LAYER-BY-LAYER ASSEMBLY OF HALOGEN-FREE POLYMERIC MATERIALS ON NYLON/COTTON BLEND FOR FLAME RETARDANT APPLICATIONS

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14. ABSTRACT

Thin films of environmentally safe, halogen free, anionic sodium phosphate and cationic polysiloxanes were deposited on a Nyco (1:1 nylon/cotton blend) fabric via layer-by-layer (LbL) assembly to reduce the inherent flammability of Nyco fabric. In the coating process, we used three different polysiloxane materials containing different amine groups including 35–45% (trimethylammoniummethylphenythyl)-methyl siloxane-55-65% dimethyl siloxane copolymer chloride salt (QMS-435), aminoethylaminopropyl silsesquioxane-methylsilsesquioxane copolymer oligomer (WSA-7021) and aminopropyl silesquioxane oligomers (WSA-991) as a positive polyelectrolyte. Thermo-gravimetric analysis showed that coated fabric has a char yield around 40% at 600 °C whereas control fabric is completely consumed. The vertical flame test (VFT) on the LbL-coated Nyco fabric was passed after a flame time of 2 s, with a char length of 3.81 cm. Volatile and nontoxic degradation products of flame retardant-coated fabric were analyzed by pyrolysis gas chromatography mass spectroscopy (Py-GCMS). Surface morphology of coated fabrics and burned fabric residues were studied by scanning electron microscopy.

15. SUBJECT TERMS

FIBERS	FLAMMABILITY	LAYER-BY-LAYER	NYCO(NYLON/COTTON) FABRICS
NYLON	FLAME TESTING	FLAME RETARDANT	THERMOGRAVIMETRIC ANALYSIS
COTTON	NYCO FABRICS	VERTICAL FLAME TEST	SCANNING ELECTRON MICROSCOPY
FABRICS	HALOGEN-FREE	FR(FLAME RETARDANT)	WATER SOLUBLE POLYSILOXANES
SILOXANES	COATED FABRICS	NYLON/COTTON BLENDS	TGA(THERMOGRAVIMETRIC ANALYSIS)
PHOSPHATES	POLYSILOXANES	ENVIRONMENTALLY SAFE	

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Layer-by-layer assembly of halogen-free polymeric materials on nylon/cotton blend for flame retardant applications

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SUMMARY

Thin films of environmentally safe, halogen free, anionic sodium phosphate and cationic polysiloxanes were deposited on a Nyco (1:1 nylon/cotton blend) fabric via layer-by-layer (LbL) assembly to reduce the inherent flammability of Nyco fabric. In the coating process, we used three different polysiloxane materials containing different amine groups including, 35–45% (trimethylammoniummethylphenythyl)-methyl siloxane-55-65% dimethyl siloxane copolymer chloride salt (QMS-435), aminoethylaminopropyl silsesquioxane-methylsilsesquioxane copolymer oligomer (WSA-7021) and aminopropyl silesquioxane oligomers (WSA-991), as a positive polyelectrolyte. Thermo-gravimetric analysis showed that coated fabric has char yield around 40% at 600 °C whereas control fabric was completely consumed. The vertical flame test (VFT) on the LbL-coated Nyco fabric was passed with after flame time, 2 s, and the char length of 3.81 cm. Volatile and nontoxic degradation products of flame retardant-coated fabric were analyzed by pyrolysis gas chromatography mass spectroscopy (Py-GCMS). Surface morphology of coated fabrics and burned fabric residues were studied by scanning electron microscopy. Copyright © 2014 John Wiley & Sons, Ltd.

1. INTRODUCTION

Fires originating from burning of textile materials often lead to large property losses, severe burn injuries, and even loss of human life. Reducing the flammability of textiles is a challenging task in both military and civilian applications to prevent fire. Textile fibers, mostly made of cotton, polyesters, and polyamides are highly flammable and thus it is necessary to increase their flame retardant (FR) property. Previously, numerous attempts have been made to impart FR property to cellulosic cotton fibers. Currently, most commonly used FR materials for fabric contain halogens, nitrogen and organo-phosphorus compounds [1]. Many of these halogenated FR materials are now recognized as toxics that are known to have adverse effects on the human body and the environment. These adverse environmental effects in animals and humans include endocrine and thyroid disruption, immunotoxicity, reproductive toxicity, cancer and undesirable effects on child development and neurologic function [2]. Some FR materials, such as polybrominated diphenyl ethers (PBDEs), have been banned by EPA or voluntarily phased out by manufacturers because of

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their environmental persistence and toxicity, only to be replaced by other organohalogens of unknown toxicity [3]. Despite restrictions on further production in some countries, consumer products previously treated with banned retardants are still used and continue to release toxic chemicals into the environment. Therefore, there is a need to develop new non-halogenated FR fabric. Silicon, nitrogen and phosphorus containing FR are considered as environmentally safe because they do not generate substances that are harmful to humans and the environment under conditions of fire [4].

Phosphorus containing flame retardants are unique since they can either act in vapor phase or condensed phase. The mode of action of their FR mechanism may be either in the vapor phase or in the condensed phase depending on the chemical structure and the interaction with the burning polymer [5–8]. Prior studies have shown that, decomposition mode of the cellulose is modified when they are treated with phosphorus containing FR compounds. Treated fibers produce a surface char layer which is relatively less toxic to the environment and humans [9]. Earlier studies have also shown that nitrogen containing FR produce non combustible and non toxic gases while degrading at high temperatures. These gases act as diluents for the oxygen concentration near the burning materials resulting in minimization or retardation of the flame and often used in conjunction with phosphorus containing FR materials. The gases originating from nitrogen containing FR materials form a swollen protective layer around burning surfaces [10, 11]. Comparatively, silicon containing FR materials are more environment-friendly since they do not produce harmful substances on catching fire. They form a layer of silicon dioxide or silica which does not react further with oxygen. This silica layer protects the burning material from decomposing further at high temperature [12, 13].

Spontaneous sequential adsorption of oppositely charged ionic materials widely known as electrostatic layer-by-layer (LbL) process is a simple and versatile method to impart desired properties to surfaces by forming thin films of polymers, colloids or molecules [14, 15]. A simple washing/rinsing (in water) step is performed after adsorption of each layer to remove weakly or nonspecifically bound charged moieties adhering to the substrate. This step also prevents the contamination of the solution in the next dipping cycle. The LbL coating can also be achieved by spray-assisted LbL coating process [16, 17]. This process allows large surfaces to be coated more rapidly than LbL dip coating process. As shown in Figure 1(b), for the same concentration of
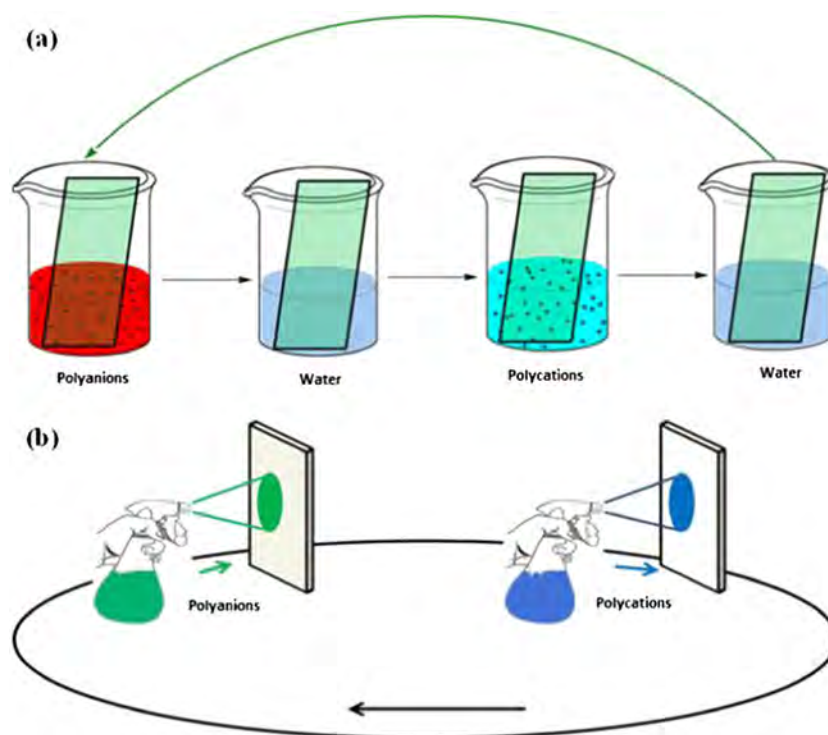

Figure 1. Schematic diagram of (a) LbL dip coating and (b) spray-assisted LbL coating processes.

polyelectrolytes, omitting the rinsing or washing step results in thicker coatings than dip coating process [17]. However, reproducibility of LbL assembly and resulted film properties depend on many factors, including concentration of coating solutions, adsorption times, pH or temperature, and applied LbL method. Monitoring of the LbL assembly can be observed by several methods, such as UV–Vis spectroscopy, elipsometry or X-ray reflectometry, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and quartz crystal microbalance (QCM).

Previously, LbL process as shown in Figure 1(a) was employed to coat fabrics for FR applications. The materials used are poly(allylamine), poly(acryl amide), poly(acrylic acid), inorganic materials such as montmorillonite, ammonium polyphosphate and poly(sodium phosphate) and renewable materials such as chitosan, phytic acid and graphene oxide [18–26]. However, polysiloxane containing FR materials have received limited attention as polyelectrolyte for aqueous LbL deposition process on fabrics. In addition, most of the research has been devoted to develop FR coating using LbL process. A Nyco fabric which is a blend of cotton and nylon has received limited attention towards developing FR coating using LbL process. Herein, we report, deposition of multilayers of phosphorus and silicon containing FR polyelectrolytes on Nyco fabric using LbL process. The goal of this study is to observe changes in the FR properties of Nyco fabric when coated with silicon, phosphorus and nitrogen containing FR materials using LbL process. The LbL dip coating process was employed to coat small samples ($3'' \times 1''$) for thermal characterization studies. We have used spray method for the large size ($12'' \times 3''$) samples to obtain faster coatings as compared to dip coatings due to the fact that we skip water rinsing step in the spray method. We observed thicker coatings when we used spray method over dip method. Other than this, we did not observe any significant differences between these two coating methods.

2. EXPERIMENTAL

2.1. Chemicals and substrates

QMS-435, a 60% milky dispersion of cationic polymer (35–45% (trimethylammonium methyl phenythyl)-methyl siloxane–55–65% dimethyl siloxane copolymer chloride salt), of molecular weight 1800–2000 in methoxypropanol was obtained from Gelest and used without further modification. WSA-7021, a 22–25% solution in water of aminoethylaminopropyl silsesquioxane–methylsilsesquioxane copolymer oligomer having molecular weight ranging from 370 to 650, was purchased from Gelest and used without further modification. WSA-9911, a 22–25% solution in water of aminopropyl silesquioxane oligomers having molecular weight ranging from 270 to 550, was obtained from Gelest and used as received. Poly (sodium phosphate) (PSP) (crystalline, +200 mesh, 96%) was obtained from Aldrich and used as received. Distilled water obtained from Poland Spring was used for preparation of all solutions. 1 M HCl and 1 M NaOH (Sigma-Aldrich) were used to adjust pH of the depositing solutions. Non dyed, bleached cotton fabrics were obtained from US Army Natick Soldier Research, Development and Engineering Center (NSRDEC) and used as substrates for monitoring LbL deposition process. The camouflaged Nyco fabric (1:1 nylon/cotton blend, 235 g/m^2) was obtained from the US Army Natick center and used for further experimental LbL deposition.

2.2. LbL assembly dip coating process and characterization

PSP (2 wt %), QMS- 435 (6.8 wt %), WSA-9911 (4 wt %) and WSA-7021 (4 wt %) solutions were prepared in distilled water as deposition solutions. The pH of these solutions was maintained at 7 for LbL process. Fabric specimens were dipped in pH 2 solution to develop initial positive charge which improves the adhesion of polyelectrolytes. LbL deposition process was performed by sequential dipping these charged specimens into anionic PSP and cationic siloxane solutions. Each successive cycle of dipping in oppositely charged polyelectrolytes added one bilayer. The first dip into each polyelectrolyte mixture was for 5 min, and consequent dips were for 1 min each. The fabric specimens were rinsed by dipping in distilled water solutions after each dip in polyelectrolyte solutions to remove loosely bound polyions and then dried using hot air gun. This procedure was iterated until desired numbers of bilayers were coated on specimens.

2.3. Spray-assisted LbL coating process and characterization

The Nyco fabric was also coated by spray-assisted LbL coating using spray bottles as shown in Figure 1(b). The common household devices such as spray bottles have been used intentionally instead of sophisticated spray coating instruments so as to demonstrate the reliability of the process. Similar concentrations of solutions PSP (2 wt %), QMS-435 (6.8%), WSA-9911 (4%) and WSA-7021 (4%) were used for spray-assisted LbL coating on Nyco fabric. In a typical spray-assisted LbL coating process, anionic solution of PSP was sprayed using spray bottles on fabric held horizontally in an aluminum frame followed by spraying QMS-435 or WSA-9911 or WSA-7021 solution. The rinsing or washing with water spraying was omitted which allowed to develop higher thickness of polyelectrolytes layers as compared to dip coating. There was no vacuum used for spray coating process. This process was repeated until desired numbers of bilayers were obtained on one side of fabric. Similar process was used to coat the other side of fabric. Coated specimens were dried in vacuum at 80° C for about two hours.

The LbL dip coating process was characterized by attenuated total reflection Fourier transform infra red (FT-IR) spectroscopy. Coated fabrics were weighed by balance from Denver instrument company model A-250. Post vertical flame test (VFT) residues from coated fabrics were studied using field emission scanning electron microscope (FE-SEM JEOL JSM-1401F) at accelerating voltage of 5 kV. Fabric specimens and post VFT char residues were sputtered with gold to prevent charging.

2.4. Thermo-gravimetric analysis

The thermal stability of control and coated fabric was measured using a thermo-gravimetric analyzer (TGA Q 50, v 6.7). Approximately 10 mg of the samples was loaded in platinum pans and heated up to 850 °C at a rate of 20 °C/min. All TGA experiments were performed under air atmosphere maintained under a constant flow of air at 30 ml/min. All tests were conducted in triplicate and average values are reported.

2.5. Vertical flame test

Vertical flame tests (VFT) were performed on control and coated Nyco fabrics (30.48 cm × 7.62 cm) according to ASTM D 6413 [27]. This test method is a qualitative pass/fail indicator of fabric flammability. It measures the relative flammability of a fabric specimen which is vertically held in a three-sided frame. The bottom edge of the fabric is ignited with a methane flame for 12 s. The char length (damaged part of the fabric); afterflame (the amount of time the flame persists on the fabric surface after the initially ignited flame is turned off), afterglow (the amount of time the fabric continues to glow after the flame stops) and relevant observations are recorded.

2.6. Pyrolysis-gas chromatography mass spectroscopy (Py-GCMS)

The pyrolysis portion of the Py-GCMS measurements was carried out with a CDS 5200 pyrolyzer which is coupled to an Agilent GCMS instrument (GC Model 7890A, MS Model 5975C). A measurable amount of sample of 1.00 mg of coated fabric was placed inside a quartz capillary tube which was then inserted in the platinum coil in the pyroprobe. The platinum filament was heated rapidly to a temperature high enough to pyrolyze the polymeric materials into volatile monomers or smaller fragments. The volatile products of pyrolysis were transferred to the gas chromatograph to be separated and eventually identified by the mass spectrometer. The pyrolysis was done under helium carrier gas at a flow rate of 54 ml/min. In this experiment, the pyroprobe temperature was raised only to 200 °C to thermally desorb the FR coating from the coated fabric. The interface and thermally insulated transfer line temperature were set at 300 °C to keep the chemicals volatilized during transport from the pyrolyzer to the GC column. The GC column was a DB-5 ms low bleed, 5%-phenyl-methyl polysiloxane column (30 m × 0.25 mm × 0.25 um), which is typical for GCMS. The GC temperature was initially held at 40 °C for 2 min, and was programmed to 300 °C at 10 °C/min ramp, and then held at 300 °C for 10 min. The mass spectra were measured using electron impact ionization energy of 70 eV. The mass detector was scanned from 35 to 400 *m/z* at scan rate of 4 scans per second. The data was searched using the NIST 2008 MS library and the CDS's pyrolysis library.

3. RESULTS AND DISCUSSION

3.1. LbL process characterization

LbL coating of materials such as QMS-435, WSA-9911 and WSA-7021 shown in Figure 2 (a), 2(b) and 2(c) as cationic polyelectrolytes and poly(sodium phosphate) (PSP) as an anionic polyelectrolyte were performed on non dyed cotton fabric using dip coating process. Different samples of Nyco fabric ($3'' \times 1''$) were coated using LbL dip coating process and desired numbers of bilayers (5, 10, 15 and 20) were achieved with each polysiloxane based polycations and polyanions pair. These coated samples were characterized by FTIR spectroscopy.

Figure 3 shows that the intensity of stretching vibrational peaks at $800\,cm^{-1}$ increased as the number of bilayers increased. The stretching frequencies at $800\,cm^{-1}$ are assigned to Si–CH$_3$ functional group in polysiloxane materials [28]. Obviously, this stretching frequency was not seen in the control cotton fabric and observed only in coated cotton fabric specimens. The stretching frequencies at $845\,cm^{-1}$ also increased as the number of coated bilayers increased which is assigned to dimethyl groups in copolymers.

3.2. Mass adsorption analysis

The coated fabrics were also characterized for mass adsorbed on them because of LbL dip coating process. The mass added was measured by difference in weight method for PSP/QMS-435, PSP/WSA-9911 and PSP/WSA-7021 coated Nyco fabric before and after LbL dip coating. Figure 4 shows that the mass adsorbed per square centimeter area on Nyco fabric as a function of the number of bilayers of deposited. The mass adsorbed per unit area increased linearly with respect to increased number of bilayers for PSP/QMS-435, PSP/WSA-9911 and PSP/WSA-7021 coated fabrics as shown in Figure 4(a), 4(b) and 4(c) respectively. The linear nature of the graphs show that mass adsorbed on Nyco fabric increases rapidly from the initial adsorbed bilayer till the final adsorbed bilayers in all the three cases depicted in Figure 4. Mass adsorbed in case of PSP/QMS-435-coated fabric is much greater than that of PSP/WSA-9911 and PSP/WSA-7021 owing to large molecular weight of QMS-435 compared to WSA-9911 and WSA-7021.

3.3. Thermal properties

The thermal stability of coated Nyco fabrics was studied using thermo-gravimetric analyzer in an air and nitrogen atmosphere. As seen in Figure 5, coated fabrics showed lower degradation temperature
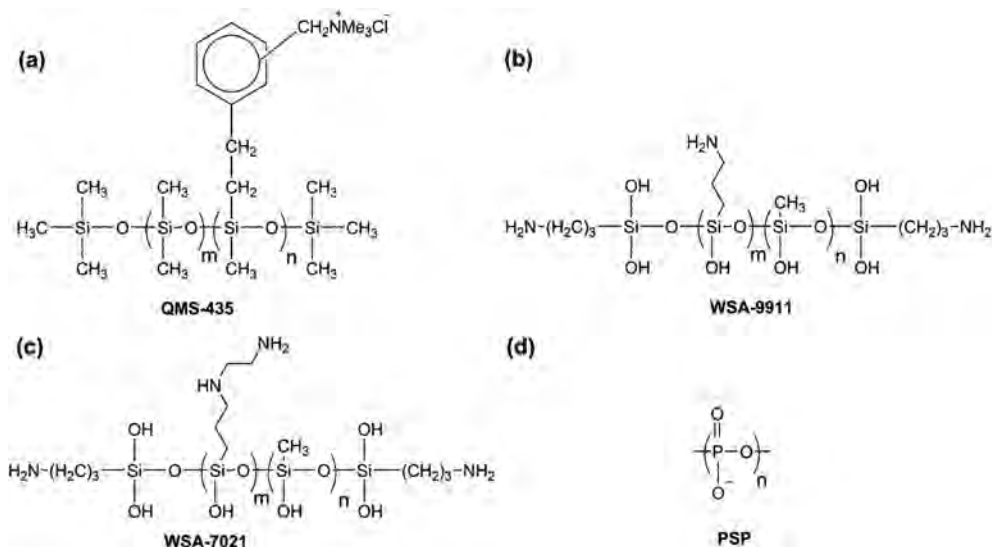

Figure 2. Chemical structures of polysiloxane materials (a) QMS-435, (b) WSA-9911, (c) WSA-7021 and containing material (d) poly(sodium phosphate), i.e. PSP.
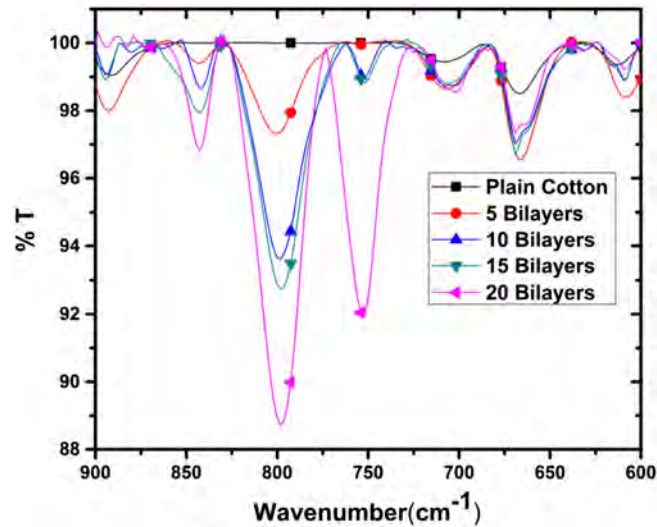
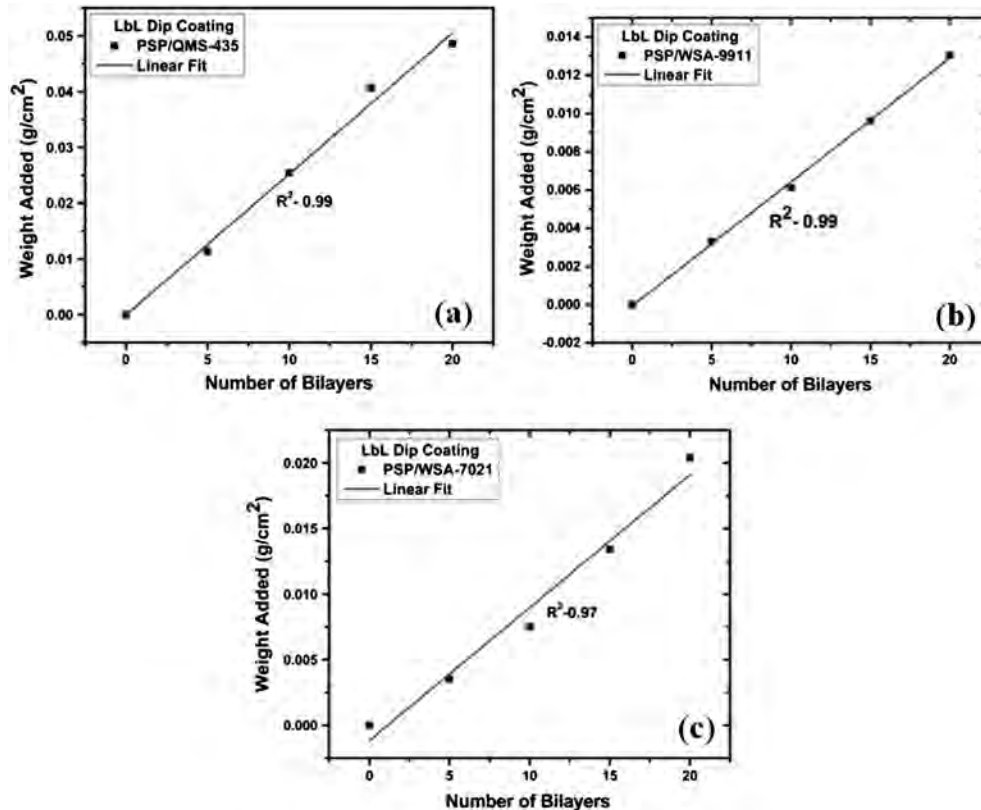Figure 3. The FT-IR spectra of QMS-435-coated cotton fabric.

Figure 4. Mass adsorbed on Nyco fabric as a function of number of deposited bilayers for (a) PSP/QMS-435, (b) PSP/WSA-9911 and (c) PSP/WSA-7021.

than control Nyco fabrics. Degradation of PSP/QMS-435-coated Nyco fabric occurred around 230 °C, about 90 °C lower than the control fabric as shown in Figure 5(a). Fabric specimens coated with PSP/WSA-9911 and PSP/WSA-7021, degradation occurred around 310 °C, approximately 20 °C lower than the degradation of control as shown in Figure 5(b) and 5(c). These lower degradation temperatures of coated fabrics suggest that coated materials degrade prior to the onset of
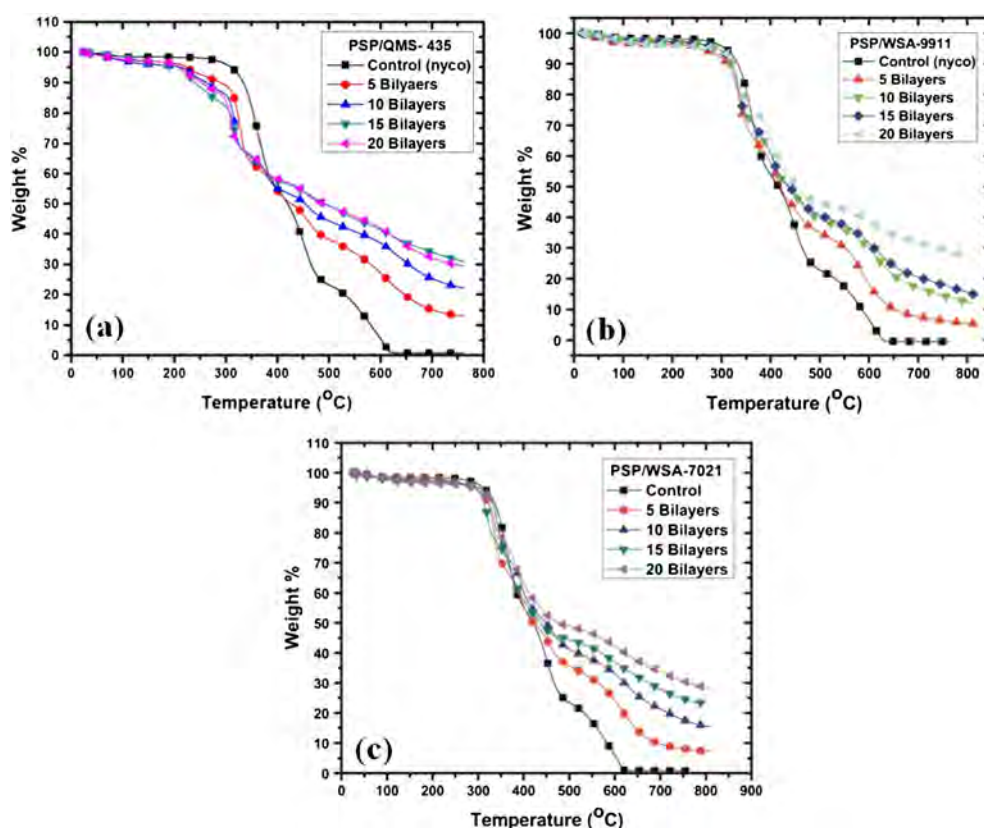
Figure 5. Thermo-gravimetric analysis of Nyco fabrics coated with (a) PSP/QMS-435, (b) PSP/WSA- 9911 and (c) PSP/WSA-7021 under air.

degradation of fabric forming char layers and non-combustible gases in the process and help to retard or extinguish the flame. The degradation of coated fabrics ceased much earlier than the fabric as shown in Figure 5(a), 5(b) and 5(c). All coated fabrics showed earlier onset of degradation (Tonset) and exhibited much higher char residues than control fabric beyond $600\,^{\circ}C$. The average char yield of these coated fabrics is tabulated as shown in Table I. In general, all these coated Nyco fabric samples gave higher char residues in nitrogen atmosphere compared to air atmosphere. However, this increase in char yield is due to the non burning nature of base fabric Nyco in nitrogen. This means that there is no difference between the char yields of these samples in air and nitrogen atmospheres.

3.4. Py-GCMS studies

The thermal decomposition of cellulose (cotton) produces many flammable fragments such as aldehydes, ketones, acid, furans and furfural [29–31]. Prior studies regarding thermal degradation of aliphatic nylons have demonstrated formation of monomers or cyclic or linear oligomers. Secondary reactions lead to evolution of volatile gases and to cross linking. Thermal decomposition of Nylon 6/6 yielded carbon dioxide and cyclopentanone as the major gaseous products [32]. The Py-GCMS was employed on coated Nyco fabric samples to thermally degrade them and provide thorough information about the degradation products.

For PSP/QMS-435-coated fabric, the total ion chromatogram (TIC) showed CO_2, hexamethyl cyclotrisiloxane, toluene, acetic acid, D-allose, Nylon 6/6, hexanedintrile and other miscellaneous substances as shown in Figure 6 [33]. Similar experiments were performed on fabric samples coated with PSP/WSA-9911 and PSP/WSA-7021, resulting TIC shows CO_2, hexanedintrile, D-allose, Nylon 6/6 and various other substances as shown in Figure 7 [34].

Table I. Thermo-gravimetric analysis and fabric weights of PSP/QMS-435, PSP/WSA-9911 and PSP/WSA-7021-coated Nyco fabric.

PSP/QMS-435

Sample	Char yield (%) at 700 °C under air	Char yield (%) at 700 °C under N$_2$	Weight added on fabric (%)
Control	0.80	11.46	0
5 bilayers	16.80	23.42	50.55
10 bilayers	27.20	27.26	102.89
15 bilayers	37.40	28.79	165.89
20 bilayers	34.20	34.35	195.67

PSP/WSA-9911

Sample	Char yield (%) at 700 °C under air	Char yield (%) at 700 °C under N$_2$	Weight added on fabric (%)
Control	0.80	11.46	0
5 bilayers	9.80	19.51	12.74
10 bilayers	19.84	23.54	24.67
15 bilayers	24.20	29.34	40.39
20 bilayers	35.00	38.13	56.13

PSP/WSA-7021

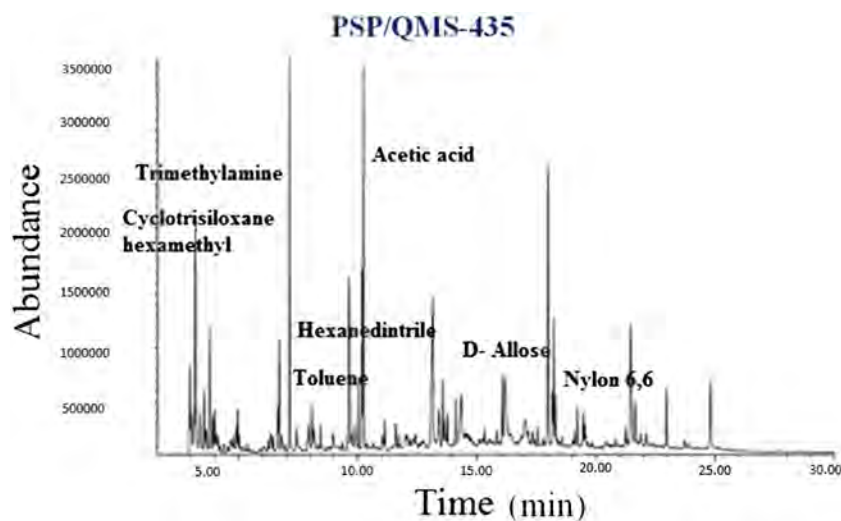| Sample	Char yield (%) at 700 °C under air	Char yield (%) at 700 °C under N$_2$	Weight added on fabric (%)
Control	0.80	11.46	0
5 bilayers	10.06	21.80	14.46
10 bilayers	21.20	25.77	29.34
15 bilayers	28.20	30.35	55.29
20 bilayers	36.00	31.89	89.23

Figure 6. Py-GCMS chromatogram of Nyco fabric coated with PSP/QMS-435.

3.5. Flame retardant properties of fabric samples

To accelerate the LbL coating on bigger samples (30.48 cm × 7.62 cm), 20 bilayers of PSP/WSA-9911 and PSP/WSA-7021 were deposited by a spray-assisted LbL coating process. The control and the spray-assisted LbL-coated fabrics samples were subjected to vertical flame test (VFT, ASTM D 6413). The control Nyco fabric was completely consumed by direct exposure to flame. The fabrics coated with 20 bilayers of PSP/QMS-435 were also burnt completely but exhibited slower burn rate across the fabric surface or higher resistance to flame because of the presence of
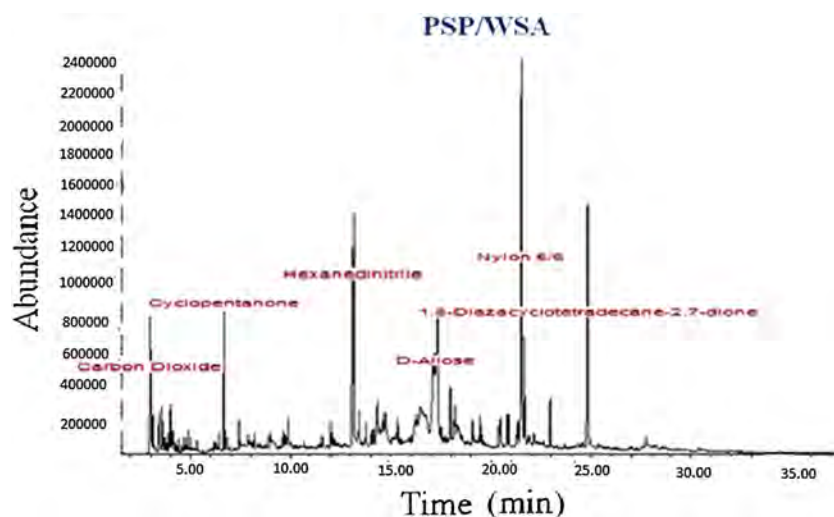
Figure 7. Py-GCMS chromatogram of Nyco fabric coated with PSP/WSA-9911.

phosphate and siloxane groups. When fabric specimens coated with 20 bilayers of PSP/WSA-9911 and PSP/WSA-7021 were subjected to VFT, the flame was extinguished for both samples, and these results are summarized in Table II. The coated fabric showed char length of 1.5 in as shown in Figure 8(a) and 8(b) for PSP/WSA-9911 and PSP/WSA-7021-coated fabrics, respectively. The reasons for flame extinguishing nature of these materials, PSP/WSA-9911 and PSP/WSA-7021, are the presence of phosphate, and siloxane coupled with presence of primary amine groups. These primary amine groups facilitated the release of ammonia gas which further reacted with oxygen to form non combustibles gases such as water vapor and nitrogen. These escaping of non combustible gases acted as a blowing agent [35] and resulted in foamy char as depicted from SEM images shown in Figure 9.

3.6. Surface morphology studies

Surface morphology of control fabric, coated fabric and burned fabric were studied by scanning electron microscope (SEM) as shown in Figure 9. Thicknesses of coated fibrils increased for all three types of coated fabric as shown in Figure 9(a), 9(b) and 9(c) compared to control fabric which showed natural striations as depicted in Figure 9(d). The coating of materials did not change the weave nature of Nyco fabric before VFT. Higher magnification images of coated fabric with PSP/WSA-9911 and PSP/WSA-7021, as shown in Figure 9(f) and the Figure 9(g) respectively, clearly showed that coatings were highly conformal. Relatively high amounts of materials were coated in case of 20 bilayers of PSP/QMS-435-coated fabric. The control fabric demonstrated a smooth surface, whereas all coated samples showed individual fibrils bridged by materials and the

Table II. ASTM D 6413 Vertical Flame Test (VFT) results on all the LBL-coated samples and untreated Nyco.

Sample	Afterflame (s)	Char length (cm)	Test result (pass or fail)
Control Nyco	–	Completely consumed	Fail
PSP/QMS-435 (20 bilayers)	–	30.48	Fail
PSP/WSA-9911 (20 bilayers)	2	3.81	Pass
PSP/WSA-7021 (20 bilayers)	2	3.81	Pass

Figure 8. Post vertical flame test images of (a) PSP/WSA-9911 and (b) PSP/WSA-7021 with char length of 1.5" (3.81 cm).
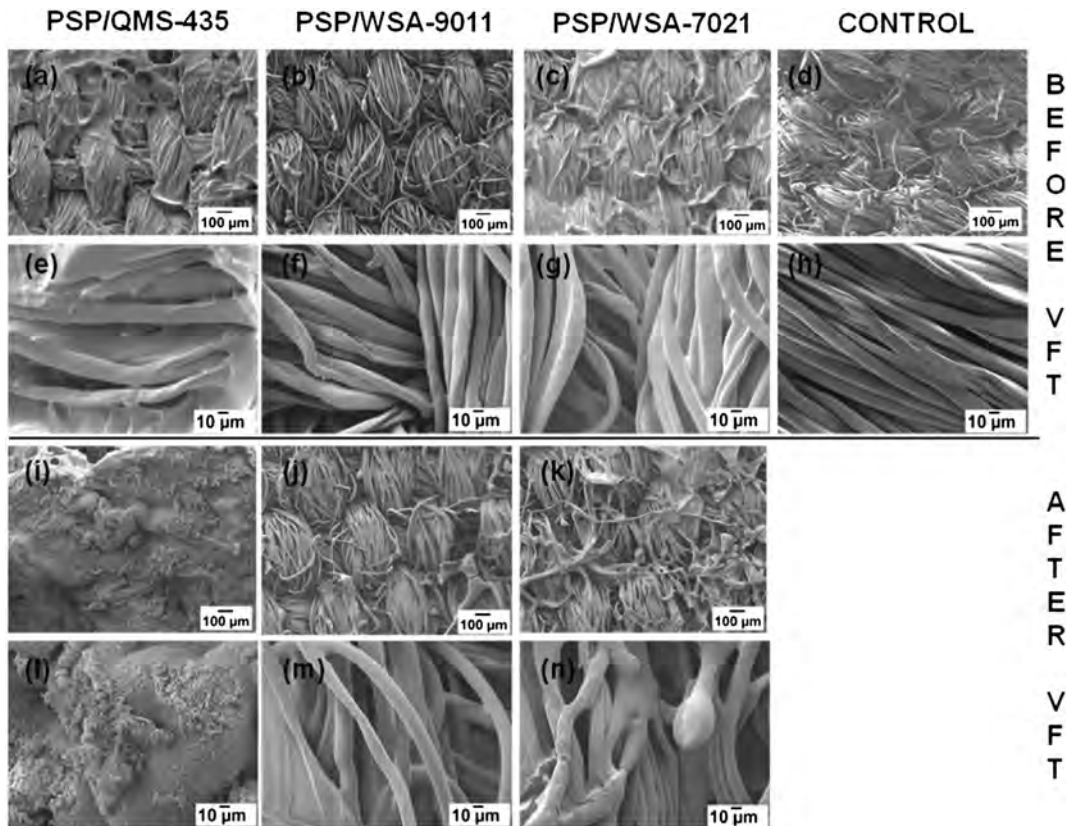

Figure 9. Low magnification SEM images of fabric samples coated with 20 bilayers of PSP/QMS-435 (a, e), PSP/WSA-9911 (b, f), PSP/WSA-7021(c, g) and control fabric (d, h) before burning. Post VFT, low magnification images of fabric coated with 20 bilayers of PSP/QMS-435 (i, l), PSP/WSA-9911 (j, m) and PSP/WSA-7021(k, n).

gap between fibrils also narrowed down. This bridging also resulted into increased stiffness of the coated fabrics.

As can be seen in Figure 9(a), the fabric swatch coated with 20 bilayers of PSP/QMS-435, has the highest amount of material deposited on the surface compared to fabric swatches coated with copolymer oligomers PSP/WSA-9911 (Figure 9(a)) and PSP/WSA-7021 (Figure 9(b)). This could be attributed to high molecular weight and consequently more number of charged groups in QMS-435. The residues after VFT tests were also observed closely in the scanning electron microscope. Fabrics coated with PSP/QMS-435 were burnt completely by the flame but showed foamy intumescent char as shown in Figure 9(i). Weave structure of PSP/QMS-435 fabric was not retained after VFT and covered by expansion of coated materials. The fabric coated with 20 bilayers of PSP/WSA-9911 showed very uneven, coarse and patchy surface as shown in Figure 9(j) and 9(m). Similar characteristics of the burnt surface were observed for fabrics coated with PSP/WSA-7021 as shown in Figure 9(k) and 9(n). These roughness and uneven surface textures of post burn images were due to enlargement and spreading out of coated materials in all three cases. Intumescent actions of coated materials in the case of PSP/WSA-9911 and PSP/WSA-7021 helped to prevent the damage of fibers and conserved the weave structure. As shown in Figure 8(a) and Figure 8(b), the foam structure formed in these samples was slightly gray and white in color. The appearance of white color is attributed to the presence of silica component whereas the gray color of char is formed due to the carbon content along with phosphorus and nitrogen.

4. CONCLUSION

We successfully achieved, LbL deposition of polysiloxane containing materials on a Nyco fabric for the first time. LbL deposition of PSP and three different cationic polysiloxane materials QMS-435, WSA-9911 and WSA-7021 were used in this study. Mass adsorption on fabric increased linearly with respect to number of bilayers. Nyco fabric coated with 20 bilayers of PSP/WSA-9911 and PSP/WSA-7021 extinguished the flame and showed char length of 1.5" (3.81 cm). Fabric coated with 20 bilayers PSP/QMS-435 did not extinguish the flame but demonstrated slow burning rate across the fabric surface as compared to the control sample. The non-extinguishing nature in this coated fabric is attributed to the difficulty in the formation of ammonia gas due to the lack of primary amino groups in QMS-435. Thermo-gravimetric analysis showed that coated materials decomposed earlier than Nyco fabric which helped to prevent Nyco fabric from burning. Post vertical flame microscopy images of char demonstrated signs of swelling and uneven surface texture. Afterglow was not observed for 20 bilayer-coated samples of PSP/WSA-9911 and PSP/WSA-7021. The LbL deposition of polysiloxane based polyelectrolytes in combination with phosphorus containing polyelectrolytes offers an environmentally benign method to develop FR textiles for military and civilian applications.

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