INFLUENCE OF ALKALINE ULTRASOUND PRE-TREATMENT ON THE CROSSLINKING ENVIRONMENTALLY FRIENDLY FLAME RETARDANT AGENT WITH CELLULOSIC MATERIAL

Sandra FLINĻEC GRGAC [1] Andrea KATOVIĹ [2] and Ivana KLJAJIĹ [1]

[1]Univesity of Zagreb Faculty of Textile Technology, Prilaz baruna Filipovi a 28 a, Zagreb, Croatia
[2] University of Calabria, Department of Environmental and Chemical Engineering, Via P. Bucci 44A, 87030 Rende (CS), Italy
sflincec@ttf.hr

Abstract: The use of ultrasounds in the textile wet processing has been found to have great utility since they alter the fibre structure increasing their absorption as well as raising the diffusion coefficient of chemical molecules. Starting from these premises, the aim of this study was to investigate the effects of alkaline ultrasound pre-treatment on the cross linking of non-halogenated hydroxyl functional organophosphorus (Non-halogenide HFOP) flame retardant agent and citric acid (CA) as a bonding agent on the cellulose material. Flame retardance was tested using Limiting oxygen index (LOI) technique according to ISO 4589-2. The thermal and physico chemical properties of the so obtained flame retardant samples were characterized by thermogravimetric analysis, coupled thermal gravimetric - Fourier transforms infrared technique (TG-FTIR) and Fourier transforms infrared spectroscopy (FTIR). The results indicate that a more stable bonding between cellulose and flame retardant agents was achieved in the sample which was pre-treated in an ultrasound alkaline bath.

Keywords: alkaline ultrasound pre-treatment, flame retardance finishing, cotton, FTIR spectroscopy, TG-FT-IR, tensile properties of fabrics.

1. Introduction

Clothing, curtains, furniture, bedding and many other things that surround us are made of flammable cellulosic materials. Cellulose fibres have functional groups, which have an important role due to their reactivity that results not always sufficient for many finishing processes. It is already known that treating cellulose material with aqueous NaOH solution has a significant effect on morphological, molecular and supramolecular cellulose properties, causing changes in crystallinity, pore structure, access to reactive areas, solidity, unit cell structure and orientation of fibrils inside the fibres. Furthermore, it is known that the using lower concentrations of sodium hydroxide solution (14-18%), it is possible to obtain Na - cellulose that is more reactive than the pure cellulose [1].The use of ultrasounds in the textile wet processing has been found to have great utility since they alter the fibre structure increasing their absorption as well as raising the diffusion coefficient of chemical molecules. Extensive research has found the intensification of the effects during the wet finishing textile materials by application of ultrasound based on physical mechanism such as reduction of the boundary-layer thickness between the textile surface and the bulk liquid, reduction in the size of the particles, and increased swelling of the fibers [2]. Starting from these premises, the aim of this study was to investigate the effects of alkaline and alkaline ultrasound pre-treatment on the cross linking of non-halogenated hydroxyl functional organophosphorus (Non-halogenide HFOP) flame retardant (FR) agent and citric acid (CA) as a bonding agent on cellulose material. Flame retardance was tested using Limiting oxygen index (LOI) technique according to ASTM D 2863-97. The thermal and physico chemical properties of the so obtained flame retardant samples were characterized by FTIR spectroscopy, thermogravimetric analysis (TGA), coupled thermal gravimetric - Fourier transforms infrared technique (TG-FTIR) white the tensile properties of fabrics were tested according to ISO 13934/1. The results indicate that a more stable bonding between cellulose and flame retardant agents was achieved in the sample which was pre-treated in a ultrasound alkaline bath which used frequency of the ultrasound waves generated by the sonicator plate 80 kHz (Ap3) with 100% power. The use of alkaline ultrasound pre-treatment enhanced the performance of Non-halogenide HFOP/CA and the treatment caused no significant changes in the fabrics physical properties.

2. Materials and methods

2.1 Materials

The desized, scoured, bleached and optically brightened 100% cotton print cloth weighing 170 gm^{-2} was used in the study.

Cellulose fibres were subject to the alkaline process or semi-mercerisation [1] to simplify the penetration of prepared bath inside the cellulose material. All samples were treated with the same bath for mutually are different in methods of pre-treatment in 8% NaOH. One part of cellulose material in stretched form was subject to pre-treatment in an 8% NaOH for one minute at 25 ± 2°C (Ap1). Second and third part of cellulose fabrics were pre-treated in ultrasound for 1 min with 8% NaOH solution. The frequencies of the ultrasound waves generated by the sonicator plate were 37 kHz (Ap2) and 80 kHz (Ap3) with 100% power. Cotton fabric pre-treated without ultrasounds and ultrasound pre-treated cotton fabrics then padded with an aqueous solution containing citric acid (70 g/l), sodium hypophosphite (65 g/l), and halogen free hydroxy- functional organophosphorus oligomer (400 g/l). pH value of the bath was 2.38.

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 170°C for 3 minutes.
The home laundering wash/dry process was performed at 40 °C according to ISO 6330:2012 with standard detergent without phosphate.

2.2 Methods

The Limited Oxygen Index (LOI) technique provided a quantitative measure for determination of reduced flammability for treated cotton materials. LOI values of the samples were determined according to the EN ISO 4589-2 and presented the maximum percentage of oxygen in an oxygen-nitrogen gas mixture that will sustain burning a standard sample for a certain time. The LOI values were calculated according to the equation (1) [3].

$$LOI\ [\%] = \frac{[O_2]}{[O_2]+[N_2]} \cdot 100 \qquad (1)$$

Thermal analyses of untreated and treated cotton materials were performed in a flowing synthetic air atmosphere (30 % oxygen; flow rate of 90 ml/min) using a Perkin Elmer analyser controlled by a PC system (Pyris 1). TG (thermal gravimetric) of the samples were obtained from 50 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 millilitres per minute.

Physical and chemical changes within the material and degree of esterification D.E., which confirm crosslinking cellulose with flame retardant agent, were analyzed by FTIR spectrometer (PerkinElmer, software Spectrum 100). The cured cotton fabric was immersed into a 0.1 M NaOH solution for 3 min to convert the free carboxyl groups to carboxylate, thus remove the unreacted acid. The sample was dried at 90 °C for 10 min [4]. 4 scans at a resolution of 4 cm^{-1} were recorded for each sample between 4000 cm^{-1} and 380 cm^{-1}.
The ester carbonyl band absorbance was normalized against the 1314 cm^{-1} band associated with the C-H bending mode of cellulose. The D.E. values were calculated according to the equation (2)[4].

$$D.E.[\%] = \frac{I_{1730}}{I_{1730} + I_{1570}} \cdot 100 \qquad (2)$$

Where is:
D.E.- degree of esterification
I ï intenzity of peak in the 1730 and 1570 cm^{-1}

3. Results and discussion

Results of Limited Oxygen Index (LOI), a convenient parameter for measuring the minimum oxygen concentration necessary for combustion, are presented in Table1.

LOI values are the most commonly used parameters to indicate the flammability of textiles and other materials, as well. The LOI value of untreated fabric was 18. The LOI values of the cotton fabric treated with Ap1, Ap2 and Ap3 was 26,6%, 26 % and 26%, while after the washing cycle the values slightly decreased to 22%, 20% and 23%.

Table1. LOI of untreated and treated cotton fabrics

Fabrics	LOI, %						
	cotton	Ap1	Ap1_w	Ap2	Ap2_w	Ap3	Ap3_w
Warp	18	26,6	22,3	26	20	26	23
Weft	18	26	22	26	20	26	23

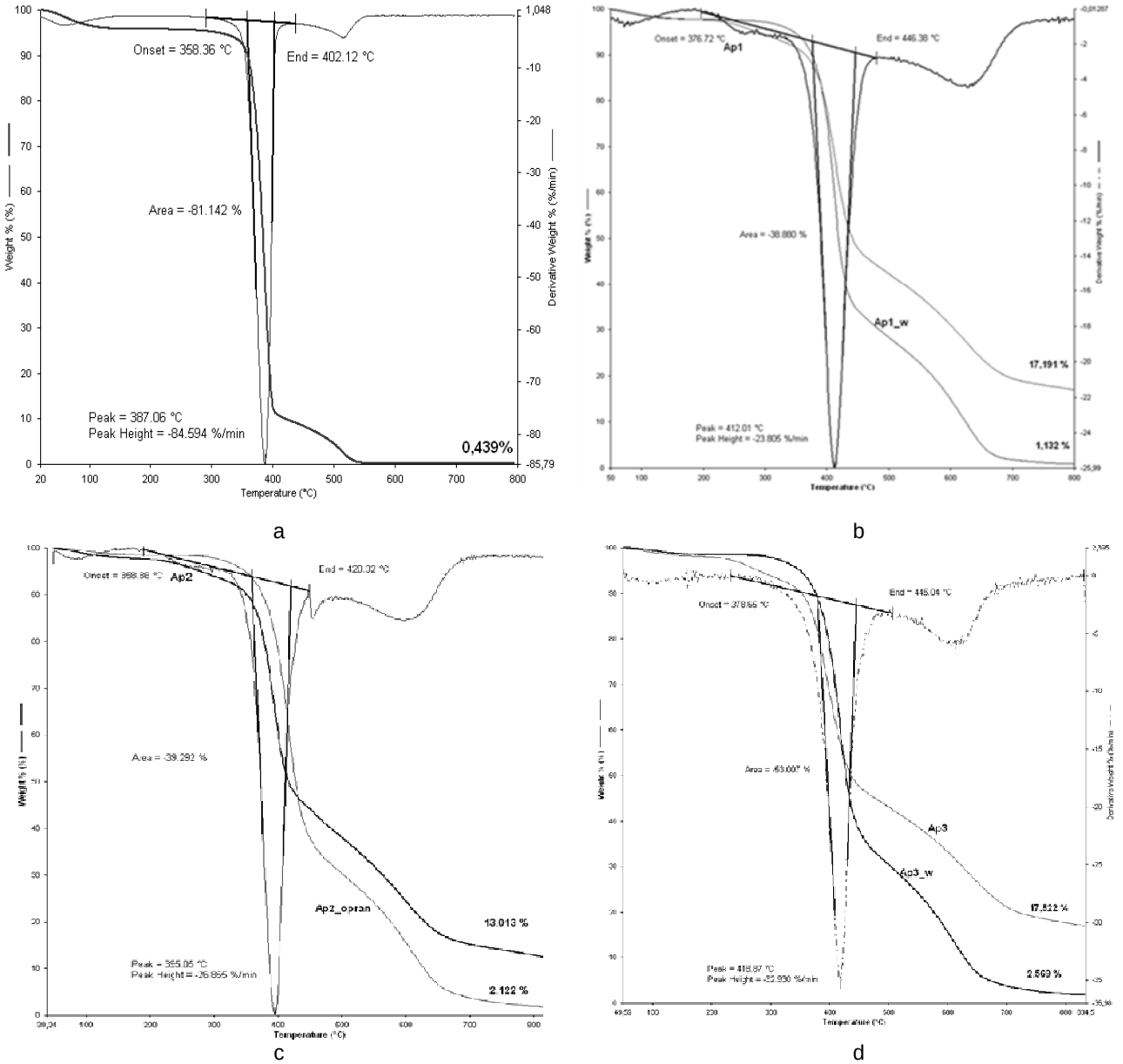

Figure 1. TG and DTG curves of fabrics samples: a) cotton, b)Ap1 before and after washing (Ap1_w),c) Ap2 before and after washing (Ap2_w), d) Ap3 before and after washing (Ap3_w), The char residue is given as % of the initial sample weight.

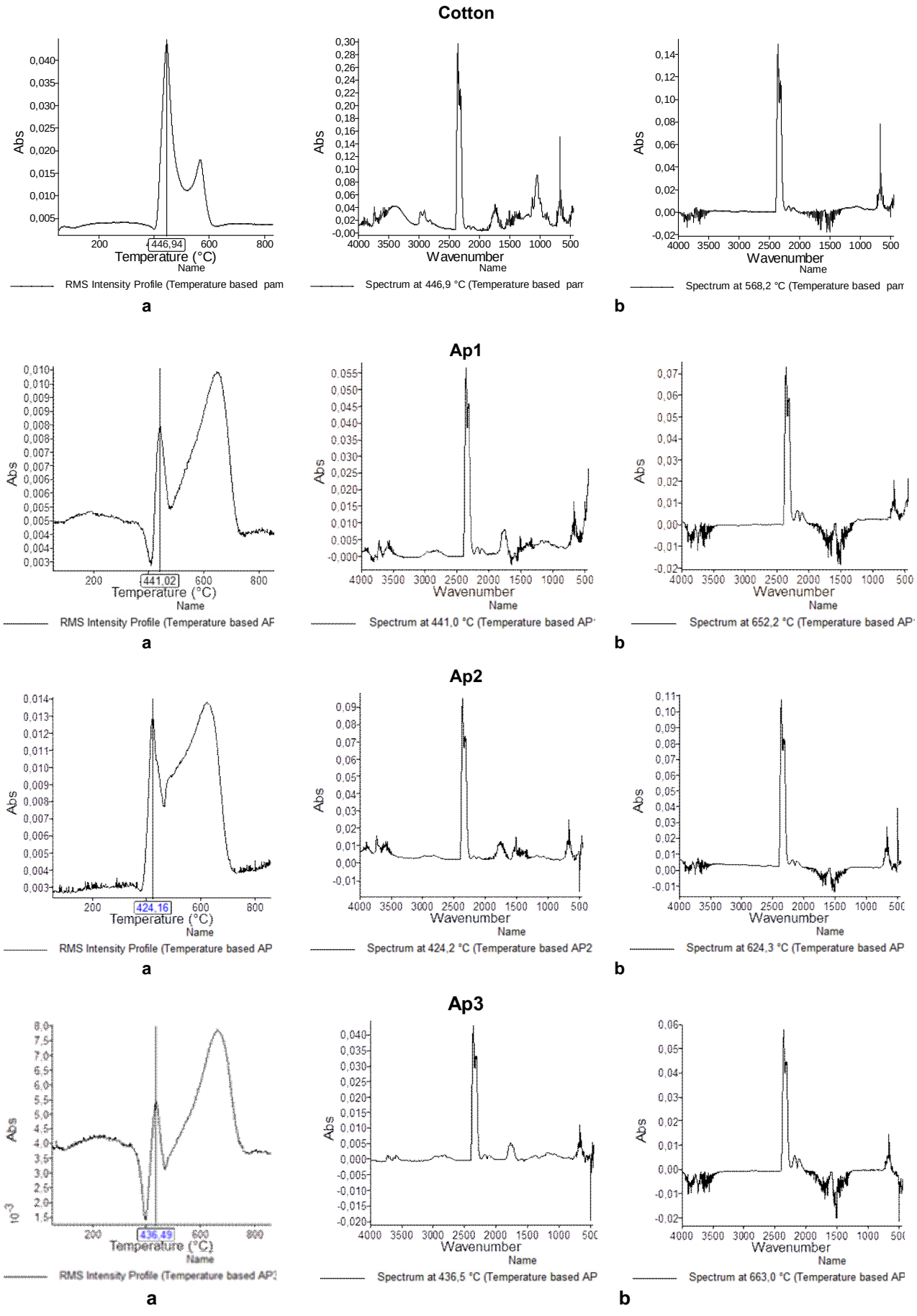

Figure 2. (a) TGï IR analysis of samples cotton, Ap1, Ap2 and Ap3 during termooxidative decomposition (b) FT-IR spectra of gas evolved (cotton, Ap1, Ap2, Ap3)

The TG analyses were applied in order to understand the impact of different pre-treatment processes on the obtained thermally stable cellulosic material after FR finishing with bath which contains halogen free hydroxy- functional organophosphorus oligomer. Figure 1 presents the TG analysis (TGA) curves of cotton, Ap1(a), Ap2(b) and Ap3(c) before and after the washing processes. In comparison to untreated cotton pyrolysis (Fig. 1a), the pyrolysis of cotton treated in Ap1 (Fig. 1 b), Ap2 (Fig.1c) and Ap3 (Fig.1 d) has a lower decomposition temperature while the concentration of the volatiles (Fig.2) are reduced. Upon being exposed to heat, the treated cotton fabric (Ap1, Ap2, Ap3) first loses moisture slowly, and then starts to decompose at a temperature of 358 to 378°C. DTG (the first derivative of TG curve) curves for all treated sample shows the rate of weight loss accelerates above 400 °C due to thermal decomposition of the organic compound. At this stage, most of the volatiles are developed (figure 2) and char residues form. The data presented here indicated that Non-halogenated HFOP, as a condense phase flame retardant, functions to promote char formation as the cotton is exposed to elevated temperatures. From the thermogravimetric curves it is visible that the best thermal stability shows sample that the pre-treated with of the sodium hydroxide and with ultrasonic at a frequency of 80 kHz and then treated with the bath for FR finishing (AP3).

The volatiles were also measured with the TG-IR interface and it can clearly be seen that the sample treated with Ap3 has less volatiles substance, which are observed at 436.49 °C and are identified as CO2 (characteristic peaks at 2359 and 2322 cm^{-1}), CO (characteristic peaks at 2171.43 cm^{-1} and 2112.48 cm^{-1}), volatilized water (characteristic peaks at 1550 and1566 cm^{-1}) and aldehyde RCHO (characteristic peaks at 2951 and 1184 cm^{-1}). Second peak on the intensity profile of evolved gas is observed at 663 °C and are identified as CO2 (characteristic peaks at 2359 and 2322 cm^{-1}), CO (characteristic peaks at 2171.43 cm^{-1} and 2112.48 cm^{-1}) [5]. Untreated and samples treated with Ap1 and Ap2 have more volatiles containing more health damaging gases.

The FT-IR spectra of cotton and flame retardant cotton fabrics are presented in the Figure 3.

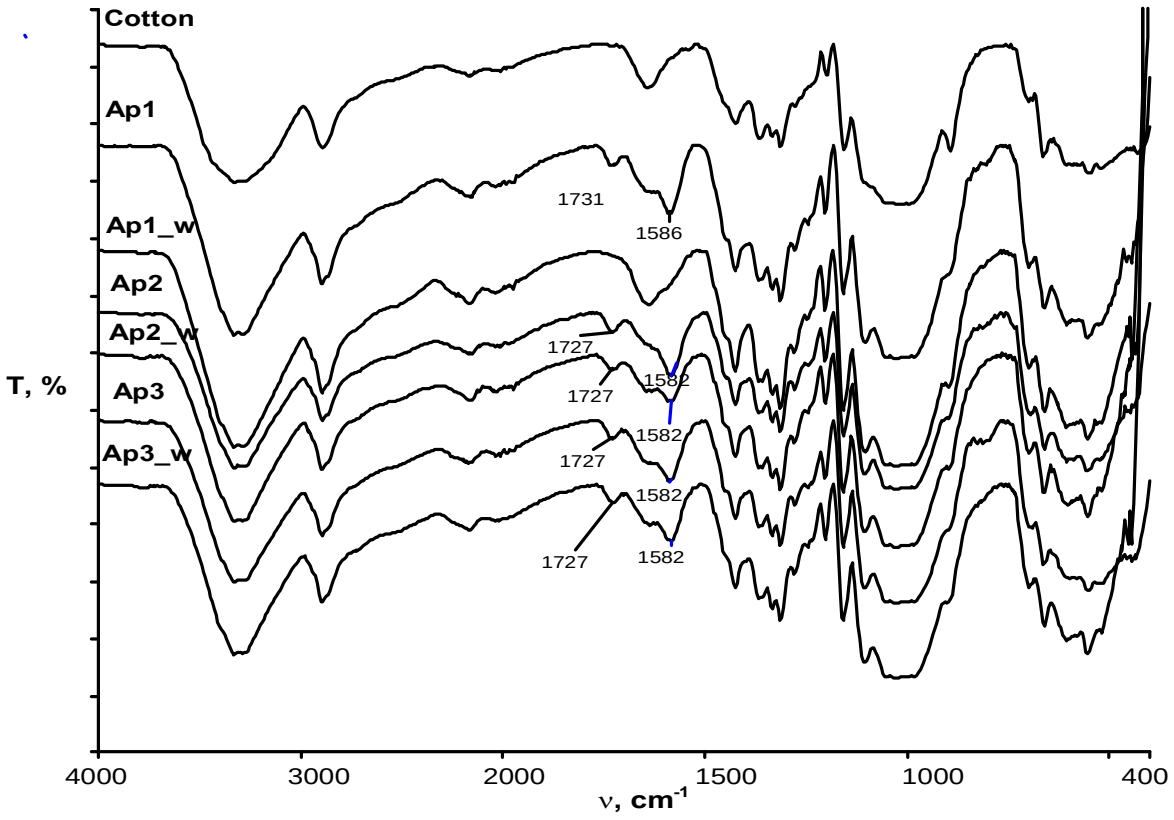

Figure 3. FT-IR spectra of cotton and flame retardant cotton fabrics before and after washing cycle

Degree of esterification (D.E.) for the treated cotton samples calculated from the ratio of the intensities of the IR bands at wave numbers 1727 cm^{-1} and 1582 cm^{-1} corresponding to ester and carboxylate groups, respectively (Tab.2). Figure 3 presents ATR spectra of untreated cotton, Ap1, Ap2 and Ap3 sample before and after washing process where the latest proved better esterification performance confirmed with higher peaks at 1730 cm^{-1} as evidenced by its degree of esterification which is before washing 37,83% and after one washing cycle 31,81%.

Table 2. Degree of esterification of flame retardant cotton sample before and after washing cycle

Sample	Degree of esterification D.E., %
Cotton	0
Ap1	39.26
Ap1_w	0
Ap2	36.36
Ap2_w	28.53
Ap3	37.83
Ap3_w	31.81

4. Conclusion

In this paper, the impact of alkaline pre-treatment in bath and with ultrasound on the mechanism of crosslinking of a new halogen free hydroxy- functional organophosphorus oligomer with environmentally friendly agent (CA) was investigated. The results indicate that a more stable bonding between cellulose and flame retardant agents was achieved in the sample which was pre-treated in an ultrasound alkaline bath which used frequency of the ultrasound waves generated by the 80 kHz sonicator plate (Ap3) with 100% power. This is evidenced by its degree of esterification which is before washing 37,83% and after one washing cycle it is 31,81%. The cotton fabrics treated with Ap1 and Ap2 before and after one washing cycle have lower levels of crosslinking that is visible after calculated degree of esterification from the sample spectra, which were recorded with ATR-FTIR technique.

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