Environmentally Friendly Flame-Retardant Materials Produced by Atmospheric Pressure Plasma Modifications

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ABSTRACT: The objective of this work was to investigate plasma modification of viscose for environmentally friendly flame-retardant cellulosic materials. Sodium silicate layers were predeposited onto viscose and cotton flannel substrates and grafted/crosslinked using atmospheric pressure plasma. The modified cellulosic fabrics tested with the automated 45° angle test chamber showed significant improvement in their flame-retardant properties. Analysis conducted by TGA and DSC exhibited enhanced thermal stability of the treated fabrics. Furthermore, the surface analysis (XPS and SEM) confirmed the presence of the SiO_2 network attached to the substrate even after intense ultrasound washes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 116–122, 2012

Key words: flame-retardant; viscose; cotton flannel; atmospheric pressure plasma; coatings

INTRODUCTION

Cellulose is the most extensively used biopolymer and represents a renewable source for organic materials. Its availability in vast quantities as well as its good mechanical properties and biodegradability make cellulose one of the most representatives of natural polymers. However, the use of regenerated cellulose fibers for specific technical applications can lead to several disadvantages such as ease of ignition, burning, and thermal degradation of cellulose. Therefore, as is well known, a number of durable flame-retardant (FR) finishes have been developed for rayon and cotton in recent years. In general, these finishes depend on first padding an aqueous solution of a phosphorus-containing monomer or prepolymer onto the textile and then drying and curing to form an insoluble resin. Another approach of flame proofing rayon involves mixing a flame-retardant with the viscose dope before spinning so that the resulting fiber contains the flame retardant entrapped in it. However, there are several requirements that the additive has to be compatible with the viscose solution and appropriate particle size distribution when solid FR agents are used.[1,2] The conventional process to impart FR to textiles involves a pad-dry-cure method. Problems with these finishes include yellowing from heat curing and acid damage, alteration of fabric hand and degradation, or total loss of mechanical properties. These concerns and limitations have led to further development of alternative physicochemical processing methods. In this field, plasma technology shows distinct advantages because it is environmentally friendly and surface properties of inert materials can be easily modified.[3–5]

In the previous article we have reported the improvement of FR properties of cellulosic materials (cotton) using a sol–gel process in conjunction with atmospheric pressure plasma (APP) treatments.[6]

In this article, we examine a different route to lower the flammability of viscose and cotton flannel fibers by forming a layer of silica particles on their surface and convert it into a grafted/crosslinked macromolecular network using atmospheric pressure plasma (APP) technology.

EXPERIMENTAL

Materials

Spun Viscose Challis, weight = 138 g/m^2 and Bleached Cotton Flannel, weight = 122 g/m^2 were purchased from Test Fabrics and cut in 2 × 6" samples. Sodium silicate solution was purchased from Sigma Aldrich Chemicals.

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TABLE I
Burning Spread Times for Rayon/Viscose

Sample	Conc (%)	Weight (g)	Dry pick up (%)	BST (s)
Viscose				
Control	0	1.60	–	10.13
APP V 2	2	1.60	1.61	45.05
APP V 3	3	1.57	1.9	44.30

Procedure

Viscose and cotton flannel fabrics were dried in the vacuum oven overnight and weighted. The samples were soaked in sodium silicate solution of different concentrations (2, 3, and 5 wt %) for 2 h, then dried in the vacuum oven at room temperature overnight. After drying, the samples were exposed to APP using an Array Electrode Reactor (AER) described elsewhere.[7] The influence of plasma parameters and FR concentrations on the burning spread times of the fabrics was analyzed according to a statistical design of experiments (Design Expert 7 software). The following plasma parameters were used: power = 70 W, plasma exposure time = 5 min and air flow rate = 500 sccm. The process parameters are the optimal ones proven and discussed in more detail in the previous studies[6–8] After plasma treatment to remove the non reacted SiO_2 particles, samples were washed for 30 min in deionized (DI) water using an ultrasound bath. Three washings for each batch were performed. Tables I and II show the dry pick up and their corresponding burning spread times of the treated and control viscose and cotton flannel samples.

45° Angle flammability test (ASTM D1230- 01)

The plasma treated and washed samples were dried in vacuum oven overnight at the room temperature and then tested for flammability with a 45° angle Auto-Flame chamber. Samples were mounted in a frame and held in a special apparatus at an angle of 45°. A standardized flame was applied to the substrate's surface near the lower end for 1 s. The flame traveled up the length of the fabric to a trigger string, which dropped a weight to stop the timer when burned through. The time required for the flame to travel the length of the fabric and break the trigger string was recorded, as well as the fabric's ignition time.[9] Five samples for each treatment were tested and the results were averaged. For further confirmation of these results the tests have been duplicated.

TABLE II
Burning Spread Times for Cotton Flannel

Sample	Conc (%)	Weight (g)	Dry pick up (%)	BST (s)
		Cotton flannel		
Control	0	–	–	17.50
APP CF 2	2	1.43	3.95	38.70
APP CF 3	3	1.40	4.25	41.30
APP CF 5	5	1.40	4.19	42.60

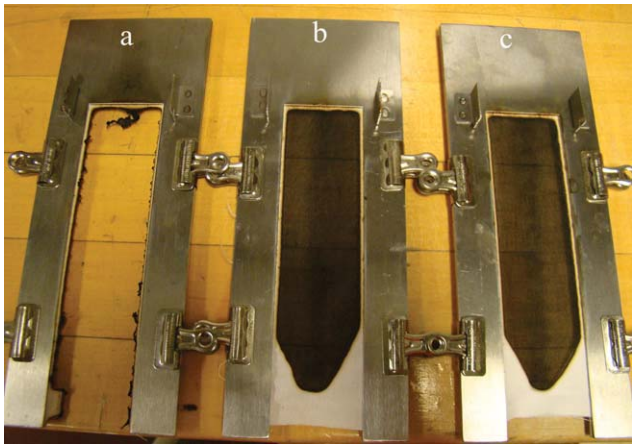

Figure 1 Burning behavior; (a) viscose control; (b) viscose with 5% FR; (c) viscose with 3% FR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermo gravimetric analysis

TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. The samples were analyzed using a TGA Q500 from TA Instruments to evaluate their thermal stability. The samples were placed into the device one at the time at a ramp temperature from 25°C till up to 700°C at a heating rate of 10°C/min. The purge gas used was nitrogen.

Differential scanning calorimeter

DSC was used to evaluate the changes in thermal behavior before and after coating using a Q100 Modulated DSC instrument from TA Instruments. The analysis was carried out under nitrogen atmosphere in the temperature range of 20–500°C using a heating rate of 10°C/min.

Surface characterization

X-ray photoelectron spectroscopy

A Perkin–Elmer Physical Electronics Phi 5400 Small Area Spectrometer (Mg source; 15kV; 300W; pass energy = 89.45 eV) was used for the XPS analysis. A 45° take-off angle was used between the sample and the detector. Survey and high-resolution (HR) scans for core levels were performed on the samples. The curve fitting of the HR peaks were done using Gaussian algorithm.

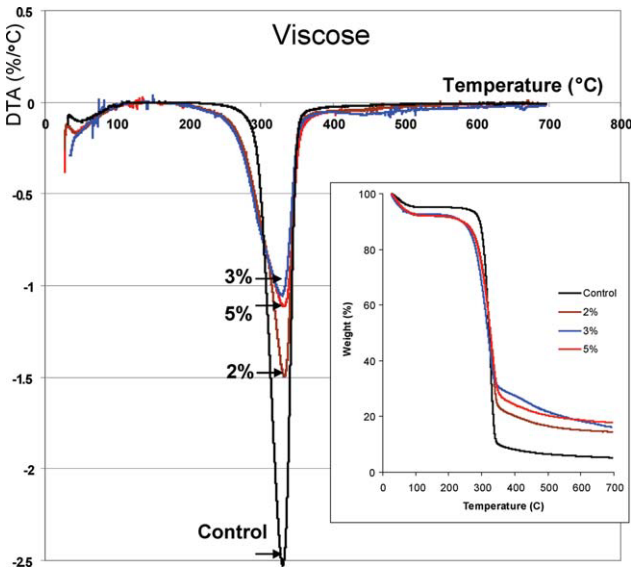

Figure 2 TGA diagram of control viscose versus plasma-modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scanning electron microscope

To characterize the morphology of the surface as well as the uniformity of the coating the samples were analyzed with a LEO DSM 1530 FE Scanning Electron Microscope. The magnification used was 20,000X.

RESULTS AND DISCUSSIONS

45° angle flammability test

The concentrations of the FR solution, dry pick up amounts and their corresponding results from burning spread time of the fabrics are presented in Tables I and II. It can be observed that the fabrics have similar dry pick up amounts regardless the FR concentration used (Tables I and II). Furthermore, the difference in burning spread times was more than four times higher for treated viscose fabrics (regardless the FR concentration used) in comparison with control ones (Table I). The burning spread time for treated cotton flannel was two and a half times higher than control one regardless the concentration of FR used (Table II). The results obtained are comparable to those reported by Konda et al.[10] and Ramachandran et al.[11]

The photo-image (Fig. 1) shows the burning behavior of treated viscose samples (b and c) compared with the untreated one (a) during the flammability test. The virgin viscose burns completely during the test, while most of the burned material is retained as a char in case of the silicate/plasma-treated samples. This is characteristic of a homogeneously silicate coating on the treated samples.

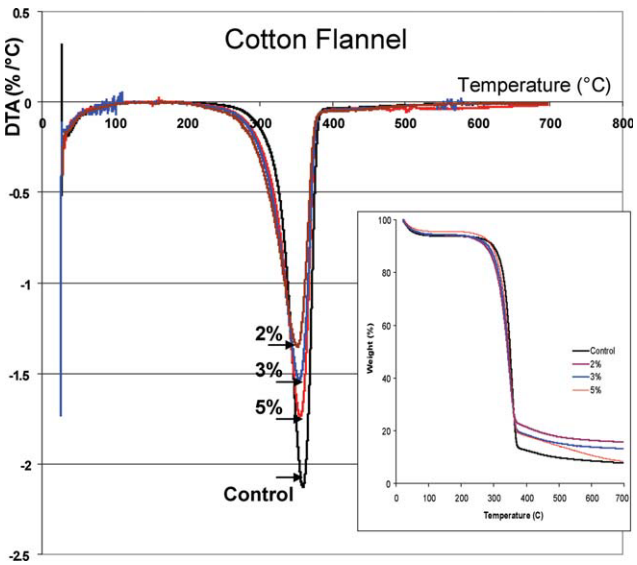

Figure 3 TGA diagram of control cotton flannel versus plasma-modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

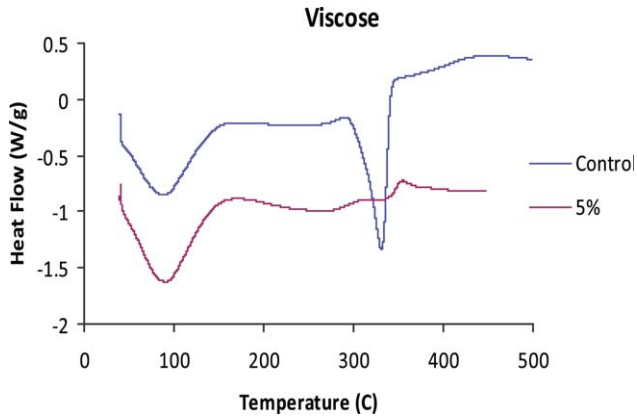

Figure 4 DSC diagram of control viscose versus plasma-modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

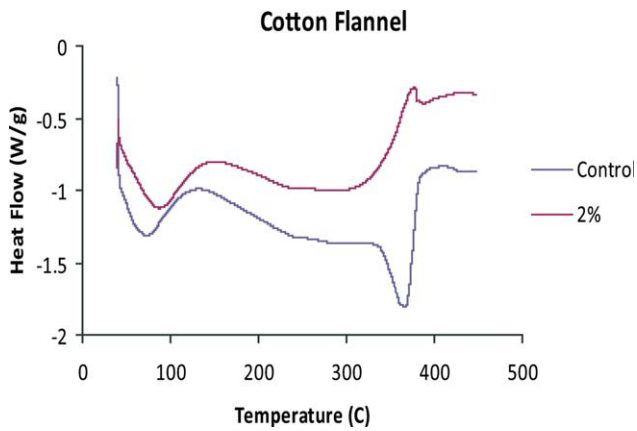

Figure 5 DSC diagram of control cotton flannel versus plasma-modified samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

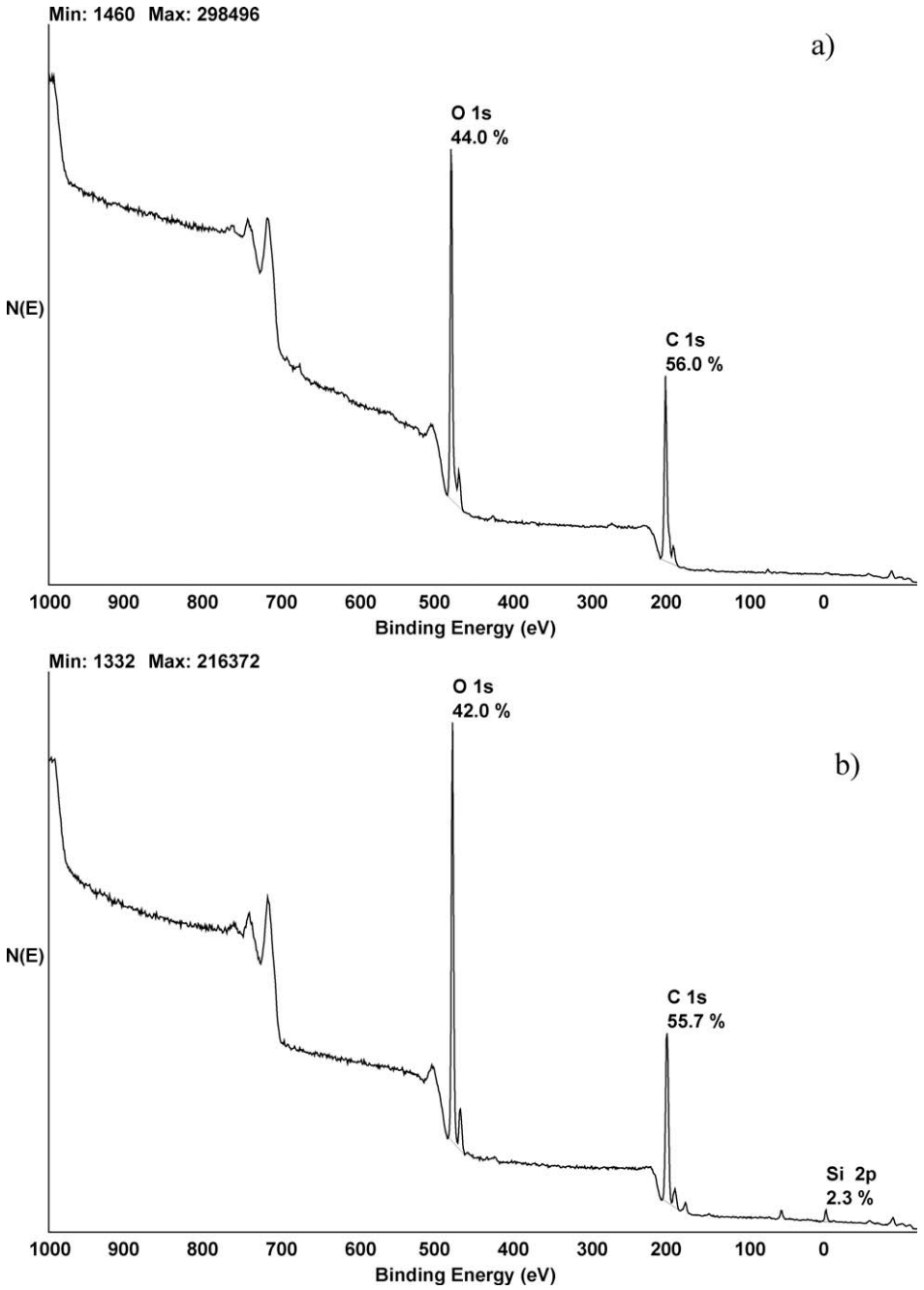

Figure 6 XPS Survey of (a) viscose control and (b) viscose with 2% FR.

Thermo gravimetric analysis

The thermal behavior of untreated and modified viscose and cotton flannel was analyzed in nitrogen atmosphere in a temperature domain of 25–700°C (inserts in Figs. 2 and 3). The weight-loss processes starts at 287°C for the control viscose and at 260°C for SiO_2 coated and plasma-treated viscose (insert in Fig. 2). At temperatures as high as 700°C the residual weight of nondecomposed substrate present in the system was between 14.5 and 17.8% for treated samples versus 5% for control.

It can be observed that the weight loss of the unmodified cotton flannel starts at 303°C and the residual weight at 700°C is 7.8% (insert in Fig. 3). Weight residuals at 700°C between 13.30 and 15.75% of silicate coated and plasma-treated substrates show a less significant weight loss comparing to nontreated cotton flannel.

The first order differential curves (Figs. 2 and 3) show clearly the reduction in decomposition rate. Viscose presents a maximum reduction (about 2.5 times lower) of the decomposition rate for the plasma treatment performed on 3% sodium silicate coated material.

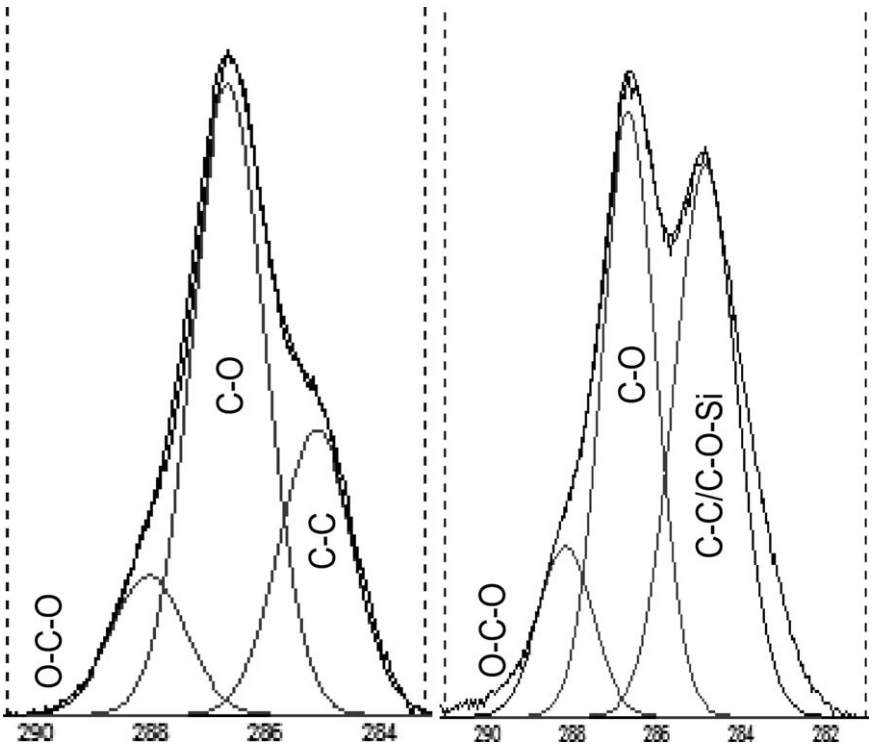

Figure 7 High resolution XPS of (a) control viscose and (b) viscose with 2% FR.

It can be noted that an increase in concentration of coating material (5%) do not produce sensible changes. Cotton flannel has the highest reduction of decomposition rate (about 1.7 times lower) for plasma treatments performed on 2% sodium silicate coated material; it can be noted that highest concentrations of sodium silicate coating are producing lower decrease in decomposition rates. It is suggested that the viscosity of the solutions play an important role in the ability of coating to follow the topography/nanotopography of the cotton flannel material.

Differential scanning calorimeter

The DSC curves for all samples heated at 10°C/min in nitrogen show (between 50 and 150°C) a peak

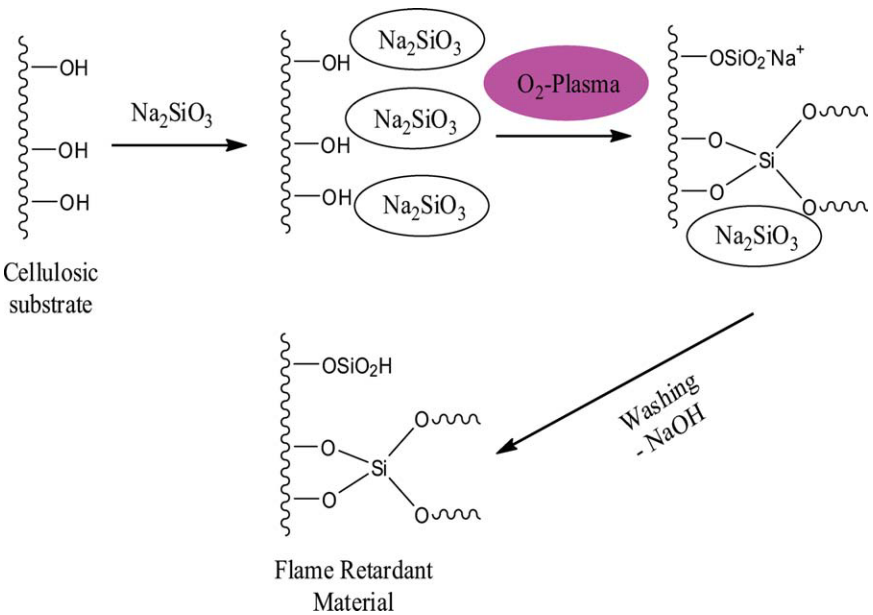

Figure 8 Suggested plasma-induced crosslinking mechanism. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

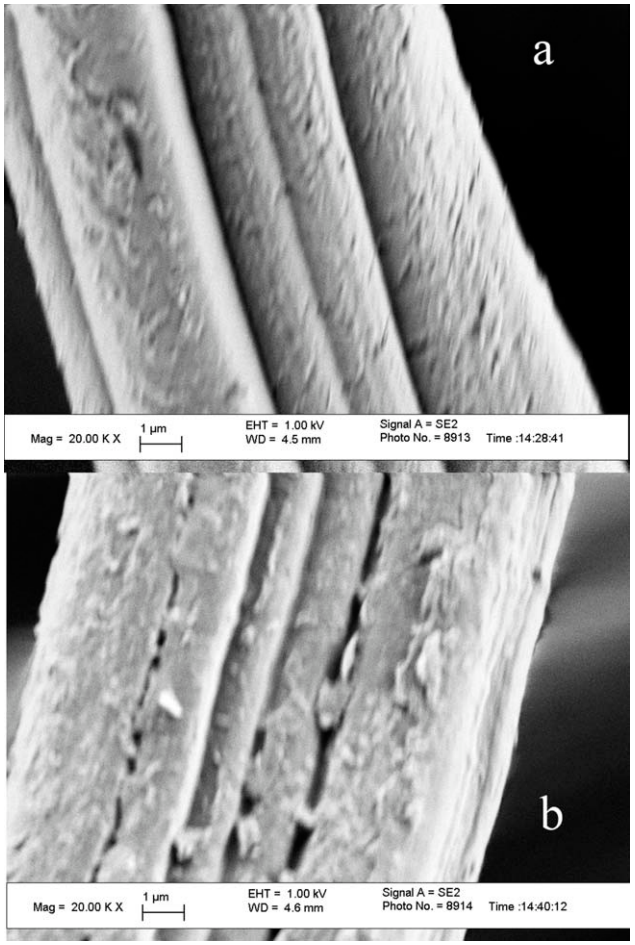

Figure 9 SEM of (a) control viscose; (b) viscose with 2% FR.

related to loss of water that was probably absorbed during processing. The DSC values of control viscose and cotton flannel (Figs. 4 and 5) show two endothermic peaks at around 350°C; this is mainly due to depolymerization of cellulose with formation of laevoglucose and its evaporation.[11] In the DSC curves of the FR viscose and cotton flannel (Figs. 4 and 5) an exothermal peak appeared between 360 and 380°C from the pyrolysis reaction of fire-retardant agent at this temperature. This peak indicates that cellulose was catalyzed to dehydrate and char rapidly by the fire retardant coating.

Surface characterization

X-ray photoelectron spectroscopy

Low resolution survey scans (Fig. 6) for elemental identification and high-resolution spectra of carbon C 1s region (Fig. 7) for identifying and quantifying differently bonded carbon atoms were used. According to the survey scan for the control viscose, fabric's surface consisted mainly of carbon and oxygen [Fig. 6(a)]. The calculated O/C ratio of the control viscose was 0.78 which is pretty close to 0.83 expected for pure cellulosic fibers.[12] Results from XPS survey data collected from SiO_2 coated and APP treated samples [Fig. 6(b)] show an increase in C/Si ratio allowing us to suggest that deposited SiO_2 layers were discharge-induced crosslinked onto viscose substrates.

Figure 7(a,b) depicts high-resolution (HR) C 1s spectra for control and SiO_2-coated fabrics. The HR peak for the control viscose was fitted in three distinct peaks: C—C (285 eV), C—O (286.7 eV), and O—C—O (288.2 eV).[12] Decreased relative surface atomic carbon content and the presence of silicon atoms incorporated into the SiO_2-coated fabrics [Figs. 6(b) and 7(b)] allow us to suggest that part of the predeposited silicate structure has been crosslinked and converted into a nonwater soluble network. The presence of a larger relative surface area peak (at 284.4 eV) in the HR C1s diagram is indicative that in addition to C—C linkages, C—O—Si bonds are parts of the plasma-modified layers, also [Fig. 7(b)]. A suggested plasma-induced crosslinking mechanism of the interface of the SiO_2 network with the cellulosic substrate is presented in Figure 8.

Scanning electron microscope

The presence of the coating can be easily demonstrated by comparing SEM photomicrograph of control and SiO_2-coated and APP treated viscose [Fig. 9(a,b)]. The surface morphology of the untreated fiber is smooth and, apart from the parallel channels that run alongside the fiber axis, no significant surface structural features can be observed [Fig. 9(a)]. On the other hand, the SiO_2-coated and APP treated viscose fiber exhibits a rough surface morphology that shows layers of SiO_2 particles present on the surface of the viscose fibers even after intense ultrasound washes [Fig. 9(b)].

CONCLUSIONS

This work was investigating the modification of cellulosic materials for flame-retardant properties using silica based formulations and atmospheric pressure plasma processes. The combustion time of the treated cellulose samples was significantly increased (between two and a half to four and a half times). The TGA and DSC results showed that silica layer acts as a thermal insulator, allowing the coated fabrics to decompose at lower rates comparing with untreated ones. Surface characterization of the substrates with XPS and SEM confirmed the presence of the silicate like structures on the surface of the fabrics even after ultrasound washes.

The results obtained in this work allow us to conclude that silica-based coatings used in conjunction with plasma processes have high potential to obtain green flame-retardant cellulosic materials. In addition to fashion, these textile materials have numerous applications such as fabrics used for interior environment, first responders and military uniforms.

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