NANOCOATING OF COTTON BY A HALOGEN-FREE FLAME RETARDANT BPEI/PA VIA LBL DEPOSITION

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Abstract: Thin films of environment friendly electrolytes, cationic branched polyethylenimine (BPEI) and anionic phytic acid (PA), were deposited on cotton via Layer-by-Layer (LbL) deposition in order to reduce the flammability of cotton. Altering the concentration of PA (5, 10, 50 wt %) at the same BPEI concentration (1 %) and the number of BPEI/PA bilayers (1, 5, 10) at each of PA concentration confirmed that number of bilayers had no significant influence on flammability of cotton. The highest content of PA (50 wt %) gave the best FR performance to cotton (LOI), while 10 BPEI/PA bilayers with 50 wt % of PA just slightly decreased the LOI value. Cotton fabric treated with 1 bilayer of BPEI/PA (50 wt %) gave the highest contest of char residue after heating in TG.

Introduction: Cotton is one of the most important textile material today used for both apparel and non-apparel due to its unique proporties such as moisture and water absorption making it comfortable to wear. However, as a celullose fiber cotton is extremely flammable and it has to be treated with flame retardants if used for safety clothes etc. The most efficient commercially available flame retardants for cellulose materials are based on nitrogen-phosphorus synergism. Due to potential toxicity risks and environmental issues associated with FR cotton treatments, there is a need for their substitute with some new green alternatives. Phytic acid (PA), as a principal phosphorus store in plant, and its salts from renewable sources, such as bran and seeds, have been used as an alternative environment friendly replacement for commercial phosphorus based flame retardans in laboratory conditions [1-8]. Branched polyethylenimine (BPEI) is used as a polyelectrolyte multilayer on charged surfaces to provide a biocompatible coating on surfaces where finds its application in detergents, adhesives, water treatment, printing inks, dyes, cosmetics, and paper industry, adhesion promoter, lamination primer, fixative agent, flocculant, cationic dispersant, stability enhancer, surface activator, chelating agent, scavenger for aldehydes and oxides. Besides, it is rich in nitrogen [9]. Theoretically BPEI and PA should be an effective cotton N-P flame retardant system. Since the cotton surface is negatively charged in neutral and alkali aqueous, it should be a good substratum for a laboratory-scale method of nanocoating called Layer-by-Layer deposition. This method includes alternate immersion of the substrate into an oppositely charged polyelectrolyte aqueous solutions building a positively and negatively charged layers on the substrate surface or bilayers [10]. Theorethically it is also expected that the increase the number of such built bilayers, the FR performance of cotton fabric is higher.

Exp. no.	BPEI (wt %)	PA (wt %)	No. of bilayers
0 - cotton	n/a	n/a	n/a
1	1	5	1
2	1	5	5
3	1	5	10
4	1	10	1
5	1	10	5
6	1	10	10
7	1	50	1
8	1	50	5
9	1	50	10

Table 1: Applied chemicals

Exp. no.	TG		LOI
	Peak (°C)	Char residue (%)	LOI (%)
0 - cotton	423,89	0,000	18,5
1	402,99	1,712	20,0
2	397,75	1,714	21,0
3	393,01	7,275	20,0
4	395,41	4,565	22,0
5	395,62	2,568	23,0
6	400,88	4,850	23,0
7	407,62	29,387	29,0
8	401,69	2,275	28,0
9	387,43	2,282	28,0

Table 2: Results

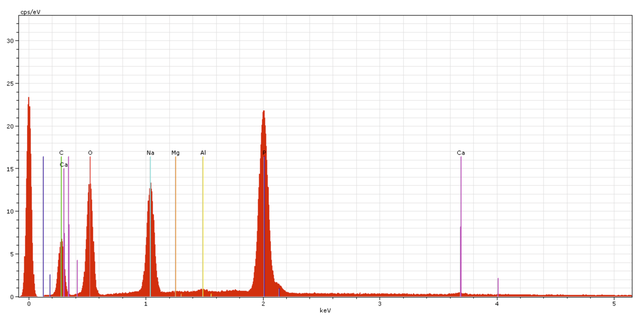

Fig.2: EDX analysis of char residue after TG – experiment 7

Methodology

Experimental: Chemically bleached, desized 100% cotton fabric with a density of 177 g/m2 was supplied by Pamucna industrija d.d. Duga Resa, Croatia. Three aqueous solutions of sodium phytate (5, 10, 50 wt %) supplied by Carbosynth Ltd, UK (CAS 14306-25-3) and branched BPEI (1 wt %) supplied by Sigma-Aldrich (CAS 9002-98-6) were prepared with 18.2 MΩ deionized (DI) water according to table 1. Nine cotton samples were immersed into aqueous solutions of positively charged BPEI and negatively charged PA forming 1, 5 and 10 bilayers. The immersing time was 10 minutes for the first layer (cotton/BPEI) and 1 min for each layer (BPEI/PA). Each immersion step was followed by rinsing in deionized (DI) water. Cotton samples were dried in the oven at 50°C.

Characterisation: The morphology was studied using a Tescan MIRA\\LMU FE-SEM Scanning Electron Microscope (BSE detector, 3,5 kV) equipped with the EDX detector for elemental analysis and SC7620 Sputter Coater equipped with gold/palladium target (Quorum Technologies). The thermal stability of the fabrics were evaluated by thermogravimetric (TG) analyses using PerkinElmer Pyris 1 TGA thermogravimetric analyzer. All samples for TGA were measured from 50°C to 700°C at the heating rate 40°C/min in the air (flow rate: 30 ml/min). Burning behavior of the fabric were evaluated by Limiting Oxygen Index (Dynisco) according to the EN ISO 4589-2.

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Results and discussion: Cotton fabric is characterized by low LOI (18.5%). Treatment by LbL enhances LOI values up to 20 % and 21 % when experiment 1, 2 and 3 was applied (PA 5 wt%) according to table 2. Further enhancement of LOI values (22 % and 23 %) is obtained with increase of PA concentration up to 10 wt% (experiment 4, 5, 6; table 2). The best LOI values (28 % and 29 %) were obtained by treating cotton samples with concentrated solution of PA (50 wt%). However, the increase in number of bilayers at the same PA concentration does not follow the LOI values as theoretically expected. The value of LOI of cotton samples treated with 5 % concentration of PA is the highest for 5 bilayers (21 %), than for 1 and 10 bilayers (20 %). The LOI values for the cotton samples treated with 10 % concentration of PA are 22 % (1 bilayer) and 23 % (5 and 10 bilayers). Between 3 cotton samples treated with 50 wt% concentration of PA, the highest LOI value were obtained with 1 bilayer (29 %) according to table 2.

Theoretically it is also expected that TG curves follow LOI values, which means that the temperature peaks of decomposition dicrease lineary with the increase of PA contest (5 wt%, 10 wt%, 50 wt%) as well as number of bilayers (1, 5, 10). Important differences between TGA curves of raw (sample 0) and LbL treated cotton samples are in initial decomposition temperature which is lower for all treated materials comparing to raw cotton. For untreated cotton (0), the decomposition temperature is around 424 °C, and the lowest decomposition temperature, around 387°C, obtained the cotton sample treated with PA 50 wt% in 10 bilayers (experiment 9) according to table 2.

Theoretically it is also expected that the mass of the final char residue after heating in TG shows linear grow from untreated cotton to LbL treated cotton (PA 5 wt%, 10 wt%, 50 wt%) as well as number of bilayers (1, 5, 10). In this paper the highest mass of the final char residue (around 29 %) was obtained by PA 50 wt% in 1 bilayer (experiment 7) according to table 2.

The EDX analysis of that char residue has mainly shown the contest of carbon, oxygen, phosphorus, sodium and others in traces (aluminum, magnesium, calcium) according to figure 2. This suggests that at high PA contest (50 wt%), the aqueous solution is saturated with sodium phytate, which deposites on the surface of fabric treated with BPEI instead of negatively charged PA. Char residues of other samples are low, suggesting that sodium was washed out through 5 and 10 cycles of rinsing in water. Aluminum, magnesium and calcium are impurities of the technical grade sodium phytate. EDX analysis did not show any traces of nitrogen suggesting that NOx gas compounds evolved during combustion.

SEM images of the char residue after heating in TGA (experiment 7, table 2) has shown the intumescent N-P flame retardant effect on cotton fabric with bubbles coming from NOx gas compounds evolved during combustion (figure 3).

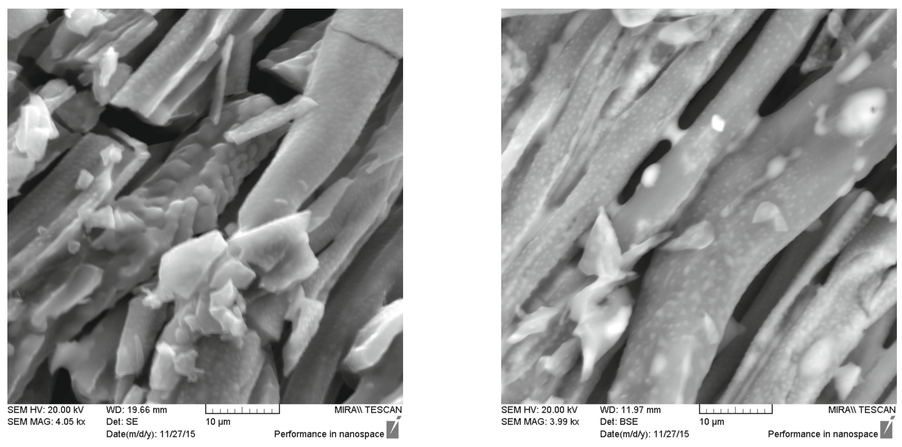

Fig.3: SEM images of char residue after TG – experiment 7 (table 2): a) SE detector b) BSE detector

Conclusion: Environmentally friendly electrolytes were successfully deposited onto cotton using LbL technology enhancing the innitally low FR properties of cotton material. Altering the number of BPEI/PA layers and the concentration of PA sodium salt hydrate in aqueous solution (1.0 and 10.0 wt %) the results of LOI, so as TGA curves indicated the reduce of flammability of cotton fabrics. Encrease of PA concentration caused continuous reduction of cotton flammability. At the same time the increase of LbL layers showed less pronounced influence on cotton flammability, using the same PA concentration. This work may open interesting perspectives of depositing environmentally friendly electrolytes using LBL technology for a variety of medical or biomedical applications.

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