENZ AG Textilmaschinen Rümlang-Zürich type, at 120°C, for 2 min.

Recipe II is very similar to the first one, it has the same components and the same work stages; the difference is in the impregnation process from the first stage we added 1.0mL of H_2O_2, 10g/L. So, in the first stage, the impregnation system Ch+A+T, an aqueous solution, contains: 20-80g/L chitosan, 20-80 g/L Tubifix MF 100, 4mL CH_3COOH conc., and 1.0mL de H_2O_2, 10g/L, dispersed in 50mL H_2O, in which was added by slightly stirring 0.25 mL H_3PO_4 conc., 200g/L Aflammit KWB, until the homogenisation, then the fabric cellulose sample was immerged at Hm = 1:10.

In the next stage, the sample was removed and squeezed, at G.S. = 80%, then dried to 120° C, for 2 min, followed by polycondensation coating at 160°C for another 2 min, in the end the samples were washed with an aqueous solution slightly alkaline Na_2CO_3, 1.0g/L, at 20°C for 10 min and then dried in the same minitherm device, ERNST BENZ AG Textilmaschinen Rümlang-Zürich type, to 120°C for 2 min.

The samples squeezing was done between the cylinders of a mini-foulard.

For the anti-creasing studies, the samples treated the same without adding chitosan.

The samples prepared for analysis were divided in 4 series, 5 samples each, for both recipes,as follows:

a) the series *pad→dry→condensation→burn,* was tested for fireproofing;

b) the series *pad→dry→condensation→ neutralization→dry→repeated wash,* was tested for the durability treatment (especially for fireproofing) at repeated washing;

c) the series *pad→dry→condensation→wash→ dry→burn*, evidentiated the fireproofing durability, when the neutralization stage (in a classic process) is replaced with a simple washing with water;

d) the series *pad→dry→condensation→wash→dry,* tested the recovery from the creasing state of the fabric.

Methods

FTIR spectrophotometry analysis was performed using a Spectrophotometer FTIR IR Affinity-1 Schimadzu (Japan), which has attached a Multiple Internal Reflectance Accessory (SPECAC, SUA) with ATR KRS-5, a bromine-iodine crystal that offers 25 reflexions, and an investigation angle of 45°.

The spectra recordings were carried out in the 4000-600 cm^{-1} range, by 250 scans. After recording the absorbance spectra were computer processed (using KnowItAll (R) Informatic System software from Bio-Rad Laboratories).

The degree of film covering in fireproofing and anti-creasing system, was determined using the following formula [7]:

$$Y_p = 100 \cdot \frac{W_a - W_b}{W_b} [\%];$$

Y_p = degree of tekeover; W_a = weight of sample before treatment; W_b = weight of sample before treatment.

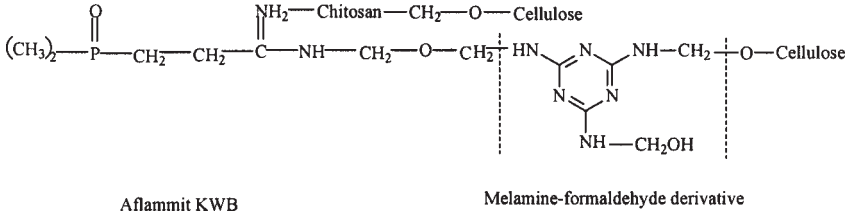
The crease recovery angle was determined using Metrimpex FF-01 device, according to the standardized German method DIN 53890 [7]. The samples treated for anti-creasing and fireproofing were tested by the vertical flame test according to DIN 53906. The amount of burned fabric was determined by calculating the difference between the weight of the samples before and after burning, because the surface of the charred area could not be determined due to the creasing of burned fabric [3]. In our case, the organophosphoric product, Aflammit KWB mixed with chitosan a biodegradable, natural polymer, with the melamine-formaldehyde derivative, by involving a catalyst (phosphoric acid) will form a resin, with coating, fireproofing, anti-creasing ability (fig. 2).

The durability of anti-creasing effects and fireproofing were determined according to SR EN ISO 105-C06:1999 standard, so the samples treated with Ch±H+A+T have undergone from 1 to 10 washes. The test was performed with the Mathis Polycolor 2002 device, followed by rinsing with distilled water and dried at room temperature. The weight of each sample was measured before and after each washing cycle.

Results and discussions

a. FTIR analysis

The FTIR spectra for the cotton samples treated with Ch+A+T and Ch+H+A+T are presented in figure 2. In order to emphasize the effects of Chitosan + Aflammit KWB + Tubifix MF 100 system, and Chitosan + H_2O_2 +



Aflammit KWB

Melamine-formaldehyde derivative

Fig. 2. Film obtaining using polycondensation

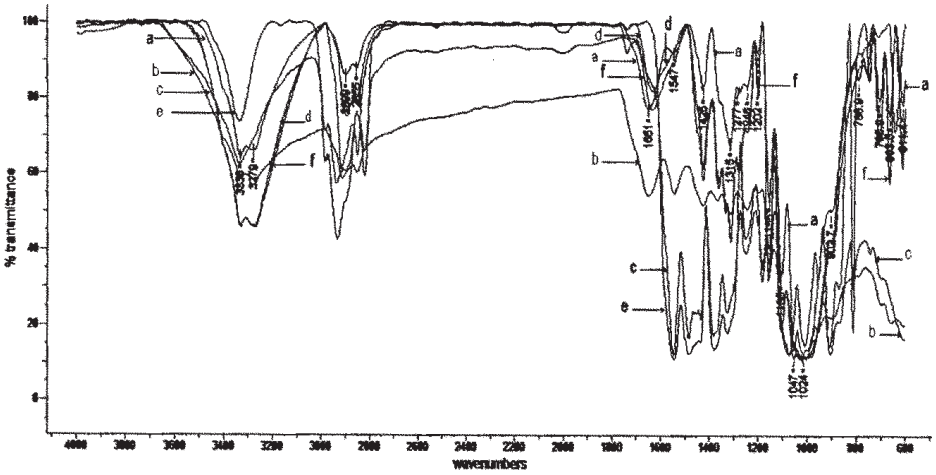


Fig. 3. FT-IR absorbtion spectra:
a. Cotton+Chitosan+Tubifix MF100+Aflammit KWB,
b. Cotton+Chitosan+ Aflammit KWB,
c. Cotton+Chitosan+Tubifix MF100,
d. Cotton+Chitosan,
e. Cotton+Tubifix MF100,
f. Cotton

C.	I n :	I n :	After burning					
			Weight [g]	Thickness [mm]	Degree of takeover after	Flame time spread[mm]	Burned area length [mm]	Weight loss [g]
0	1.172	0.350	1.365	0.366	16,46	3.02	2.0	0.030
20	1.171	0.345	1.377	0.385	17.33	3	1.5	0.027
30	1.276	0.355	1.476	0.373	16.93	3.35	5.3	0.098
40	1.243	0.346	1.435	0.386	16.20	2.5	9	0.183
60	1.270	0.346	1.395	0.393	15.02	1.74	6.7	0.124
80	1.273	0.346	1.440	0.440	16.99	1.83	6.0	0.110

Table 1
RESULTS OBTAINED USING PAD-DRY-CURE-BURN PROCEDURE

Chitosan [g/L]	After burning		
	Incandescent time [s]	Burned area length [mm]	Weight loss [g]
0	1	0	
20	2.01	6.9	0.120
30	1.86	8.2	0.151
40	6.34	17.9	0.470
60	1.46	8.9	0.177
80	2.72	7.4	0.126

Table 2
RESULTS OBTAINED USING PAD-DRY-CURE-BURN PROCEDURE

Chtiosan [g/L]	Initial data		Data before washing		Data after repeated washes					
					1 wash		5 washes		10 washes	
	Weight [g]	Thickness [mm]	Weight [g]	Thickness [mm]	Weight [g]	Thickness [mm]	Weight [g]	Thickness [mm]	Weight [g]	Thickness [mm]
0	1.281	0.365	1.394	0.395	1.388	0.392	1.382	0.383	1.379	0.380
20	1.276	0.343	1.506	0.380	1.500	0.376	1.547	0.370	1.540	0.369
30	1.264	0.350	1.464	0.386	1.359	0.380	1.351	0.279	1.340	0.370
40	1.261	0.350	1.456	0.433	1.448	0.430	1.442	0.430	1.437	0.430
60	1.258	0.330	1.449	0.370	1.440	0.370	1.437	0.367	1.430	0.365
80	1.243	0.350	1.455	0.420	1.449	0.418	1.439	0.415	1.409	0.410

Table 3
RESULTS OBTAINED USING PAD-DRY-CURE-NEUTRALIZATION-DRY-REPEATED WASH PROCEDURE

Aflammit KWB + Tubifix MF 100, were represented in the same spectra of the untreated cotton samples, the cotton samples treated only with chitosan, and the cotton samples treated with chitosan + oxygenated water.

The specific literature suggests that FTIR analysis is the most appropriate method to predict the performances of anti-creasing fabrics treatments. It can also be used as an convenient instrumental method for quality control in the textile industry [7, 8].

The main absorption bands are assigned according to the specific literature [9]. According to KnowItAll database, the presence of amines is also confirmed, -NH_2 peaks at 3333, 3279cm^{-1}, then those specific to CH_2 groups, responsible for increasing the molecular chain, at 2899, 2855cm^{-1}, the absorption peak 1651cm^{-1}, corresponding to CO group in amides, the peak 1547cm^{-1} for -NH, C-N groups; the peak 1425cm^{-1} for P=O group, the flame retardant Aflammit KWB compound, etc. Between 1315-1024cm^{-1} are absorption peaks for CO group and in 902-611cm^{-1} are those that demonstrate the presence of the flame retardant compound.

Quantitative analyses on work series

The four series, 5 samples each, were treated differently. They were put to four different tests, and experimental data were obtained, which permit the evaluation of the fireproofing and anti-creasing behaviour, respectively. Thus, for series a) *pad→dry→cure→burn,* the results are in tables 1 and 2; for series b) *pad→ dry→ cure→ neutralization→ dry→ repeated wash,* in tables 3, 4 for

Chtiosan [g/L]	Initial data		Data after repeated washing	
	Weight [g]	Thickness [mm]	Weight [g]	Thickness [mm]
0	1.225	0.352	1.278	0.395
20	1.319	0.350	1.329	0.390
30	1.234	0.356	1.315	0.397
40	1.255	0.353	1.280	0.399
60	1.312	0.363	1.412	0.541
80	1.289	0.350	1.436	0.600

Table 4
RESULTS OBTAINED USING PAD-DRY-CURE-NEUTRALIZATION-DRY-REPEATED WASH PROCEDURE

Chitosan [g/L]	After burning		
	Incandescent time [s]	Burned area length [mm]	Weight loss [g]
0	1.17	11.06	
20	2.19	8.0	0.172
30	2.17	9.1	0.148
40	6.45	17.6	0.467
60	1.36	10	0.175
80	1.55	9.9	0.123

Table 5
RESULTS OBTINED USING PAD-DRY-CURE-WASH-DRY-BURN PROCEDURE

Chitosan [g/L]	After burning		
	Incandescent time [s]	Burned area length [mm]	Weight loss [g]
0	3.07	10.67	-
20	1.64	11.90	0.126
30	1.29	10.29	0.144
40	1.80	13.38	0.144
60	0.89	13.61	0.074
80	1.27	15.05	0.106

Table 6
RESULTS OBTAINED USING PAD-DRY-CURE-WASH-DRY-BURN PROCEDURE

Chitosan [g/L]	Initial weight [g]	Initial thickness [mm]	After treatment		Crease recovery angle	
			Weight [g]	Thickness [mm]	Dry(W+F)	Wet (W+F)
0	1.287	0.370	1.401	0.380	145.5	146
20	1.290	0.350	1.485	0.400	200	203
30	1.310	0.373	1.532	0.403	164	160
40	1.442	0.373	1.666	0.420	168	180
60	1.285	0.370	1.540	0.426	168	172
80	1.285	0.360	1.540	0.426	200	208

Table 7
RESULTS OBTAINED USING PAD-DRY-CURE-WASH-DRY-BURN PROCEDURE

Chitosan [g/L]	Initial weight [g]	Initial thickness [mm]	After treatment		Crease recovery angle	
			Weight [g]	Thickness [mm]	Dry(W+F)	Wet (W+F)
0	1.329	0.356		0.495	138.2	152
20	1.265	0.356	1.460	0.390	164	208
30	1.241	0.356	1.431	0.400	186	204
40	1.267	0.360	1.375	0.443	150	206
60	1.347	0.363	1.600	0.510	162	222
80	1.280	0.360	1.529	0.433	142	242

Table 8
RESULTS OBTAINED USING PAD-DRY-CURE-WASH-DRY PROCEDURE

series c) *pad→dry→cure→ wash→dry→burn*, in table 5, 6 and for the last series d) *pad→ dry→ cure→ wash→ dry,* in tables 7 and 8.

According to data in table 1, we conclude that whereas the chitosan concentration increases, the percentage of weight loss after treatment with chitosan and Aflammit KWB solution will increase. The loss is not very big, so this procedure is appropriate for a favourable fireproof effect, table 2. The durability of fireproofing does not depend only on the concentration of the flame retardant agent, Aflammit KWB, reflected by the weight loss in the washing process, but also by the thickness of the samples; tables 3 and 4.

In table 5 we conclude that once the chitosan concentration increases, the flame spreading time and the weight loss due to burning also increases. So, when adding chitosan in the impregnation bath it results a weaker fireproof effect.

This treatment is favourable for anti-creasing due to high concentration of chitosan, showed by the crease recovery angles (table 7). This is due to the formation of a crosslink between the macromolecular chains of cellulose, chitosan and the flame retardant agent. The presence of oxygenated water in the impregnation bath determines a slight degradation of the chitosan and cellulose, so the flame retardant effect becomes weaker, according to the bigger weight loss after burning (table 7). In table 7 we see that the weight loss after 10 washes is big, meaning that the effect is not durable. In this case there are very big loses, proving that the oxygenated water does degrade chitosan and cellulose in cotton. In the same time, the good crease recovery angles are presented; demonstrating that it is a good treatment for the anti-creasing effect (table 8).

Conclusions

Using a mixture of fireproof and anti-creasing agents selected according to certain criteria and characteristics, it was obtained an acceptable flame retardant effect by using Recipe I, the durability of the effect depended on the existence or the absence of neutralization after

condensation, the presence of chitosan declined the crease recovery angle in the presence or the absence of the oxygenated water.

Further studies will be made on the possibility of increasing the flame retardant effect according to the anti-creasing one by using other procedures, or the mixture of a natural polymer, chitosan and the phosphorus flame retardant agents.

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