LBL DEPOSITION – AN INNOVATIVE METHOD OF SURFACE MODIFICATION OF COTTON WITH ENHANCED FR PROPERTIES

Eva MAGOVAC; Sandra BISCHOF & Jaime C. GRUNLAN & Igor JORDANOV

Abstract: *Due to the numerous environmental problems that occur in the production, usage and disposal of textile materials treated with durable flame retardants for cotton there is a need for their partial or complete replacement by new alternative environmentally friendly agents and one of the possible ways is "Layer-by-Layer" (LbL) deposition. In this work the renewable, eco-friendly polyelectrolytes from natural sources were deposited onto cotton fibres via LbL assembly in an effort to reduce the flammability of cotton. Positively charged chitosan coupled with urea was paired with negatively charged phytic acid forming different number of bilayers (BL) on cotton. Thermal behaviour of the treated cotton samples was investigated by thermogravimetric analysis (TGA/DTA) and compared to the untreated one. The mass residue at characteristic temperatures of thermal degradation was analysed in order to investigate the correlation between the increase of the mass residue with the increase of the number of bilayers. The elemental analysis of the char residue after heating in TGA was performed with EDS detector in order to investigate its chemical composition.*
Keywords: *cotton, layer-by-layer, flame retardancy, eco-friendly, TGA, EDS*

1. Introduction

Current commercially available flame retardants for cotton fabrics have numerous ecological drawbacks. Halogen, organo-halogen and antimony organo-halogen flame retardants are toxic, and those based on organophosphorus compounds are now considered safe to use partially due to a lack of data on their impact on the environment and health [1, 2]. The main commercial durable FR finishes on cellulose textiles are those based on tetrakis (hydroxyl methyl) phosphonium salt (THPC) and N-methylol dimethylphosphonopropionamide (MDPPA). The main disadvantage of these flame retardants is a gradual release of toxic formaldehyde during the production and use of such a treated fabric [3]. Due to the numerous environmental problems that occur in the production, usage and disposal of textile materials treated with flame retardants there is a need for their partial or complete replacement by new alternative environmentally friendly agents and / or technological solutions, and one of the possible ways is "Layer-by-Layer" (LbL) deposition. LbL deposition means the surface adsorption of long-chain polyelectrolyte molecules of one charge onto the substrate of the opposite charge followed by washing with deionized water. The next step is adsorption of the positively or negatively charged polyelectrolyte onto the opposite charged polyelectrolyte and so on. In this way it is possible to arrange several layers of the same or completely different electrolytes to one another as a bilayer (BL), a trilayer (TL) and a quadlayer (QL) of different properties [4]. LbL deposition is tested in the experimental stage on textile, plastics and foams materials using a variety of flame retardants [5]. Among all eco-friendly flame retardants for cotton materials based on organophosphorus compounds the most promising one are phytic acid and urea. Phytic acid is well known food additive in food industry which could in theory replace polyphosphates since it contains phosphorus in its structure [6]. Urea as a natural source of nitrogen is principal end product of nitrogenous metabolism in mammals [7]. Chitosan is a linear polysaccharide consisting of randomly distributed β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine. Being a positively charged biopolymer in an acidic environment, chitosan is bio adhesive and is easily bonded to negatively charged surfaces such as phytic acid. In this work we wanted to investigate the correlation between the number of bilayers and characteristic temperature points of the decomposition as well as the influence of the number of bilayers on mass residue after heating. Secondly, we wanted to analyse the chemical composition of the char at specific temperatures.

2. Method used

2.1. Experimental

Chemically bleached, desized 100% cotton fabric with a weight of 119 g/m2, was supplied by the USDA Southern Regional Research Centre (New Orleans, LA). A 5 wt % aqueous solution of positively charged branched polyethylene – BPEI (MW 25 000 g/mol), supplied by Sigma-Aldrich was prepared with 18.2 deionized water (DI) and used as a primer layer for better adhesion to cotton. A 2 wt % aqueous solution of

negatively charged phytic acid sodium salt hydrate - PA, supplied by Sigma-Aldrich USA was prepared with 18.2 deionized water (DI). A 0.5 wt % aqueous solution of positively charged chitosan – CH (MW 50−190 kDa, 75−85% deacetylated), supplied by Sigma Aldrich USA was prepared with 18.2 deionized water (DI). The solutions were magnetically stirred for 24 hours until the solutions were completely dissolved. A 10 wt % urea was added to 0.5 wt % aqueous solution of positively charged chitosan and magnetically stirred. The pH of these solutions was adjusted to 4, with 1 M NaOH or 1 M HCl prior to LbL deposition. Four cotton samples were immersed into aqueous solutions of negatively charged PA and positively charged CH-UREA forming 8, 10, 12, 15 bilayers (8BL, 10BL, 12BL, 15BL). One cotton sample was used as a control sample. The immersing time was 5 minutes for the first layer (CH-UREA/PA) and 1 min for each layer. Each immersion step was followed by rinsing in deionized (DI) water. Cotton samples were dried in the oven at 50°C.

2.2. Characterisation

The thermal stability of the fabrics was evaluated by thermogravimetric (TG) analyses using PerkinElmer Pyris 1 TGA thermogravimetric analyser. All samples for TGA were heated from 50°C to 850°C at the heating rate 30°C/min in the air (flow rate: 30 ml/min). The chemical analysis of the char left after heating in TG at 600°C was studied using a Tescan MIRA\\LMU FE-SEM Scanning Electron Microscope (BSE detector, 10 kV, magnification 300 X, WD 25.000) equipped with the EDS detector for elemental analysis. No sputter-coating was performed prior EDS analysis.

3. Results

As it is visible from the group TGA curves (Figure 1) as well as from the group DTA curves (Figure 2) of untreated and LBL treated cotton fabrics there is an important difference between thermal stability at characteristic temperature points of raw (control) cotton and LbL treated cotton samples (8BL, 10BL, 12BL, 15BL). The difference is in initial decomposition temperature which is significantly lower for all treated materials comparing to raw cotton. For untreated cotton the decomposition temperature starts at 357 °C (T_{onset1}) and reaches its maximum at 389 °C (T_{peak1}). For cotton treated with 8BL, 10BL, 12BL, 15BL the decomposition temperature starts at around 305.75 °C (average) and reaches its maximum at around 333.75 °C (average).

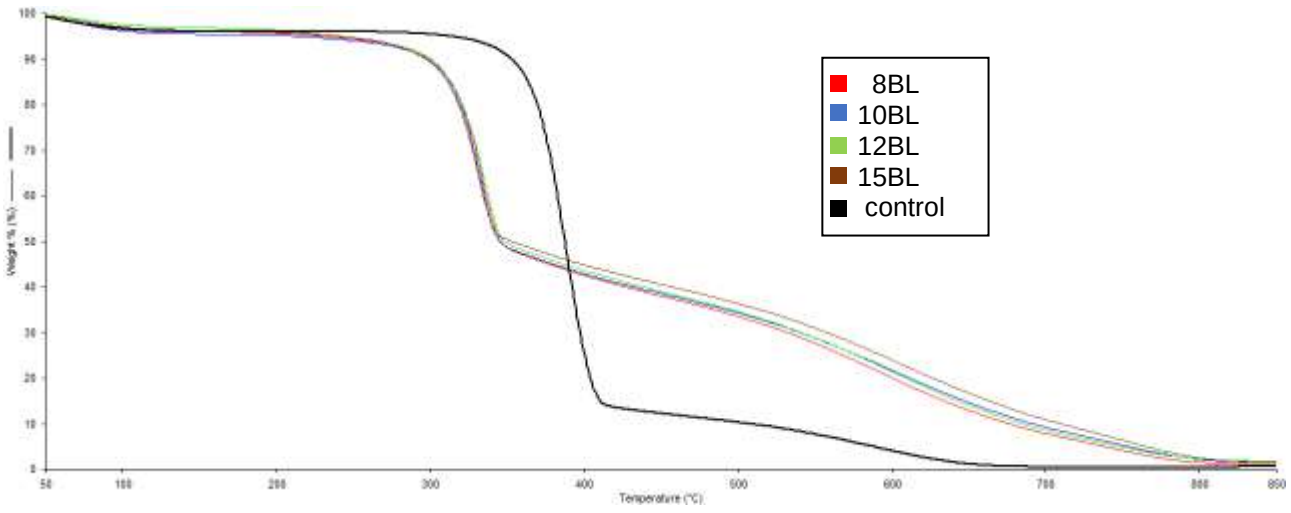


Figure 1: TGA curves of untreated and LbL coated cotton fabrics

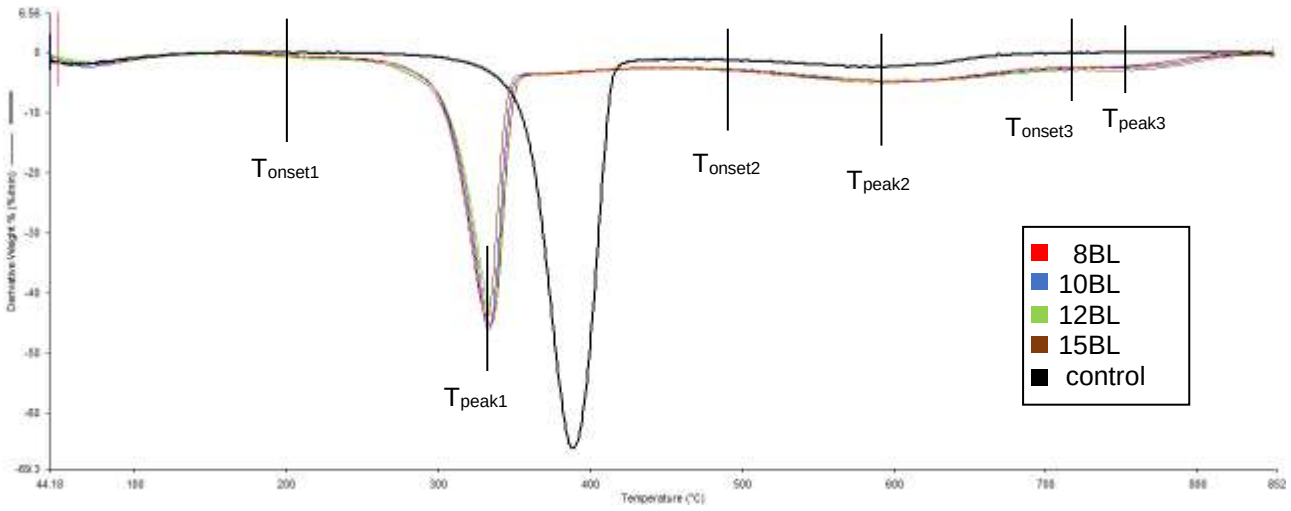


Figure 2: Group DTA curves of untreated and LbL coated cotton fabrics

However, it is visible from the Table 1 that there is a slight decrease in start of decomposition (T_{onset1}) as well as decomposition maximum (T_{peak1}) with the increase in number of bilayers (BL). For the cotton treated with 8BL, the decomposition starts at 307 °C and reaches its maximum at 334 °C. For the cotton treated with 10BL, the decomposition starts at 306 °C and reaches its maximum at 334 °C. For the cotton treated with 12BL, the decomposition starts at 306 °C and reaches its maximum at 336 °C. For the cotton treated with 15BL, the decomposition starts at 304 °C and reaches its maximum at 331 °C. The difference between average T_{onset1} of all treated samples and the untreated one is 51.25 °C. The difference between average T_{peak1} of all treated samples and the untreated one is 55.25 °C. However, the linear correlation between number of bilayers and characteristic temperature points at the second stage of the decomposition (T_{onset2}, T_{peak2}) as well as the third stage cannot be found (T_{onset3}, T_{peak3}).

Table 1: Characteristic temperatures of untreated and LbL coated cotton fabrics

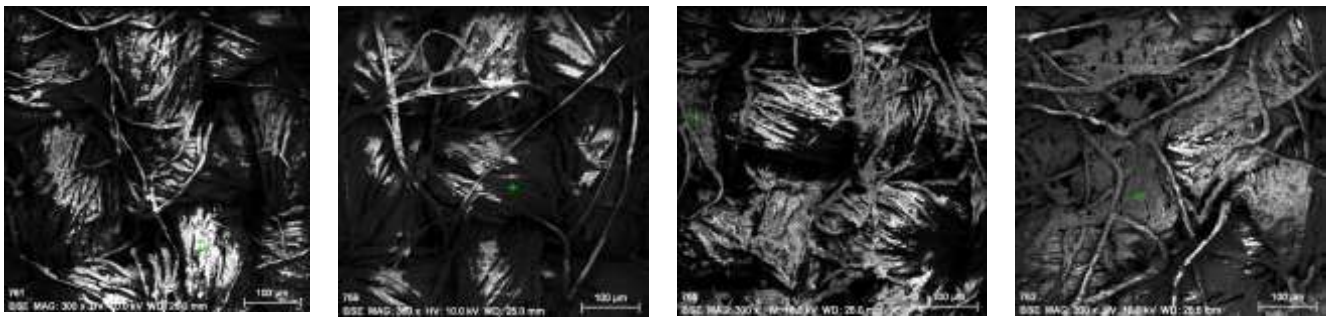
Sample	T_{onset1} /°C	T_{peak1} /°C	$T_{onset\ 2}$ /°C	T_{peak2} /°C	T_{onset3} /°C	T_{peak3} /°C
Control	357	389	506	593	/	/
8 BL	307	334	576	585	712	761
10 BL	306	334	511	604	785	779
12 BL	306	336	528	598	734	766
15 BL	304	331	509	609	721	758

Table 2 shows the correlation between mass residues at different temperature peaks of untreated and LbL coated cotton fabrics. At the first decomposition stage (T_{peak1}) the percent of mass residue of the untreated cotton is 47 % meaning that untreated cotton lost 53 % of its original mass. At the second decomposition stage the untreated cotton lost 95.4 % of its original mass. At the end of heating at 850 °C nothing is left. On the contrary, LbL treated cotton samples show almost linear grow of percent of mass residue with the increase of number of layers at all decomposition stages. At the first decomposition stage (T_{peak1}) the mass residue grows from 63 % to 65 % at 8BL and 15BL. At the second decomposition stage (T_{peak2}) the mass residue grows from 21.5 % to 23 % at 8BL and 15BL and at T_{peak3} the residue grows from 3 % to 6 %.

Table 2: Mass residue at different temperature peaks of untreated and LbL coated cotton fabrics

Sample	T_{peak1} /°C	Residue / %	T_{peak2} /°C	Residue / %	T_{peak3} /°C	Residue / %
Control	389	47	593	4.6	/	/
8 BL	334	63	585	21.5	761	3
10 BL	334	62	604	21	779	3
12 BL	336	63	598	22	766	4
15 BL	331	65	609	23	758	6

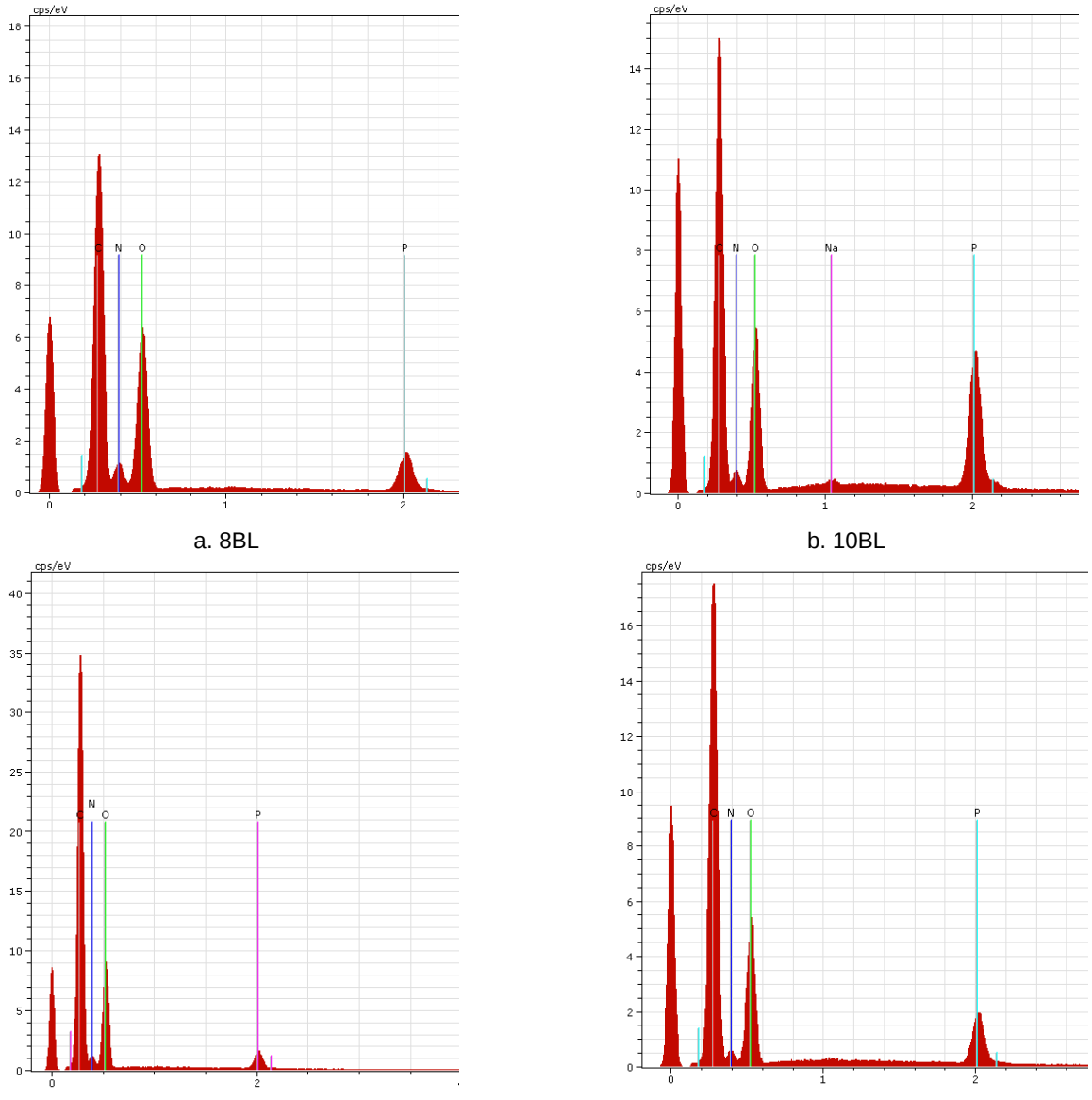
The EDS images of char left after heating of all treated cotton samples show consistent structures with visible traces of fibres and coatings (Figure 3).



a. b. c. d.

Figure 3: EDS images of char of untreated and LbL coated cotton fabrics at 600 °C: a. 8BL, b. 10BL, c. 12BL, d. 15BL

The EDS spectra of the char residue has mainly shown the contest of carbon, oxygen, phosphorus and sodium in traces as impurity which means that the deposition of CH-UREA/PA was successful (Figure 4).



a. 8BL b. 10BL

c. 12BL d. 15BL

Figure 4: EDS char spectra of untreated and LbL coated cotton fabrics at 600 °C: a. 8BL, b. 10BL, c. 12BL, d. 15BL

It is expected that the quantitative EDS char elemental analysis of LbL coated cotton shows the grow of phosphorus and nitrogen contest with the increase of number of bilayers. The results in Table 3, however, did not show any relation between the number of bilayers and contest suggesting that LbL coating was not

uniform as expected. The values of nitrogen vary from 7.39 % for 15BL to 13.22 % for 8BL. At the same time the values of phosphorus vary from 1.84 % for 12BL to 9.17 % for 10BL.

Table 3: Quantitative EDS char elemental analysis of LbL coated cotton fabrics

			8BL	10BL	12BL	15BL
Element	AN	Series	wt %	wt %	wt %	wt %
Carbon	6	K	52.92979	60.54145	65.19882	64.24413
Oxygen	8	K	30.22418	22.07647	24.08708	24.20605
Nitrogen	7	K	13.22064	7.952004	8.864816	7.394884
Phosphorus	15	K	3.625404	9.175615	1.849278	4.154928
Sodium	11	K	/	0.254467	/	/
		Sum:	100	100	100	100

4. Conclusion

Environmentally friendly electrolytes CH-UREA/PA were successfully deposited onto cotton using LbL technology enhancing the initially low FR properties of cotton material. TGA/DTA curves of all LbL treated samples (8BL, 10BL, 12BL, 15BL) indicated the reduce of flammability of cotton fabrics by decreasing the starting temperature of the first decomposition stage (T_{onset1}) as well as the decomposition maximum temperature (T_{peak1}) for around 50 °C relating to untreated cotton. At the same time LbL treatment of cotton fabrics increased percent of mass residue for 16.25 % at T_{peak1} relating to untreated cotton. At the second decomposition stage the percent of the mass residue at T_{peak2} increased for 17.27 % relating to untreated cotton. The increase in number of bilayers (8BL, 10BL, 12BL, 15BL), except slight linearity, did not show significant influence on main decomposition points and mass residue as well. EDS elemental analysis of the char residue after heating at 600 °C did not prove the increase in phosphorus or/and nitrogen contest with the increase in number of bilayers.

5. References

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Author(s):

Eva MAGOVAC, BSc.
University of Zagreb, Faculty of Textile Technology, Department of Textile Chemistry and Ecology
Prilaz baruna Filipovića 28a, HR-10000 Zagreb, Croatia
E-mail: eva.magovac@ttf.hr

Prof. Sandra BISCHOF, PhD.
University of Zagreb, Faculty of Textile Technology, Department of Textile Chemistry and Ecology
Prilaz baruna Filipovića 28a, HR-10000 Zagreb, Croatia
E-mail: sandra.bischof@ttf.hr

Prof. Jaime C. GRUNLAN, PhD.
Texas A&M University, Department of Mechanical Engineering
3123 TAMU, College Station, TX 77843, USA
E-mail: jgrunlan@tamu.edu

Prof. Igor JORDANOV, PhD.
Ss. Cyril and Methodius University, Faculty of Technology and Metallurgy, Textile Department
Ruger Boskovic 16/6, Skopje, Republic of Macedonia
E-mail: jordanov@tmf.ukim.edu.mk

6. Corresponding Address

E-mail: eva.magovac@ttf.hr