APPLICATION OF ZEOLITE *FAU* FOR FLAME-RETARDANT FINISHING OF CELLULOSE

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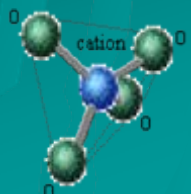
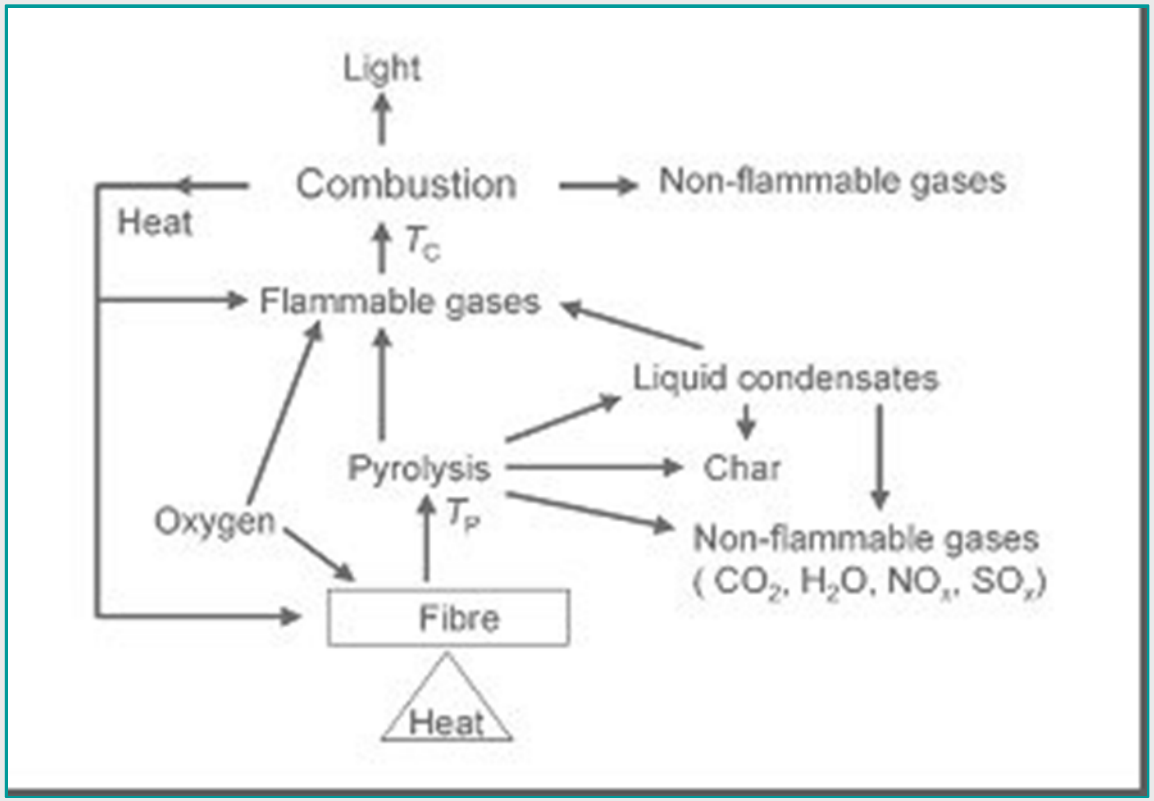
TSRC Competition 2010/2011



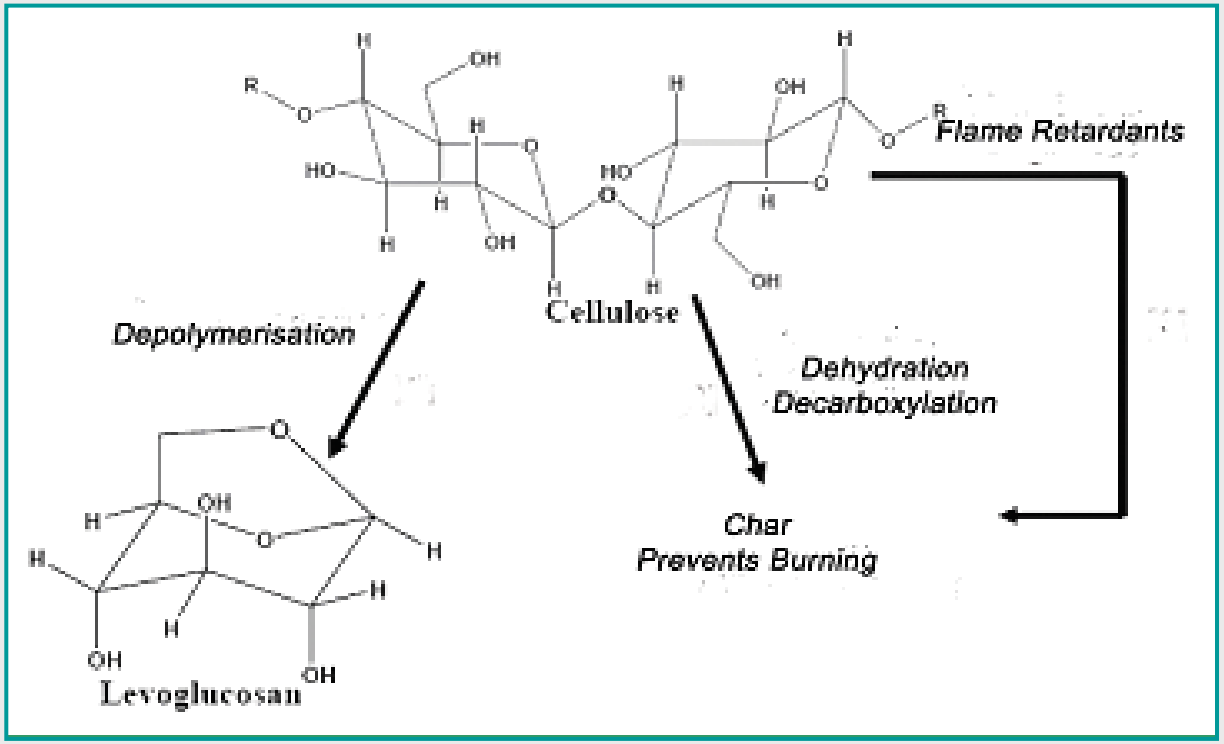
Introduction

- Cotton fabrics, which have a major share of the textile market, are highly inflammable and the development of successful flame retardant (FR) systems for cotton is of major interest.
- The idea of implementation of flame retardant into the materials dates back to 450 BC, when the Egyptians used alum to reduce the flammability of wood
- Fabric flammability is affected by various factors such as fiber composition, fabric construction, oxygen concentration, and the environmental conditions (moisture content, heat, air flow), but the effects of finishing material fabrics cannot by overlooked.
- It is well known that the laundering additives, i.e., bleaches, detergents and softeners, are flammable and if they are deposited on the surface after washing, they may enhance fabrics flammability as opposite, while in contrast the direct dye agents reduce the flammability of fabrics, or enhance fabrics LOI value.

- The burning process is comprised of five fundamental steps, which are heating, decomposition, ignition, combustion, and propagation.



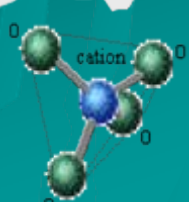
Mechanism of pyrolysis of untreated and flame retardant treated cotton fabrics



- Flame retardant agent can be classified into the following groups: (1) non-durable, (2) semi-durable, or (3) permanent.

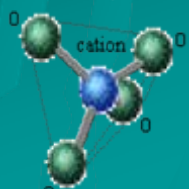
- The most desirable FR agent would be the one which could be easily applied to a fabric, preferably in a finished form ready for use, and would render that fabric permanently FR without appreciably altering the fabric char-acteristics for consumers use.

- As a consequence of the complex nature and poor reproducibility of fire there are many techniques for estimating the flammability characteristics of polymeric materials. The most widely used laboratory test is the limiting oxygen index (LOI) technique, a very convenient, precise and reproducible.



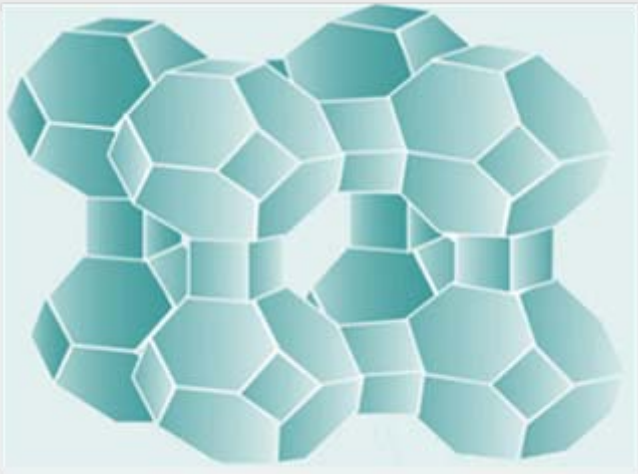
- Thermal and flame retardant properties of representative natural and synthetic fibre

Natural and synthetic fibre	LOI [%]	Glas transition T_g [°C]	Melt T_m [°C]	Pyrolysis T_p [°C]	Combustion T_c [°C]
Wool	25	-	-	245	600
Cotton	18,4	-	-	350	350
Viscoze	18,9	-	-	350	420
Triacetate	18,4	172	290	305	540
Nylon 6	20-21,5	50	215	431	450
Nylon 6.6	20-21	50	265	403	530
Polyester	20-21,5	80-90	255	420-477	480
Acrylic	18,2	100	>320	290	>250
Polypropylene	18,6	~20	165	469	550
Modacrylic	29-30	<80	>240	273	690
Nomex	28,5-30	275	375	310	500
Kevlar	29	340	560	590	>550

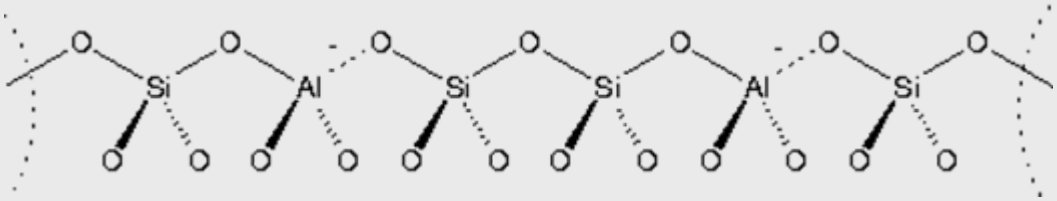


- In this paper the possibility of using aluminosilicate microporous compounds (zeolites) for the treatment of cellulosic materials to obtain flame retardant properties has been investigated.

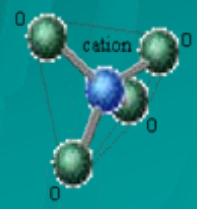
- Zeolites, a family of aluminosilicates containing pores and cavities in the range of 4-18 Å, are well-known sorbents, catalysts, molecular sieves and ion exchange. Structure of zeolites consists of three-dimensional network $[AlO_4]^{5-}$ / $[SiO_4]^{4-}$ polyhedra connected with oxygen atoms



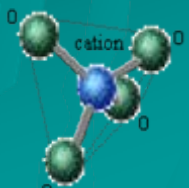
Structure of Zeolite FAU



Tetrahedra linked by oxygen atoms



Experimental



- The desized, scoured, bleached and optically brightened 100% cotton fabrics weighing 170 g/m^2 was used in the study. Commercially available reagent grade chemicals were used in the fabric treatment with Organophosphorus agents (OF) and alumino-silicate gel which was prepared in TTF laboratory. Impregnation was performed at a laboratory padder Benz Zürich, Switzerland

- Hydro gel with bulk composition (in moles)

  $6\ Na_2O - 10\ SiO_2 - 0{,}5\ AI_2O_3 - 1\ H_3BO_3 - 240\ H_2O$

  was prepared in beaker under intensive stirring.

  The pH value of the Bath I was 13.5.

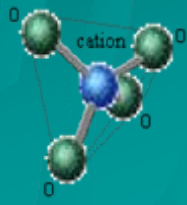
- Cellulose fabrics were treated for 1 min. in a 18 wt.% NaOH solution and then padded with prepared gel solutions (Bath I) having a wet pick- up of approximately 100 %. Crystallization was accomplished in a microwave oven during 10 min, at 900 W in steam atmosphere.

Cotton fabric sample was impregnated with an aqueous solution containing

- citric acid (70 g/l),
- sodium hypophosphite (65 g/l),
- halogenide free hydroxy- functional organophosphorus agent (400 g/l) (Bath II)

The treated sample was passed through a two-roll laboratory padder, and dried at 110°C for 2 minutes. Wet pick-up was in the range of 95-100%. The fabric was then cured at a 160 °C for 180 s.

The home laundering wash/dry process was performed at 80 °C according to ISO 6330 with a standard detergent.

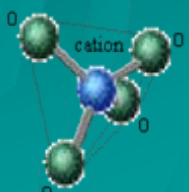


Thermal analyses of cotton materials were performed in a flowing synthetic air atmosphere (30 % oxygen; flow rate of 90 ml/min) using a Perkin Elmer analyzer controlled by a PC system. TG (thermal gravimetric) of the samples were obtained from 20 to 800 °c in air at a heating rate of 30 °c/min. prior to the thermal analysis runs the cotton fabrics were cut into small pieces having an average weight of ca. 1 mg, whereas the analyzed samples weighed approximately 6 mg.

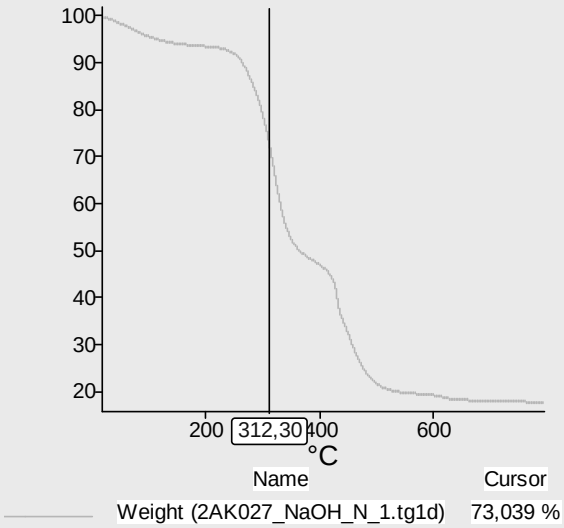
Samples were studied by the coupled TG-IR technique in order to better understand the decomposition process of differently FR-treated cotton fabrics. A Thermal Analysis Gas Station (TAGS), equipped with a detector, was used for the FT-IR analysis. The transfer line, high-temperature flow cell, and TG interface were held at 280°C for the duration of the run to prevent gas condensation. The evolved gases were transferred through the FT-IR flow cell by a peristaltic pump with a flow rate of 60 milliliters per minute.

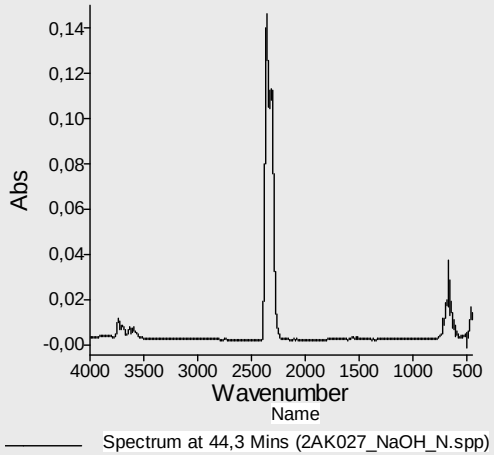
Scanning electron microscopy (SEM) was used to characterize the surface morphology and confirm bonding of zeolite particles to cellulose fibers. For SEM study, the samples were mounted on stubs and coated with gold in a sputter coater.

Results and discussion

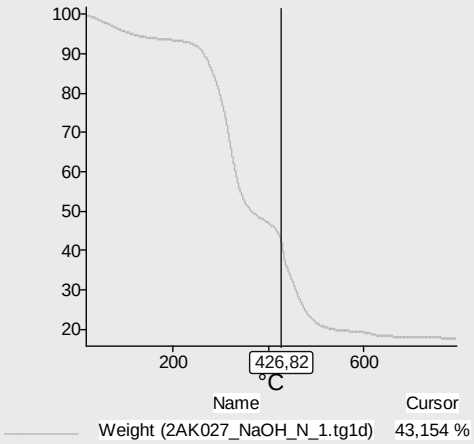


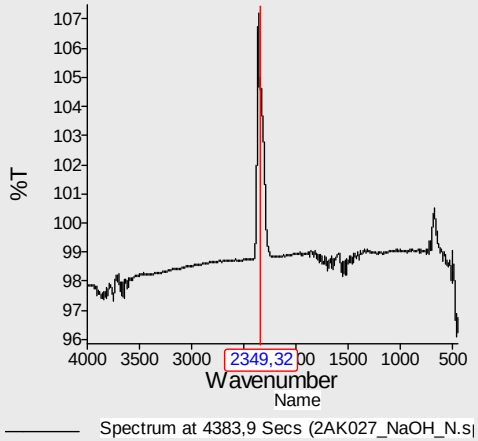
TG – FTIR analysis treated cotton fabric with bath I during thermooxidative decomposition





TG curve and FTIR spectra of gas evolved at 312, 30 °C

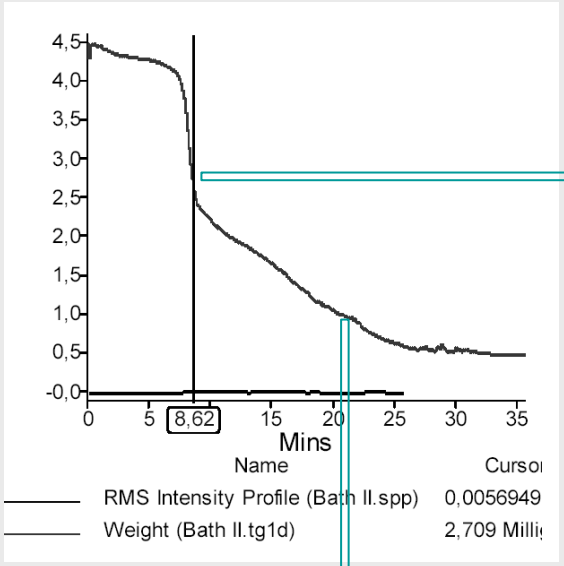


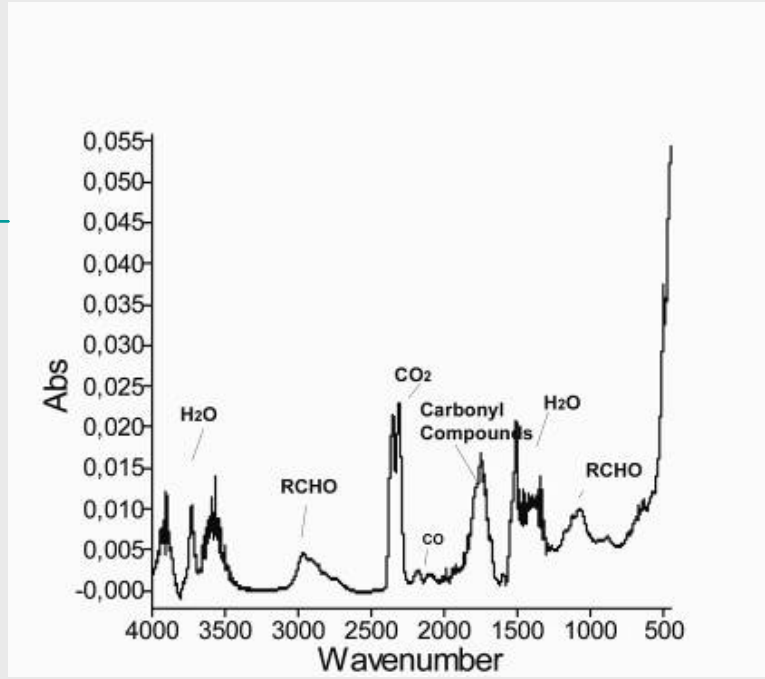


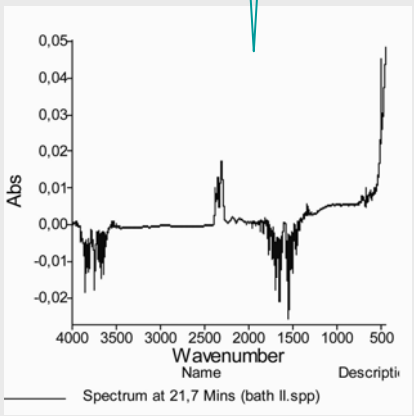
TG curve and FTIR spectra of gas evolved at 426, 82 °C

The volatilized products of sample treated with bath I observed at 312, 30 °C and 426, 82 °C are identified as CO_2 (characteristic peaks at 2359 and 2322 cm-1) and volatilized water characteristic peaks at 1550 and 1566 cm-1).

TG – FTIR analysis treated cotton fabric with bath II during termooxidative decomposition at 258,6 °C



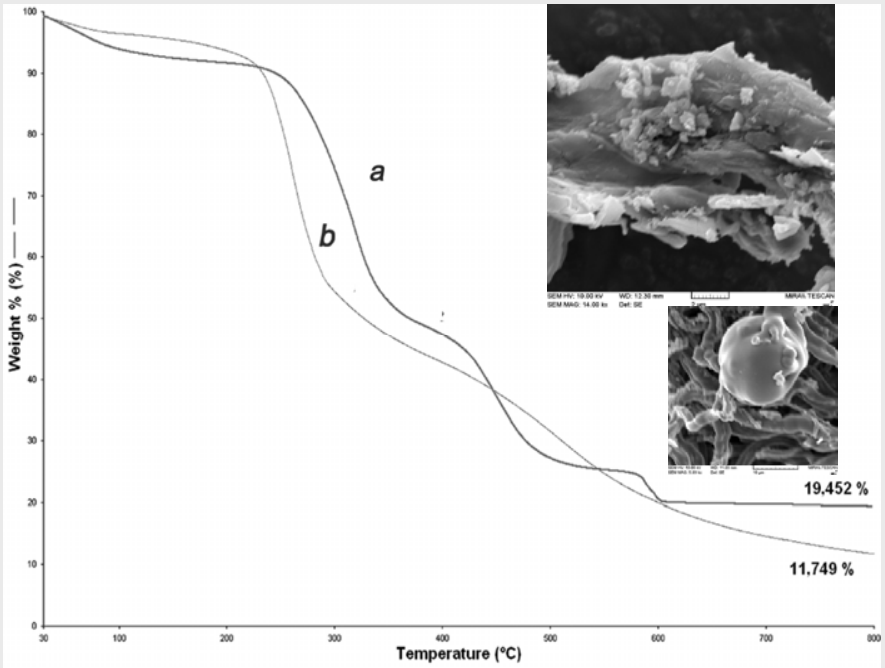


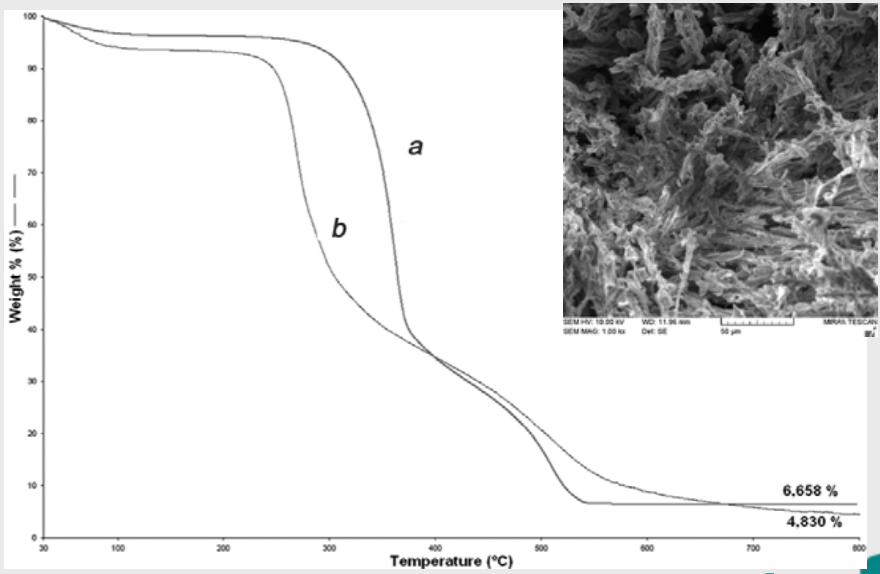


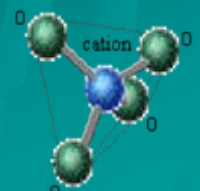
The pick at 1050 cm-1 indicates the formation of levoglucosan. The maximum levoglucosan concentrations found at the temperature of 258 °C is visible in Figure 4b. Here, the damage of the cellulose occurs mostly in amorphous region of the polymer. The volatilized products observed at 258,6 °C is identified as aldehyde RCHO (characteristic peaks at 2951 and 1184 cm-1), CO (characteristic peaks at 2179 and 2110 cm-1), CO2 (characteristic peaks at 2359 and 2322 cm-1) and volatilized water (characteristic peaks at 1550 and 1566 cm-1). The strong CO2 absorption at 2359 cm-1 saturated the IR beam visualized at 450 °C. It is clear from Figure 4c that at higher temperatures the combustion of flame retardant cellulose results in the formation of carbon monoxide as well as carbon dioxide and water.

- The sample treated with Bath I has a higher decomposition temperature respect to the sample treated with a Bath II (232,4 °C curve 1b). The amount of char formed in the TG analysis of the sample treated with Bath I (19.19 %) is higher then the amount of char formed in the analysis of the sample treated in Bath II (11,62 %). TG curves for the treated samples after one cycle of laundering indicate a progressive reduction of residue after TG analysis. The decrease in the decomposition temperature of sample treated with Bath II is due to the catalyzed dehydration of cellulose by the phosphorus acid, which was formed by decomposition of phosphorus flame retardants under lower temperatures.

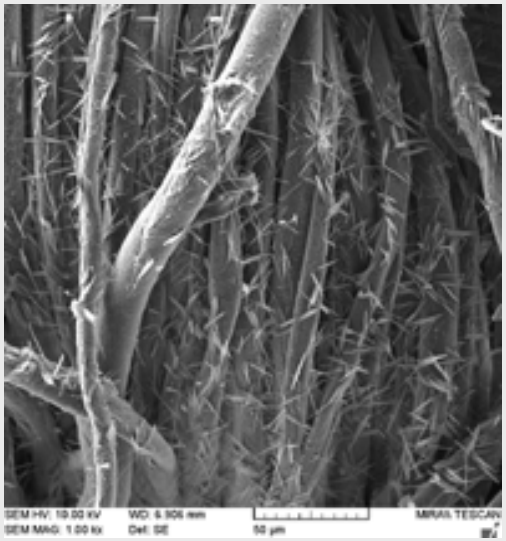
- The presence of flame retardants on the fabrics causes reduction of the decomposition temperature of cotton and also increases the amount of char content at 800 ºC. From the SEM images of the residues after TG analysis at 800 °C, presence of inorganic zeolite FAU and an organic part which belongs to cellulose are well distinguished.



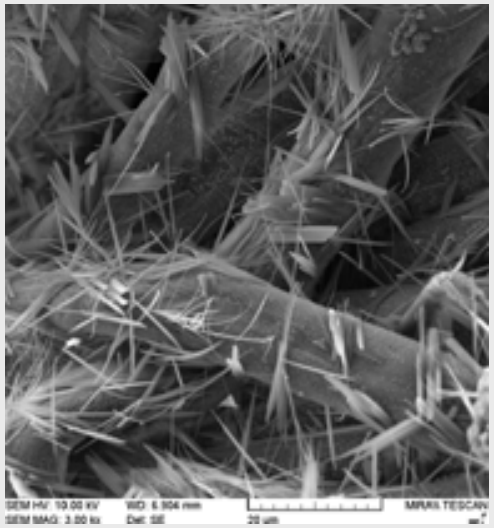




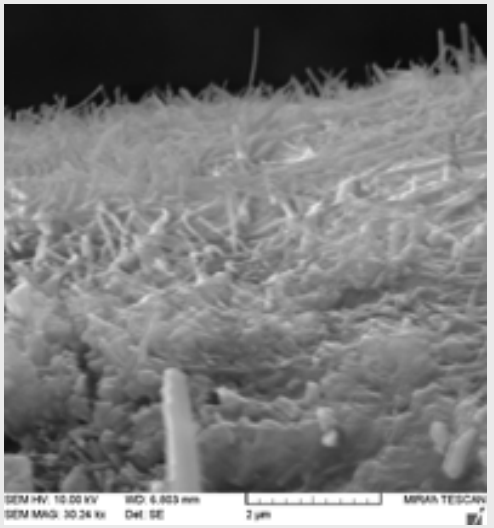
SEM images of cellulose composites at different magnifications: a) 1,00kx b) 3,00kx c) 30,24kx



a)



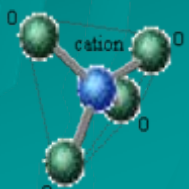
b)



c)

SEM images at different magnifications show that the coating procedure applied by direct synthesis has been successful and the entire surface of cellulose material appears homogeneously covered with FAU zeolite crystallites.

Conclusions



- The SEM pictures of the obtained composite material exhibits a homogeneous coating of the cellulose material with FAU zeolite crystallites.

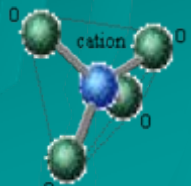
- From the results of the TG analysis it can be seen that the sample treated with the flame retardant has a lower decomposition temperature than the sample of the composite material obtained from the in situ synthesis of the FAU zeolite on cellulose material.

- It is also seen that a larger share of char remains after the TG decomposition of the composite material, indicating that apart from the inorganic (FAU zeolite) there is also a organic leftover is cellulose. As expected the char leftovers decreased after one cycle of laundering.

- The volatiles with the TG-IR interface were also measured and it can clearly be seen that the sample treated with Bath I forms less volatiles which are composed of CO_2 and H_2O while the sample treated with Bath II has more volatiles containing more health damaging gases.

- The results show that the sample treated with Bath I is more flame resistant and more ecologically acceptable.

- In further studies other parameters, necessary for the classification of the sample as ecologically acceptable flame resistant materials, will be considered.



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