MODIFICATION OF COTTON MATERIAL WITH PRECURSORS OF SILICON ALKOXIDES FOR IMPROVED FLAME RETARDANCY

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ABSTRACT
The application of natural zeolite in cotton finishing bath suggested that this complex silicone compound may have a considerable influence on cotton flammability. Silicone has excellent thermal stability and high heat resistance with very limited release of toxic gases during the thermal decomposition. In this paper cotton material has modified with sol-gel method. Material was treated with two precursors of silicon alkoxydes - 3-Aminopropyltrietoxysilane and 3-Methacryloxypropyltrimethoxysilan. These two precursors were combined with conventional flame retardants to improve their initial flame retardancy. For better understanding the changes in cotton structure under the heat conditions limited oxygen index (LOI), thermogravimetric method (TGA), micro combustion calorimeter (MCC) was used.

Key Words: 3-Aminopropyltrietoxysilane, 3-Methacryloxypropyltrimethoxysilan, conventional flame retardants, MCC, LOI, TGA

1. INTRODUCTION

Cotton was among the most widely used textile fiber in history and is still the most commonly used and most important textile fiber today. It is one of the most flammable textile fibers as well. The fire hazards of cotton clothing represent genuine risk to consumers because of cotton's ease of ignition and vigorous burning [1]. Therefore, it is necessary to improve its flame retardancy.

In the most cases flame retardant cottons are produced by chemically after-treating fabrics as a textile finishing process which, depending on chemical character and cost, yields flame retardant properties having varying degrees of durability to various laundering processes [1]. Cellulose textiles are treated with those flame retardants that increase char or non-combustible products, usually organic phosphorous-based flame retardants.

In last few years the effect of natural zeolite to flame retardancy was investigated by Grancarić et al. [2-4]. Natural zeolite applied, e. g. clinoptilolite is microporous hydrated crystals containing alumino-silicates with well-defined structures containing AlO_4 and SiO_4 tetrahedral linked through the common oxygen atoms. It has unique absorption and catalyst properties and therefore and for that multiple uses in industry, agriculture, water purification and detergents. In medicine they are attributed antitumor, antiallergic, antiseptic, antireumatic and other properties. Tribomechanical activation of natural zeolite in patented machine results in zeolite grinding to submicron levels so that their reactive ability and biological activity is exchanged several hundreds times. Applied on textile material they can absorb, but mostly scatter the UV-R, resulting in UV protection. It also gives off good antimicrobial protection on Gram positive bacteria [4].

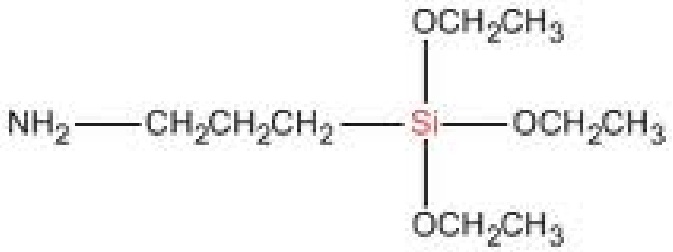
From the results applying natural zeolite clinoptilolite in cotton finishing bath suggested that this complex silicone compound may have a considerable influence on cotton flammability

[2-4]. Since silicone has excellent thermal stability and high heat resistance with very limited release of toxic gases during the thermal decomposition its application as flame retardant by sol-gel method was researched in this paper.

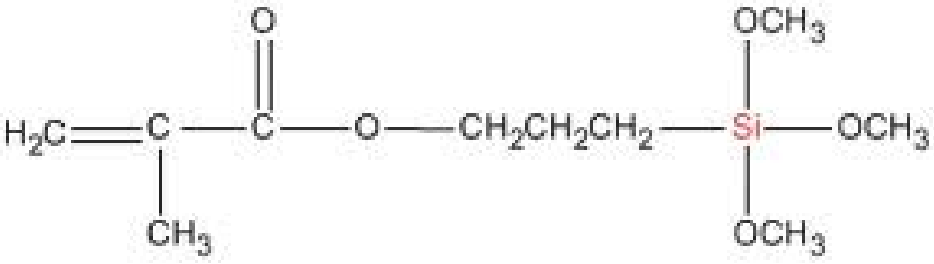
2. EXPERIMENTAL

2.1. Material

In this paper cotton material has been modified with two silicon-based precursors by sol-gel method. Textile material used was twill woven chemically bleached cotton fabrics of mass per surface area 211 g/m^2. The precursors applied are silicon alkoxydes shown in Figure 1: 3-Aminopropyltrietoxysilane and 3-Methacryloxypropyltrimethoxysilan.



a. 3-Aminopropyltrietoxysilane



b. 3-Methacryloxypropyltrimethoxysilan

Figure 1. Precursors applied for cotton modification

Cotton fabric was treated with two precursors of silicon alkoxydes by sol-gel process. The sol-gel, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of a sol to form a network in a continuous liquid phase (gel) [2-3]. These two precursors were combined with conventional flame retardants to improve their initial flame retardancy.

The cotton fabric was firstly treated by pad-dry procedure in with conventional compound ammonium hydrogen phosphate (Ap2). For sol-gel method in padding bath firstly the precursors, 3-Aminopropyltrietoxysilane (A) or 3-methacryloxypropyltrimethoxysilane (M) has been added. For the third treatment both components ammonium hydrogen phosphate and precursors, 3-Aminopropyltrietoxysilane (Ap2A) or 3-Methacryloxypropyltrimethoxysilane

(Ap2M) have been added to the padding bath, dried at 110 °C for 2 min and cured at 150 °C for 5 min. In the case of ammonium hydrogen phosphate cotton samples has been only dried.

The labels and procedures are listed in Table 1.

Table 1. The labels and procedures

Label	Procedure
0	Untreated chemically bleached cotton fabric
A	Sol-gel with 3-Aminopropyltrietoxysilane
M	Sol-gel with 3-methacryloxypropyltrimethoxysilane
Ap2	Pad-dry with conventional compound ammonium hydrogen phosphate
Ap2A	Pad-dry with conventional compound ammonium hydrogen phosphate with addition of 3-Aminopropyltrietoxysilane
Ap2M	Pad-dry with conventional compound ammonium hydrogen phosphate with addition of 3-methacryloxypropyltrimethoxysilane

2.2. Methods

Burning behavior of fabrics was determined according to ISO 4589:1996 - *Plastics - Determination of burning behavior by oxygen index*. Limiting Oxygen Index (LOI) was determined in LOI Chamber (Dynisco).

For better understanding the thermal changes of cotton structure under the heat conditions thermogravimetric analyser (TGA) and micro combustion calorimeter (MCC) have been used.

Thermogravimetric Analysis (TGA) Pyris1 (PerkinElmer) analysed of the mass loss in function of the temperature applying elevation of temperature 10 °C/min.

Microscale Combustion Calorimeter (MCC) MCC-2, Govmark, USA measured multiple fire properties of micro laboratory scale samples applying pyrolyzer operating temperature range of min. 25 to 1000°C, detection sensitivity limit of min. 5 mW, and repeatability of : ± 2 % (5 mg sample).

3. RESULTS AND DISCUSSION

In this paper cotton material was treated with two precursors of silicon alkoxides by sol-gel method. These two precursors were combined with conventional flame retardants to improve their initial flame retardancy. The burning behavior of such modified cotton fabric was determined by Limiting Oxygen Index. The results are collected in Table 2.

Table 2. Burning behaviour of Limiting Oxygen Index, LOI according to ISO 4589:1996

Fabric	$t_{100\ mm}$ [s]	LOI
0	105	19
A	107	19
M	104	19
Ap2	80,7	25
Ap2A	64	30
Ap2M	52	32

The conventional compound for cotton flame retardancy, ammonium hydrogen phosphate (Ap2) shows expected high LOI values (LOI 25). Cotton fabric treated by sol-gel method with only precursors of silicon alkoxydes shows no improvement compared to untreated cotton (LOI 19). By addition of ammonium hydrogen phosphate and precursors in padding bath flame protection reached the high LOI values (LOI 30 and LOI 32) presented in Table 1. The proposed fire retardancy of these compounds seems to be the formation on the cotton surface the barrier against heat transfer. This high LOI values could be explained by eventually synergism between silicones and phosphate.

The results of thermogravimetric analysis (TGA) carried out in the area of 50°C to 800°C, with a temperature change of 10°C per minute presented in Figure 2 confirm that. The TGA curve of pure cellulose has two-steps mass loss characteristic of cotton cellulose degradation [4]. Cotton treated with combination of ammonium hydrogen phosphate and precursors (Ap2A and Ap2M) show the higher temperature needed for full degradation and more char residue then cotton treated with conventional flame retardant, only (Ap2).

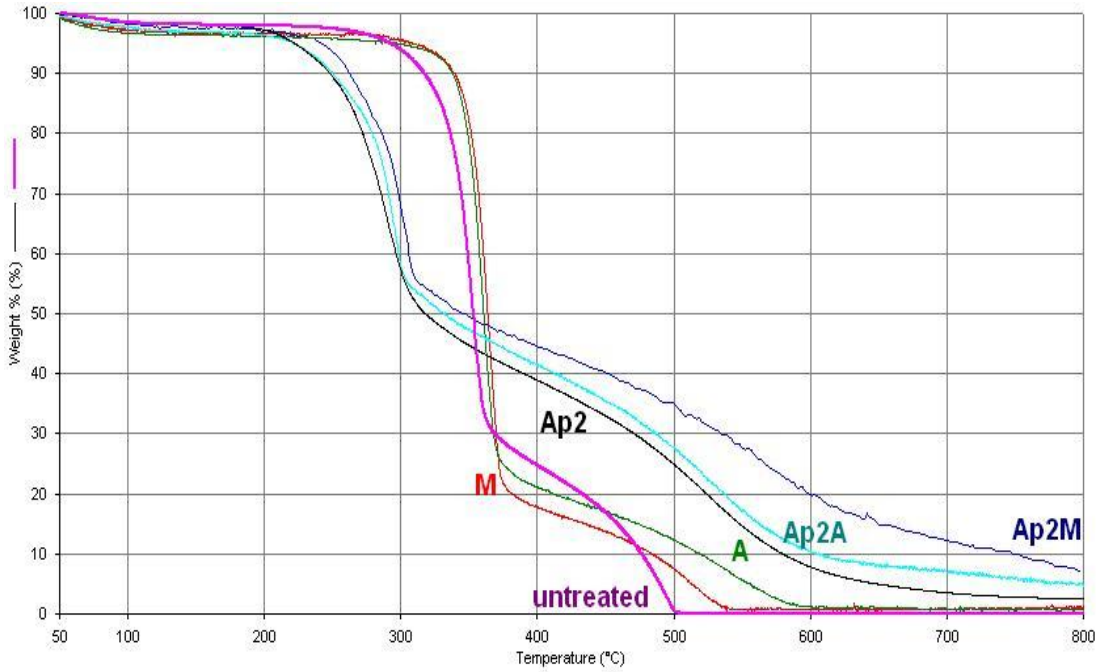


Figure 2. TGA curves of cotton fabrics recorded in air, heating rate 10 °C/min

Micro combustion calorimeter (MCC) results are presented in Figure 3.

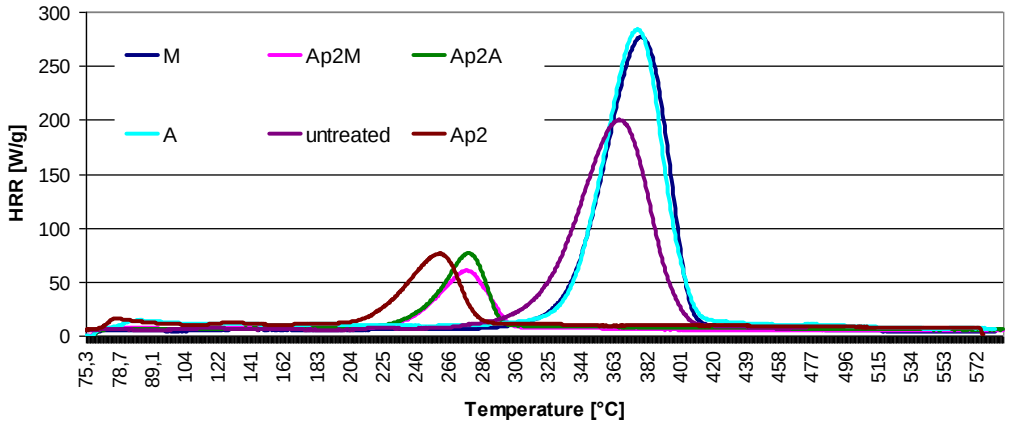


Figure 3. Cotton fabrics HRR curves

From Figure 3 it is clear that cotton material treated with ammonium hydrogen phosphate and silicon alkoxides (Ap2A, Ap2M) precursors has much lower Heat Release Rate (HRR). This confirms the lower total system energy and better thermal properties that are crucial in every material flame retardancy. For both silicon alkoxides in the bath with ammonium hydrogen phosphate it is evident that HRR curves are shifted slightly to the right as the consequence of present precursors with the high HRR.

4. CONCLUSION

Silicon alkoxides precursors visibly help in cotton flame retardancy when conventional compound ammonium hydrogen phosphate is used. This combination increased the value of the LOI for 5 to 7 units and has the better thermal properties then pure conventional treatment. The conventional compounds and agents reach very high flame retardancy but accompanied by low wash fastness. It is needed to continue this research work on the new and green technology to find enough good wash fastness and the higher flame retardancy.

ACKNOWLEDGEMENTS

The paper is a part of the results of the COST action project FLARETEX *Sustainable flame retardancy for textiles and related materials based on nanoparticles substituting conventional chemicals* (MP1105). The authors would like to thank European Commission COST for the funding of the project.

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