INVESTIGATING POSSIBILITIES OF APPLYING ENVIRONMENTALLY-FRIENDLY FLAME RETARDANT AGENT IN THE PROCESS OF TEXTILE PRINTING

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ABSTRACT

In this paper, the possibility of binding environmentally-friendly halogen-free hydroxy functional organophosphorous (HFOP) flame retardant agent on cellulosic material using printing pastes was investigated. The following methods of analysis were used for physico-chemical and flame retardant characterization: thermal gravimetric analysis (TG), coupled TG-FTIR technique and limited oxygen index (LOI). Colour yield and colourfastness before and after the washing process of the printed fabrics were measured on a DATACOLO FS600 PLUS spectrophotometer. The results indicate the possibility of applying the printing paste as a crosslinking agent for eco-friendly flame retardant agent.

Keywords: flame retardant cotton finishing, textile printing, TGA, TG-IR analysis, LOI, L*a*b* value

1. INTRODUCTION

Cotton fabrics printed with various patterns have found their wide application in the interior decoration use and special use, such as camouflage clothing. A correctly guided procedure of textile printing resulted in binding dyes to the fibers, and thus we obtained a coloured printed pattern resistant to washing. This characteristic led us to think about designing functional samples which would have aesthetic and protective properties. Due to the chemical composition, cotton fabrics are highly flammable and many scientists are investing substantial efforts to achieve durable flame retardant finishing with environmentally-friendly agents and procedure (Cheng 2009). Our previous researches (Flinčec Grgac 2015) were directed to investigate the possibilities of crosslinking environmentally-friendly flame retardant (HFOP) on cotton fabric using different binding agents generally based on melamine resin and polycarboxylic acids. However, the results did not show durability after more washing cycles. In this paper, the possibility of binding environmentally-friendly halogen-free hydroxy functional organophosphorous (HFOP) flame retardant agent on cellulosic material using printing pastes was investigated.

2. EXPERIMENTAL

The desired, scoured and chemically bleached 100% cotton fabric weighing 170 g/m2 was used in the study. A cotton fabric sample (Cotton) was printed with the paste which consisted of the printing paste Printperfect 226-3 (60 g/l), pigment Colormatch 210-rot (0,4 g/l) (PP226-3) and HFOP flame retardant agent (6 and 12 g/l) (PP226-3_6HFOP and PP226-3_12HFOP). All the samples were printed by screen-printing. The printed samples were dried at 110°C for 2 minutes and then cured at a 165 °C for 360 s. The stability of the obtained printed cellulose materials to washing was determined according to ISO 6330 with a standard detergent (HLWD). Limiting oxygen index (LOI) values of the samples were determined according to the EN ISO 4589-2 standard method. Thermogravimetric (TG) experiments were carried out using a PerkinElmer TGA Pyris1 thermogravimetric analyzer. Samples weight is in the range of 5 - 6 mg. All samples for TGA were measured from 50 °C
to 750 °C at the heating rate 30 °C/min with a continuous airflow. TG-FTIR analysis of a cotton fabric and all cotton printed fabric were performed using a PerkinElmer Pyris TG analysis, PerkinElmer FT-IR spectrometer and TG-FT-IR interface. A Thermal Analysis Gas Station (TAGS), equipped with a detector, were 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 sample 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. Colour yield and colourfastness before and after the washing process of the printed fabrics were measured on a DATACOLO FS600 PLUS spectrophotometer.

3. RESULTS AND DISCUSSION

LOI values are the most commonly used parameters to indicate the flammability of textiles as well as other materials. The LOI of the untreated cotton woven fabric was 18.0%. It increased to 19% when the fabric was printed with PP_226-3, and further increased to 20% after one cycle of washing processes. The LOI values of the printed cotton fabric with printing paste in which 6 g/l and 12 g/l of HFOP were added was 27% and 29%, while after the washing cycle (HLWD) the values slightly decreased to 24% and 26%.

TG-IR method is a very important method for monitoring impact of sample on environment and humane halt. TGAs and TG-IRs of cotton and printed cotton samples with and without HFOP agent before and after the washing are presented in Figures 1. to 4.

Figure 1. TG and DTG curves for the cotton sample (a) with TG-IR analysis during termooxidative decomposition at 464.7 and 627.4°C: I) and III) Intensity profile of gas evolved, II) and IV) FTIR spectra of gas evolved.

Untreated cotton fabric (Fig.1. a) starts to decompose at 393 °C, having the maximum weight loss rate at 425 °C and losing 99% of weight at 627 °C. Changes in adsorbing intensity of identified pyrolysis products as a function of temperature for cotton fabric are shown in fig.1. I) and III) and FTIR spectra of gas evolved at II) and IV).
At the initial stage, where the temperature range is below 300 °C, the most important changes of the fibers are some of the physical properties and a little weight loss. The results indicated that untreated cotton fabric formed considerable concentration of levoglucosan (C6H10O5), CO, CO2, CH4 and aldehyde RCHO [3,4,5] at 465°C, this temperature is near on the temperature in which sample has maximum degradation (DTG curve (Fig.1a)). Here, the damage of the cellulose occurs mostly in the amorphous region of the polymer. The volatilized products formed during the thermal degradation of the sample printed with

Figure 2. TG and DTG curves for the cotton printed samples (a) with TG–IR analysis during termooxidative decomposition at 491.5 and 642.6°C: I) and III) Intensity profile of gas evolved, II) and IV) FTIR spectra of gas evolved and TG and DTG curves for the cotton printed samples after the washing process (b) with TG–IR analysis during termooxidative decomposition at 443.8 and 560.4°C: I) and III) Intensity profile of gas evolved, II) and IV) FTIR spectra of gas evolved
PP_226-3 before and after washing were also characterized by TGA/FT-IR technique, as shown in Fig. 2a II) and IV) and 2b II) and IV). This sample shows similar properties to the raw cotton fabrics. Printed sample PP-226-3 shows the same gaseous decomposition products as well as raw cotton but to a much lesser intensity. After one cycle of washing processes, intensity and composition of gaseous degradation products is the same as the untreated cotton.

**Figure 3.** TG and DTG curves for the PP226-3_6HFOP samples (a) with TG–IR analysis during termooxidative decomposition at 364.8 and 649.7°C: I) and III) Intensity profile of gas evolved, II) and IV) FTIR spectra of gas evolved.
The printed fabrics with the printing paste in which HFOP was added (PP_226-3_6HFOP, PP_226-3_12HFOP) have lower decomposition temperatures of the cotton and printed cotton (PP_226-3) because of the catalytic dehydration of cellulose by the flame retardant. Differences between the PP_226-3_6HFOP and PP_226-3_12HFOP TGA curves (Fig. 3a and 4a) are the initial decomposition temperature which is lower for sample printed with higher amount of HFOP added in printed paste (PP_226-3_12HFOP) and the final char residue is greater. TG curves of the printed cotton fabrics (PP_226-3_6HFOP_1xHLWD, PP_226-3_12HFOP_1xHLWD) after one washing cycle Fig. 3. b) and Fig. 4. b) shows partial decrease of the durability of the flame retardant.
Figure 4 clearly shows that the sample which contains a higher concentration of HFOP flame retardant agent has recorded lower intensity of decomposition gases. The flame-retardants added in the printing paste may have catalytic actions to dewatering and carbonizing reactions and inhibiting functions to the reactions that produce l-glucose, so the production of combustible gases are reduced, the quantities of H$_2$O, CO$_2$ and CO were increased at higher temperatures.

![L*a*b* Chart](image)

Figure 5. L*a*b* values for each printed samples

The results in chart shows minor influence of HFOP addition on value of colour parameters (hue, chromaticity and lightness). Addition of HFOP affects on decrease of chromaticity value and on increase of lightness value, more significant at higher concentration. However, the addition of HFOP has no a major impact on colour parameters of printed samples, his influence can be easily predict with colour matching. All of samples show very good fastness on washing treatment.

4. CONCLUSION

The TG, TG-IR and LOI results indicate the possibility of applying the printing paste as a crosslinking agent for eco-friendly flame retardant agent. L*a*b* values show that the addition of flame retardant agent in the printing paste have not no major impact on the change in colour parameters (hue, chromaticity and lightness) due to represent a quality addition to improving the properties of textile materials.

In further research we will consider the impact of higher amounts of HFOP agent in combination with a variety of print pastes in order to obtain durability of flame retardant finishing for cotton material.
5. REFERENCES


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