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COMMUNICATION

Covalent functionalization of cellulose in cotton and a nylon-cotton blend with phytic acid for flame retardant properties

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Abstract A new and versatile method to covalently functionalize cellulose in cotton and Nylon/cotton (Nyco) blends with plant-based renewable material, phytic acid to impart flame retardant characteristics that is durable is presented. This involves functionalization of 1,1′-carbonyldiimidazole to the cellulose structure of cotton followed by the attachment of diamine and phytic acid through carbamate bonds. In the vertical flame test, phytic acid functionalized cotton and Nyco fabrics exhibit self-extinguishing behavior, whereas control samples burned completely. Pyrolysis combustion flow calorimetry confirmed that phytic acid functionalized cotton and Nyco fabrics showed a reduction in the heat release capacity and the total heat release. In this short communication, we present synthesis, chemical characterization using Fourier transform infrared spectroscopy and Scanning electron spectroscopy, Energy dispersive spectroscopy and study of thermal and flame retardant properties using thermogravimetric analysis, Pyrolysis combustion flow calorimetry and Vertical flame test of phytic acid functionalized cotton and Nyco fabrics.

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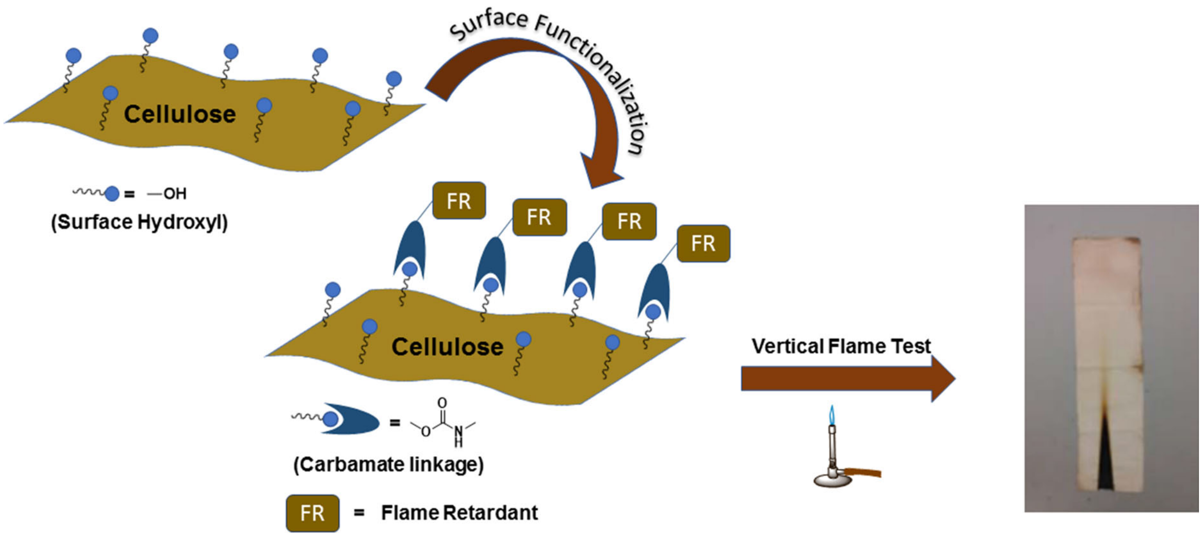
Graphic abstract



Keywords Flame retardant · Cotton · Nylon-cotton · Nyco · Phytic acid · Surface-functionalization

Introduction

The inherent flammability of some natural, as well as synthetic fabrics, makes their usage limited to only certain kind of applications. For instance, cotton, polyesters, and aliphatic polyamides (Nylon) commonly used for soldier apparel, which are inherently flammable. Thus, there is a significant need to impart fire retardancy to the fabric without compromising its durability and other physical properties such as breathability and mechanical strength. It can be addressed through different pathways, including incorporation of flame retardant (FR) additives into the fibers during manufacturing stage, surface modification of existing fibers with FR materials, and integrating inherently fire-resistant polymers.

Among all the techniques, for producing a flame retardant fabric, surface modification techniques have attracted considerable attention in recent years because they are efficient and convenient (Narkhade et al. 2016; Galina et al. 2013; Yu-Chin et al. 2011). Notably, surface coating by layer-by-layer (LbL) (Li et al. 2010) assembly and plasma treatment involved surface modifications (Edwards et al. 2012; Lam et al. 2011; Tsafack and Levalois-Grützmacher 2007) have recently been proven to be more popular in fabricating FR coatings on different fabrics. However, these surface coatings interact with the surface of the fabric through weak and non-covalent bonds that are not stable during washing (multiple laundry cycles) of the fabric. Therefore, to avoid these less durable, non-covalent interactions as well as to attach additional functional groups covalently on the surface of the fabric, new chemical methods should be introduced.

On the other hand, the best-known approach for the surface modification of cellulose is the condensation reaction of available hydroxyl groups in the cellulose structure of cotton (Kadla and Gilbert 2000; Klemm et al. 2005). In the past few years, phosphorous containing compounds have shown remarkable flame retardancy to cotton fabrics (Gao et al. 2015; Jia et al. 2017a, b). Phytic acid with 28% phosphorous content has proven its potential as a flame retardant to cotton and other fabrics which is evidenced by the previous literature (Cheng et al. 2016a, b; Feng et al. 2017; Liu et al. 2018). To mention a few, Zhou et al. (2015) prepared flame retardant polyaniline paper composite using phytic acid as a doping acid, Laufer et al. (2012) prepared flame retardant cotton using phytic acid/chitosan and Wang et al. (2015a, b) using phytic acid/nitrogen-containing silane hybrid via layer-by-layer technique.

In this work, we developed a permanent surface chemical functionalization on cotton and Nyco fabrics via covalent bonds unlike most common surface coating methods done through electrostatic interaction, which are weak and non-durable. Here, we used 1,1′-carbonyldiimidazole (CDI) reagent as an activating agent for hydroxyl functional groups of cellulose in the fabric followed by addition of nucleophile such as ethylenediamine to bring amine functional groups onto to the surface of the fabric. Finally, the coupling between newly introduced amines of the fabric and acid groups of the phytic acid gave strong and stable carbamate bonds while imparting flame-retardant properties to the fabric. We have characterized these functionalized fabrics using attenuated total reflectance—Fourier transform infrared spectroscopy (ATR-FTIR) spectroscopy, scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy. Furthermore, we have studied the thermal degradation behavior and flammability properties using thermogravimetric analysis (TGA), Pyrolysis combustion flow calorimetry (PCFC) and flammability properties using vertical flame test (VFT) according to ASTM D6413 test method.

Experimental section

Materials

All chemicals and solvents purchased were used without further purification. 1,1′-Carbonyldiimidazole (CDI) was purchased from ICN Biomedical Inc. Ethylenediamine (EDA), aqueous 50% phytic acid solution (PA), and anhydrous dimethylformamide (DMF) were purchased from Sigma-Aldrich. Cotton and Nyco fabrics were obtained from US Army Natick.

Functionalization of fabric with CDI (**2** and **6**)

In a typical procedure, each fabric sample (1 × 1 inch) was taken into a 20 mL glass vial which contains 4 mL of anhydrous DMF solvent. To this reaction vial, 100 mg of CDI was added followed by shaking the reaction vial a few times in the first 30 min of the reaction and then left for 12 h at room temperature. At the end of this reaction time, DMF solvent was decanted from the reaction vial and fabric was washed with acetone (3 × 10 mL) to remove unfunctionalized CDI followed by drying the fabric sample at 90 °C for four hours to obtain CDI functionalized cotton fabric, **2** and CDI functionalized Nyco fabric, **6**.

Functionalization of fabric with Ethylenediamine (**3** and **7**)

CDI functionalized fabric (1 × 1 inch) was taken into a 20 mL glass vial which contains 4 mL of anhydrous DMF solvent. To this reaction vial, 0.5 mL of ethylenediamine was added followed by shaking the reaction vial intermittently in the first two hours of reaction then left it for five hours at room temperature. Then the solvent was decanted from the reaction vial and fabric was washed with acetone (3 × 10 mL) followed by drying the fabric sample at 90 °C for four hours to yield the EDA functionalized cotton fabric, **3** and EDA functionalized Nyco fabric, **7**.

Functionalization of fabric with Phytic acid (**4** and **8**)

EDA functionalized fabric (1 × 1 inch) was dipped in 5 mL solution of 25% aqueous phytic acid solution for five minutes, followed by drying in an oven at 80 °C for 12 h. At the end of the drying period, the fabric swatches were cooled down to room temperature and then washed with distilled water (3 × 50 mL) followed by drying the fabric sample at 90 °C for four hours to obtain PA functionalized cotton fabric, **4** and PA functionalized Nyco fabric, **8**.

Characterizations

Fourier-transform infrared spectroscopy was carried using a Nicolet 4700 Fourier-transform infrared spectrometer (Thermo-Scientific) equipped with attenuated total reflectance (ATR) accessory to characterize the functionalized fabrics over a range of 4000–400 cm^{-1}. Each spectrum was obtained with 16 scans at a resolution of 4 cm^{-1}. Thermal degradation studies of the fabrics were conducted using a TGA Q50 (TA Instruments). Around 5 mg was heated at a rate of 20 °C/min from room temperature to 800 °C under nitrogen atmosphere. Pyrolysis combustion flow calorimetry (PCFC) was performed to study the heat release characteristic of the fabrics according to ASTM D7309. Around 3 mg of sample was heated from 80 to 750 °C at a heating rate of 1 °C/s under the nitrogen/oxygen flow rate of 80/20 mL/mL. The oxygen consumption was measured and used to calculate heat release rate (HRR), heat release capacity (HRC), and total heat release (THR). All the samples were tested at least three times. The vertical flame test was performed according to ASTM D 6413. The fabrics of size 12 × 3 inches fitted in a metal frame were ignited from the bottom with 12 s ignition time at a distance of 0.75 inches from the burner. The distance between the ignition spot of the fabric and the farthest point that the flame reached was measured as char length. Surface morphology of fabrics was observed using an SEM (JEOL JSM-6390). A thin layer of gold was deposited on the surface of all samples before imaging. Residue analysis was performed on the samples using energy-dispersive X-ray spectroscopy (EDX).

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Nexsa X-Ray Photoelectron Spectrometer (Thermo Fisher Scientific) using monochromated Al Kα X-ray source (hν = 1486.6 eV). All the XPS survey spectra were energy referenced to C1 s at 284.8 eV. XPS peak fit software was used for curve fitting and background subtraction for all the scanned surveys. The breaking strength of the fabrics was determined using the Instron universal testing machine according to the ASTMD5034. The durability of flame retardant on the fabric was evaluated by performing the normal home laundry cycles according to the AATCC 135-2004 standard. The pH values of the fabrics were measured according to ISO 3071:2005.

Results and discussion

Functionalization of cotton and Nyco fabrics

The functionalization of cotton fabric (and Nyco fabric) was carried out through three consecutive reaction steps. As shown in synthesis scheme (Scheme 1), in the first step, the reaction occurred between hydroxyl groups of cotton fabric (and cotton part of Nyco fabric) and the reactive carbonyl group of CDI resulted in the formation of carbamate bonds on the surface of the fabric. In this reaction, some of the hydroxyl groups of the cotton fabric (and cotton part of Nyco fabric) were substituted by one of the imidazole groups of CDI. Successful formation of carbamate in the fabrics **2** and **6** was confirmed by the ATR-FTIR spectra (Figs. 1, 2), with the appearance of newly formed carbamate characteristic carbonyl stretching band at 1761 cm^{-1} apart from retaining other stretching frequencies from the control fabric such as 1632 cm^{-1} corresponding to the carbonyl amide stretching. Furthermore, we observed around 10% (for Nyco-7%) weight gain to the functionalized cotton fabric swatch compared to the weight of control fabric. In the second step, to introduce amine functional groups onto the surface of the CDI functionalized fabric, we used EDA as a nucleophilic reagent in excess. One of the EDA primary amine groups has replaced the imidazole group in the fabric **2** and **6** to afford EDA functionalized fabric **3** and **7** and assuming the other primary amine group in EDA are still available for further chemical reactions. We have further confirmed the conversion of this reaction by using ATR-FTIR spectra (Figs. 1, 2) of the functionalized fabrics. The FTIR spectra of **3** and **7** possessed the characteristic urethane peaks at 1702 cm^{-1} (carbonyl urethane stretching) and 1530 cm^{-1} (C-NH vibration) and moreover the carbonyl stretching peak at 1761 cm^{-1} related to the starting CDI functionalized fabrics vanished completely which all together clearly indicated the successful completion of these reactions on the fabric surface. However, in the case of the third step, the final reaction to make PA functionalized fabric **4** and **8**, we could not observe any clear distinction of IR peaks between EDA functionalized fabrics and PA functionalized fabrics. This could be because of many of the characteristic IR bands of PA groups merging with the starting EDA functionalized fabric IR peaks. However, there is a significant weight gain (cotton-12% and Nyco-8%) observed in the PA functionalized fabrics. The final step which is reaction between the amine groups and phytic acid to form phosphoramide was proved using a model reaction between orthophosphoric acid and propyl amine under same conditions (Supporting Information). Functionalization of the fabrics with phytic acid led to decrease in the pH of the fabrics. The pH values were found to be 7.1 and 3.6 for cotton control and PA treated cotton fabric. The decrease in the pH value after functionalization can be attributed to the presence of free phosphoric acid group in phytic acid. The pH values of Nyco control and PA treated Nyco fabric were found to be 6.9 and 4.0 respectively.

Scheme 1 Schematic representation for possible chemical functionalization of cotton and Nyco fabrics; reagents and reaction conditions: (i) 1,1′-Carbonyldiimidazole, DMF, r.t., 12 h; (ii) Ethylenediamine, DMF, r.t., 5 h; and (iii) Phytic acid, 80 °C, 12 h

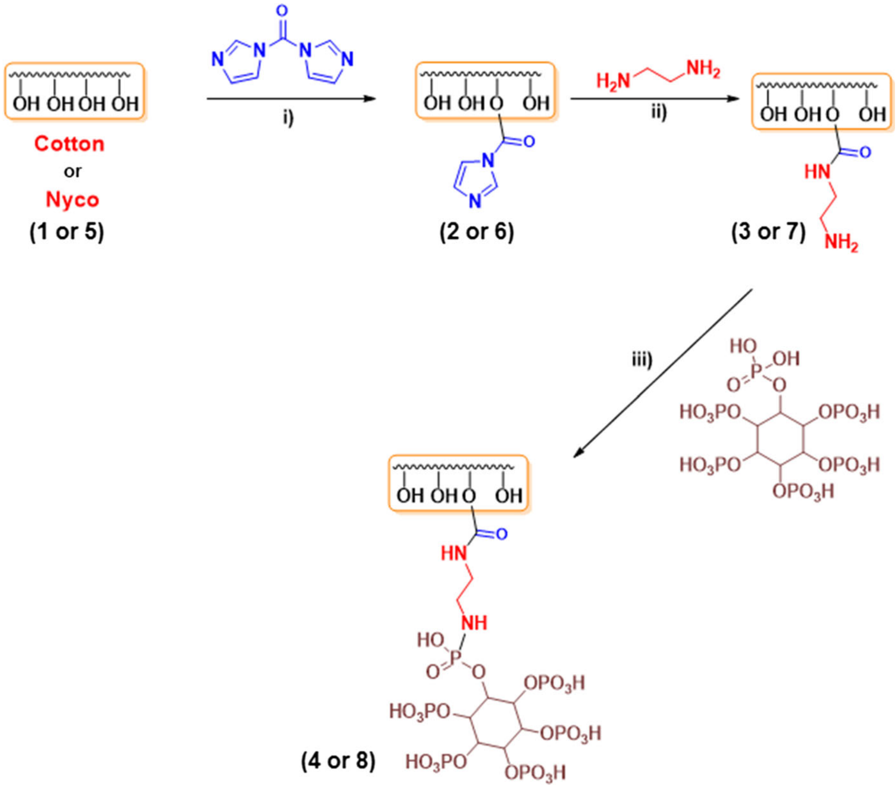
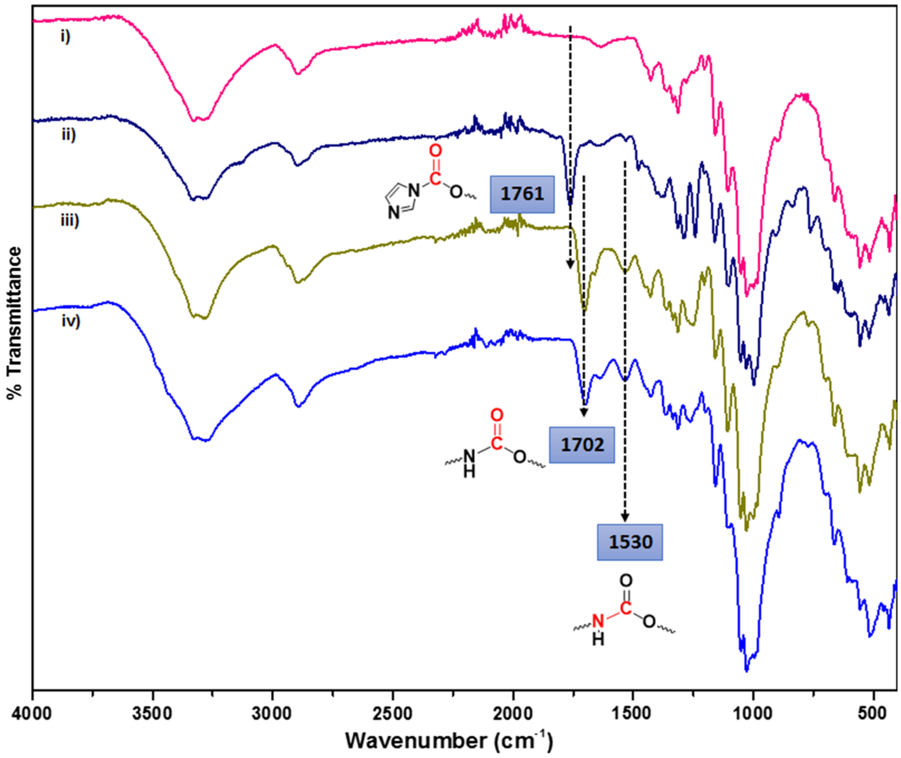


Fig. 1 FTIR-ATR spectra of (i) cotton fabric, (ii) cotton fabric with CDI functionalization (iii) EDA functionalized cotton fabric, and (iv) PA functionalized cotton fabric



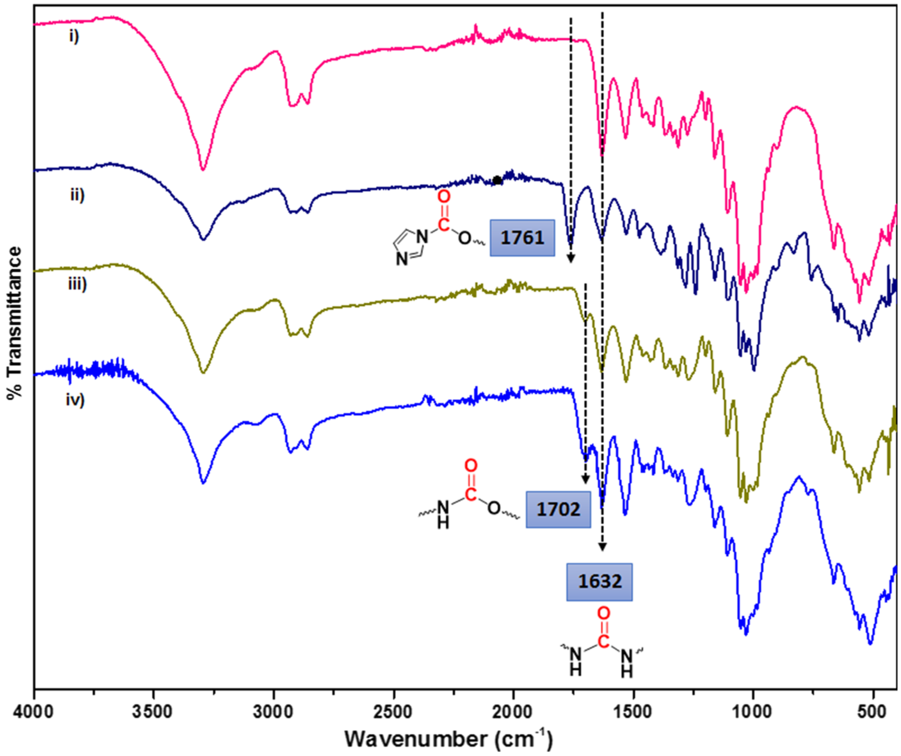


Fig. 2 FTIR-ATR spectra of (i) Nyco fabric, (ii) Nyco fabric with CDI functionalization, (iii) EDA functionalized Nyco fabric, and (iv) PA functionalized Nyco fabric

Thermogravimetric analysis

Thermal degradation behavior and thermal stability of the functionalized cotton and Nyco fabrics were investigated using TGA Q50 (TA Instruments) under nitrogen atmosphere. The TGA decomposition graphs comprising the data of weight loss versus temperature and their derivative plots for cotton and Nyco fabrics are shown in Figs. 3 and 4. All the functionalized cotton and Nyco fabrics showed the lower onset degradation temperatures than the control fabrics due to the presence and degradation of newly introduced functional groups. The control cotton fabric has followed a single degradation step which is due to the dehydration reaction between hydroxyl groups leading to the char formation and/or direct

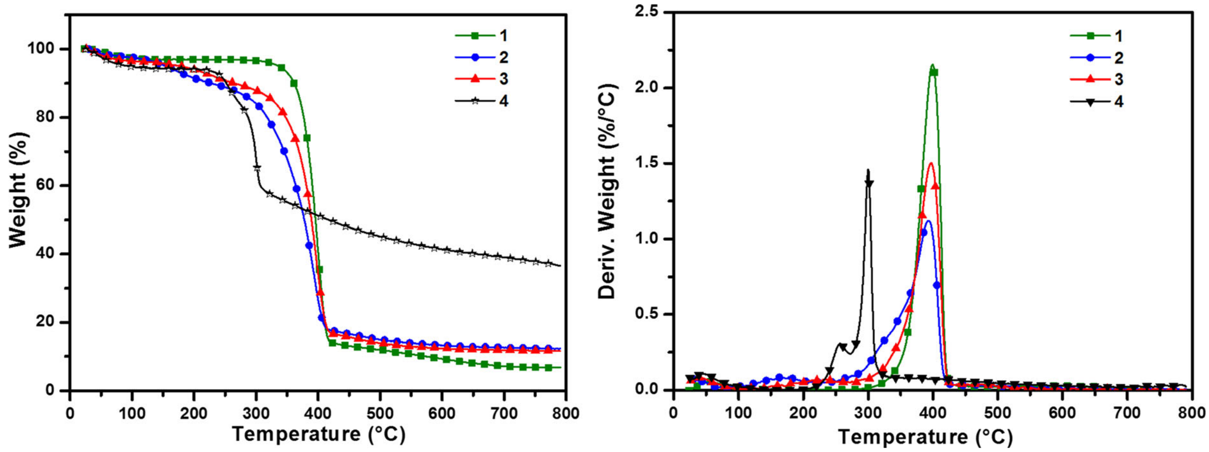


Fig. 3 Thermogravimetric analysis (TGA) curves of (1) Cotton fabric, (2) CDI functionalized cotton, (3) EDA functionalized cotton and (4) PA functionalized cotton fabric under N_2 atmosphere

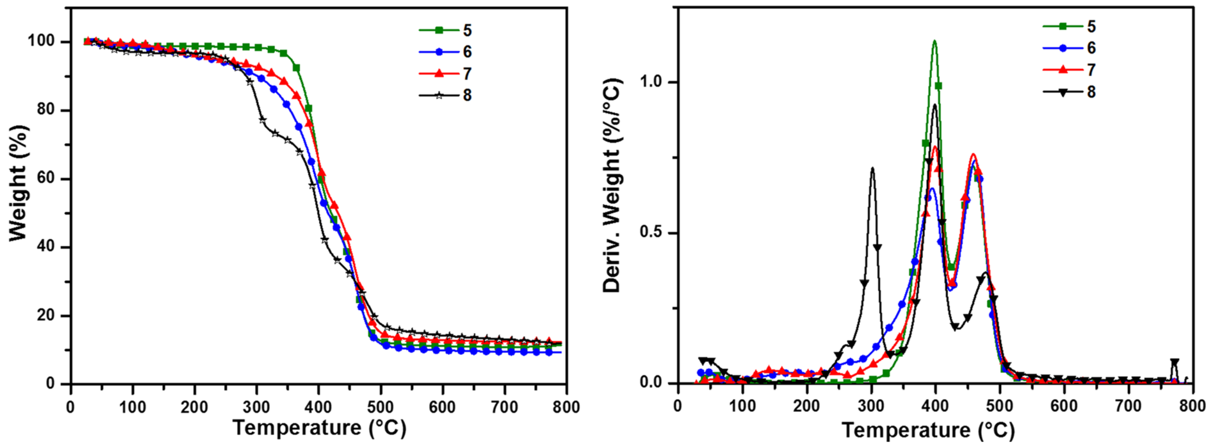


Fig. 4 Thermogravimetric analysis (TGA) curves of (5) Nyco fabric, (6) CDI functionalized Nyco, (7) EDA functionalized Nyco, and (8) PA functionalized Nyco fabric under N_2 atmosphere

decomposition of the cellulose structure to generate flammable volatiles (Soares et al. 1995). The PA functionalized cotton followed the degradation pattern similar to the control but with lower degradation temperature and higher amount of char residue. The presence of the phosphate group in PA structure releases phosphoric acid which promotes the char formation by catalytic dehydration as reported earlier (Cheng et al. 2016b). The formed char acted as a barrier between the surrounding atmospheric oxygen and the fabric making it self-extinguishing thus flame retardant.

In the case of Nyco fabric, a two-step degradation was observed owing to its 50:50 nylon and cotton. The Nyco fabric functionalized with PA went through a three-step degradation process. The first degradation at around 300 °C corresponded to the phosphate groups in the PA structure. Char residue was increased by 18% for PA functionalized Nyco fabric compared to the control Nyco. However, this improvement is less compared to that of functionalized cotton fabric. Since Nyco is a 50:50 blend of cotton and nylon 66 and the functionalization of PA is only for cotton part of Nyco, the nylon 66 part thermally degrades completely leaving less char residue. All the corresponding data of cotton and Nyco fabrics are tabulated in Tables 1 and 2.

Pyrolysis combustion flow calorimetry

The flammability characteristics of functionalized and control fabrics were studied using a small-scale flammability technique called Pyrolysis combustion flow calorimetry (PCFC) which evaluates the combustion parameters based on consumption of oxygen during the non-flammable combustion process. The essential parameters obtained from this technique are furnished in Tables 3 and 4. The heat release capacity (HRC) and total heat release (THR) values gives information about the heat release characteristics of the material. The cotton fabric functionalized with PA showed lowest heat release capacity of 36 J/g K and lowest total HR value of 0.6 kJ/g which are remarkably lower than that of control cotton fabric. This result suggests that the functionalization of PA to cotton fabric led to the significant reduction of about 86.7% for HRC and 94% for THR. In the case of Nyco functionalized with PA, a significant reduction in HRC and THR values was observed. These results indicate that functionalized cotton and Nyco fabrics have better heat release properties compared to control fabrics.

Vertical flame test

In order to evaluate the flammability behavior of the fabric, vertical flame test (VFT) was performed on control as well as phytic acid functionalized cotton and Nyco fabrics (12 × 3 inches). In VFT, the sample size within the frame was 12 × 3 inches. A Bunsen burner was used for sample ignition. The flame height was 1.5 inches, and the distance between the lower edge of the sample and the burner was 0.75 inches. The ignition time was 12 s. The images taken after the VFT of control and PA functionalized fabrics are shown in Fig. 5. Both the control fabrics (cotton & Nyco) burnt

Table 1 TGA results of control and functionalized Cotton fabrics

Fabric codes	T_{ON} (°C)[a]	T_{MAX} (°C)[b]	Char residue at 700 °C (%)
1	373	398	7.1
2	347	392	12.5
3	366	396	11.8
4	239	299	39.0

[a] Onset decomposition temperature

[b] Maximum decomposition temperature

Table 2 TGA results of control and functionalized Nyco fabrics

Fabric codes	T_{ON} (°C)	T_{MAX} (°C)			Char residue at 700 °C (%)
		[a]T_{1MAX}	[b]T_{2MAX}	[c]T_{3MAX}	
5	370	398	457	–	10.9
6	346	394	460	–	9.5
7	366	398	457	–	12.5
8	282	300	398	477	12.9

[a] Maximum decomposition temperature in first step degradation

[b] Maximum decomposition temperature in second step degradation

[c] Maximum decomposition temperature in third step degradation

'–'represents not available

Table 3 Heat Release properties of functionalized cotton fabrics

Fabric codes	HRC (J/g K)	Total HR (kJ/g)
1	258	10.0
2	207	10.0
3	275	13.7
4	36	0.6

Table 4 Heat Release properties of functionalized Nyco fabrics

Fabric codes	HRC (J/g K)	Total HR (kJ/g)
5	354	18.4
6	284	15.6
7	299	18.0
8	229	12.3

away completely on exposure to ignition, leaving behind some amount of char only in the case of Nyco. Interestingly, when the PA functionalized fabrics (cotton & Nyco) were tested according to the same standards, they self-extinguished within 2 s after the ignition source was removed. The average char lengths for three replicants of the cotton and Nyco fabrics functionalized with PA are 4.66 and 6.26 inches, respectively. The VFT results indicate that phytic acid functionalized cotton and Nyco fabrics are self-extinguishing which is a critical step going forward with this chemical functionalization method.

Scanning electron microscopy

Surface morphologies of control and phytic acid functionalized fabrics were examined by scanning electron microscope (SEM). The different magnification images were taken for clear observation before and after burning of the fabrics and are depicted in Fig. 6. From the Fig. 6, we can say that there is no difference in the thickness of fabrics surfaces between control and functionalized fabrics since the functionalization occurred through covalent bonds and it is a conformal level functionalization unlike non-covalent

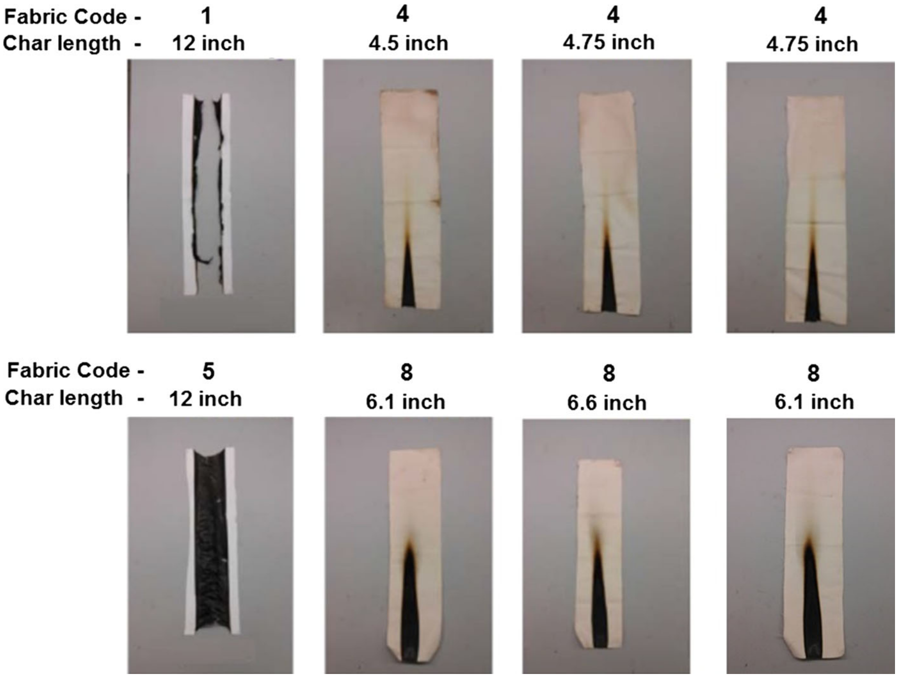


Fig. 5 Post vertical flame test images of phytic acid functionalized cotton (top row) and Nyco fabrics (bottom row) including their control fabrics

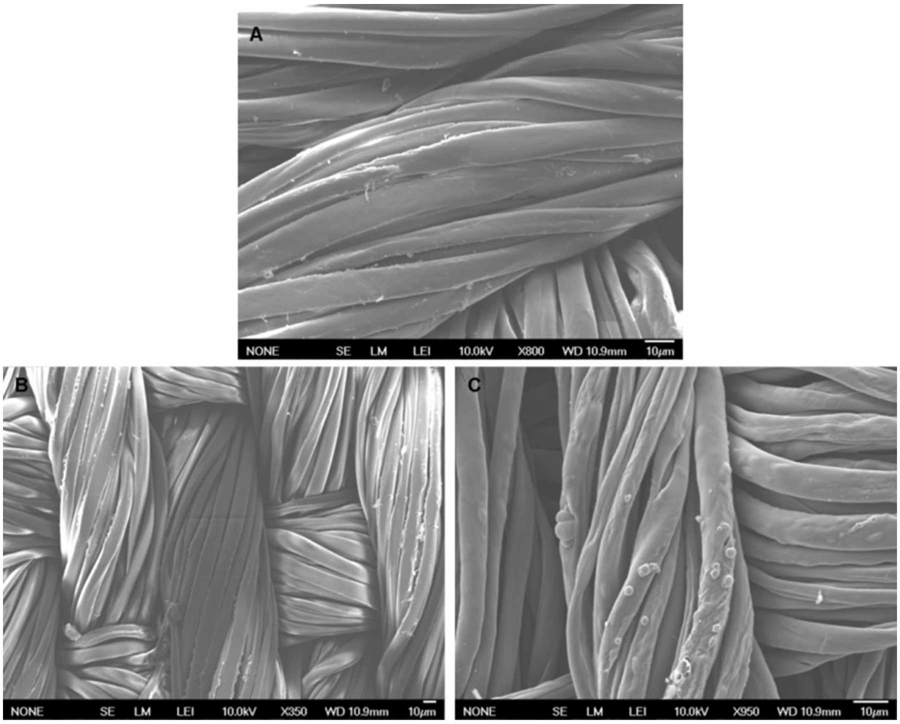


Fig. 6 Low magnification SEM images of fabric samples. (**A**) Cotton control fabric, (**B**) Phytic acid functionalized cotton fabric before burning, (**C**) Phytic acid functionalized cotton fabric after burning

surface coatings most of them are physical adsorptions, and thickness increases from microns to millimeters. Moreover, burned sample surface morphology of treated fabric indicates the formation of inorganic phosphate/polyphosphate based char formed by the catalyzing action of phytic acid on carbonization of cotton fibers which prevented the functionalized fabric from burning (Schartel 2010).

EDX analysis

The elemental compositions were estimated by performing EDX spectra analysis of phytic acid functionalized cotton fabric before and after burning the fabrics. The EDX spectra of the fabrics are shown in Fig. 7, along with the elemental composition details. The presence of phosphorous composition indicated the functionalization of PA to the fabric where control fabric showed just background noise. As expected, the carbon content increased after burning the sample because of char formation with a decrease in the oxygen content which is lost as volatile gases. In addition to that, importantly, there is no significant amount of change in the phosphorous content, which indicated its total contribution to the char formation upon heating.

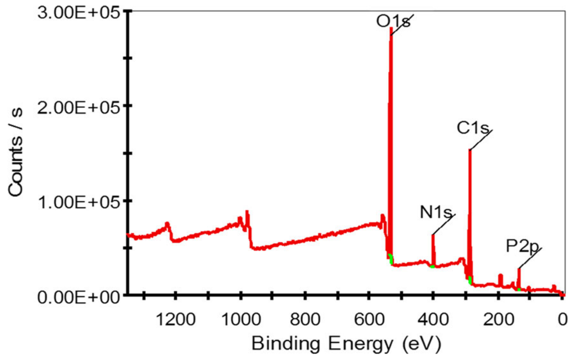
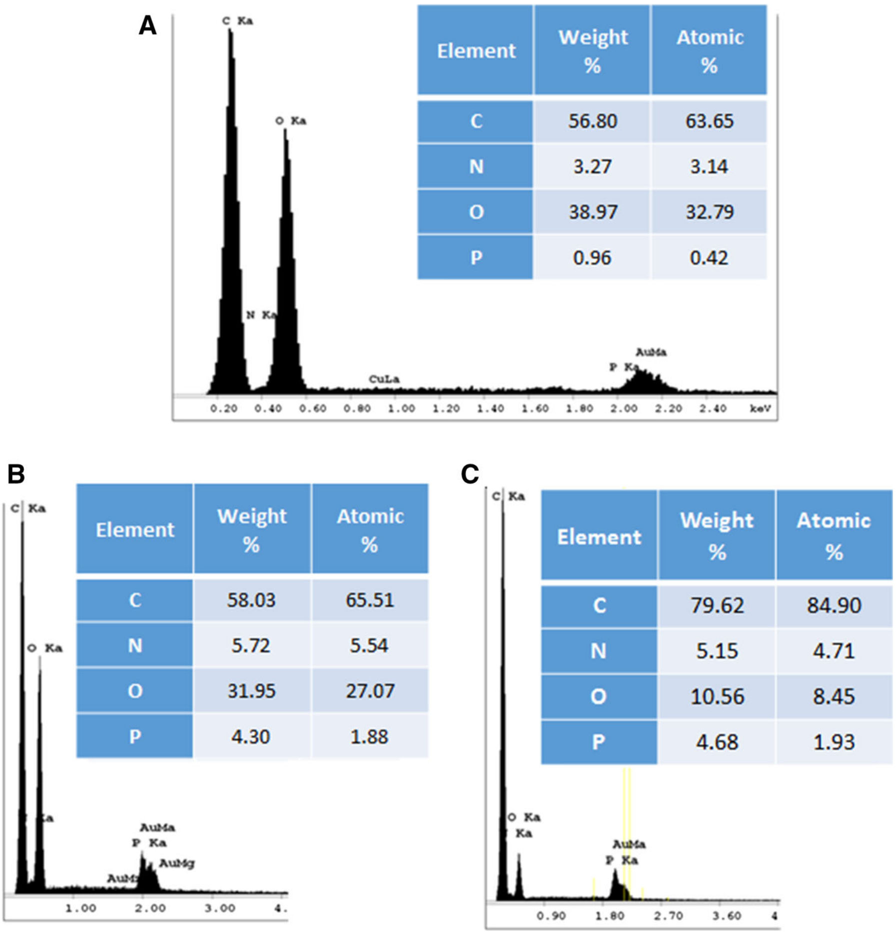


Fig. 8 XPS survey spectrum of phytic acid functionalized cotton fabric

Fig. 7 EDX spectra: (**A**) control cotton fabric, (**B**) phytic acid functionalized cotton fabric before burning, and (**C**) phytic acid functionalized cotton fabric after burning in VFT



A

Element	Weight %	Atomic %
C	56.80	63.65
N	3.27	3.14
O	38.97	32.79
P	0.96	0.42

B

Element	Weight %	Atomic %
C	58.03	65.51
N	5.72	5.54
O	31.95	27.07
P	4.30	1.88

C

Element	Weight %	Atomic %
C	79.62	84.90
N	5.15	4.71
O	10.56	8.45
P	4.68	1.93

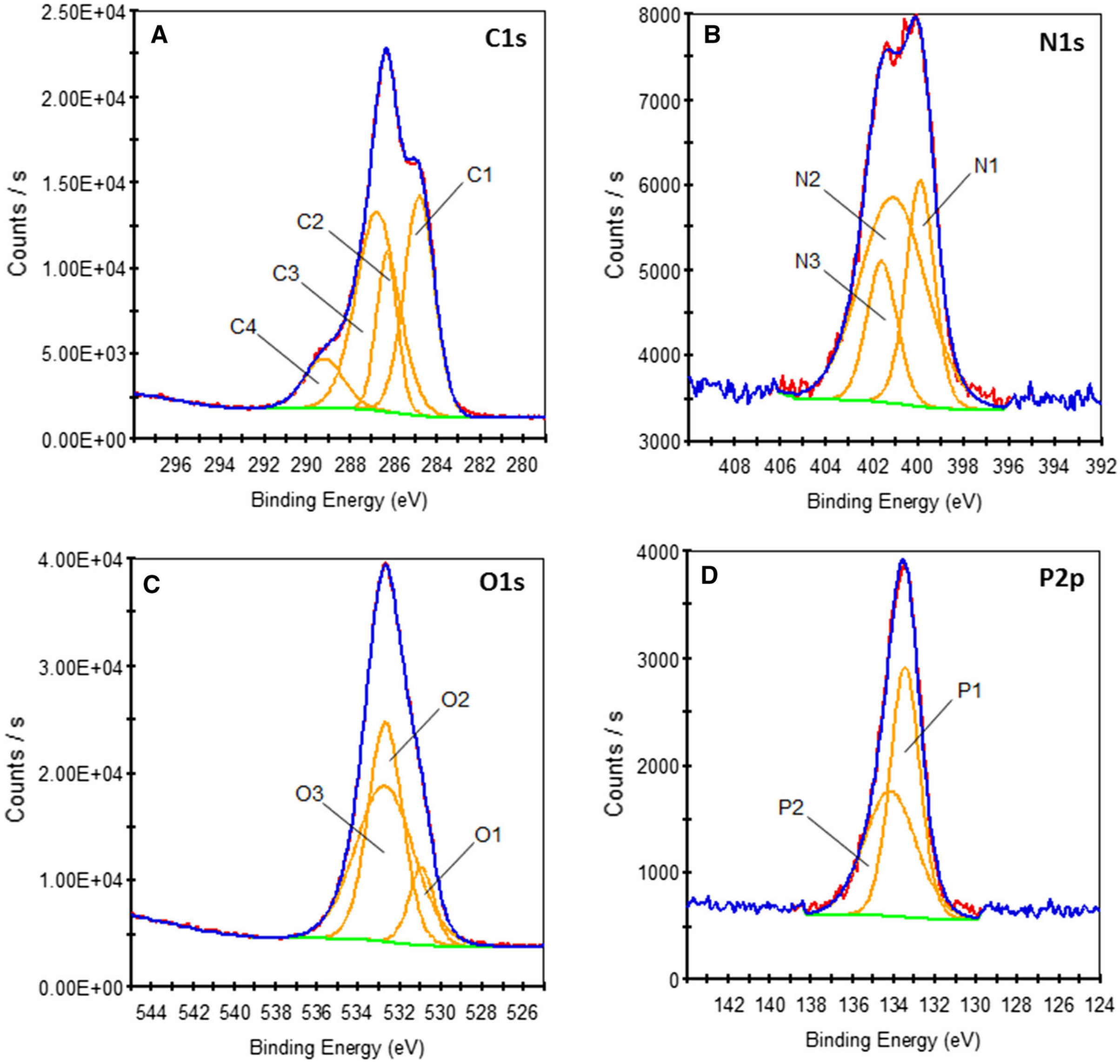


Fig. 9 Deconvoluted XPS survey spectra of **A** C1s, **B** N1s, **C** O1s and **D** P2p of phytic acid functionalized cotton fabric

XPS analysis

X-ray photoelectron spectroscopy was performed to investigate the chemical environments on the surface of the treated fabric to a depth of a few micrometers. The XPS survey spectrum of phytic functionalized cotton fabric is shown in Fig. 8. In the full survey spectrum, the peaks with binding energies in the range of 282–292, 396–406, 528–538, and 130–138 eV were identified as carbon (C1s), nitrogen (N1s), oxygen (O1s) and phosphorous (P2p) respectively. The peak deconvolution for high resolution reveals the different chemical environments corresponding to the elements. The high-resolution spectrum (Fig. 9) of C1s can be deconvoluted into five signals: C1-284.79, C2-286.29, C3-286.76, and C4-289.21 eV. The binding energies corresponding to C1 and C3 can be assigned to C–C/C–H, and C–O bonding in the cellulosic structure of cotton, whereas, the functionalization through CDI introduces C–N and –NH–C=O(O)– (Carbamate linkage) binding to the surface which can be identified as C2-286.29 and C4-289.21 eV, respectively (Li et al.2013; Liu et al. 2013). The binding energy at 289.21 eV further confirms the covalent attachment

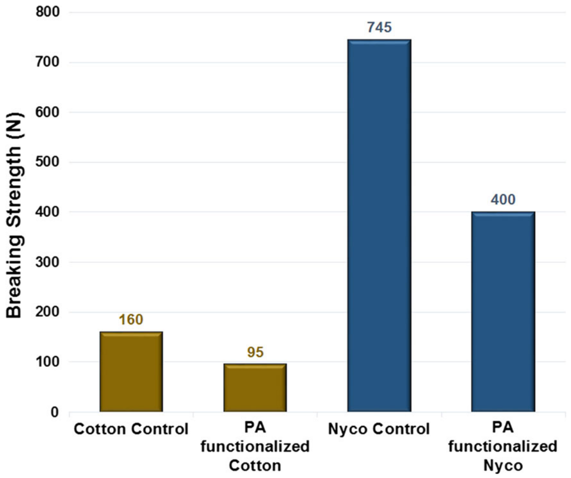


Fig. 10 Breaking strength of treated and untreated fabrics

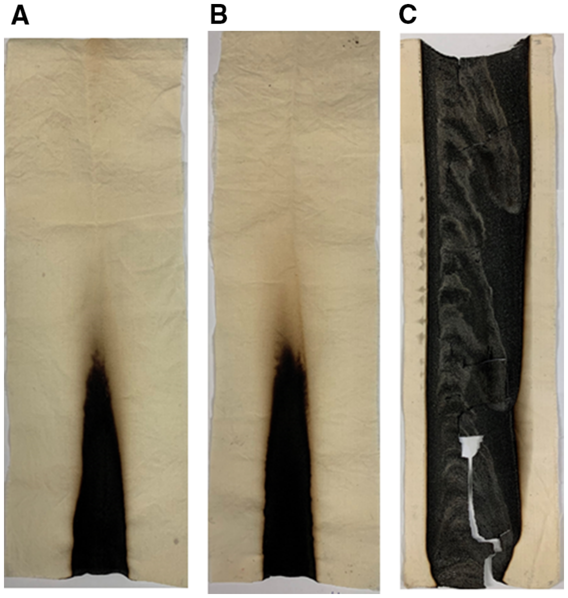


Fig. 11 Post vertical flame test images of (**A**) Phytic acid treated cotton fabric after 1 laundry cycle, (**B**) after 5 laundry cycles, and (**C**) Phytic acid treated nyco after 1 laundry cycle

through carbamate bonding (Ireni et al. 2016). Similarly, the O1 s high-resolution spectrum (Fig. 9) deconvoluted into three signals: O1-530.91, O2-532.66, and O3-532.69 eV. The O1 peak corresponds to –C=O and –P=O present in the carbamate linkage and phytic acid, whereas O2 and O3 correspond to the –C–O/–P–O and –C–OH/–P–OH respectively (Zhao et al. 2008; Zheng et al. 2015). Moreover, the convolution spectra of N1s (Fig. 9) and P2p suggests the attachment of phytic acid through the P-N bond. The deconvolution spectra of N1 s showed three peaks: N1-399.89, N2-401.07, and N3-401.55 eV corresponded to the nitrogen environment in amine, urethane and phosphoramide [–NH–P=O(OH)–O-] group, formed between the amine and phytic acid (Yu et al. 2014). The P2p spectra (Fig. 9) deconvoluted to two peaks: P1-133.43 and P2-134.14 eV. The lower binding energy peak P1 corresponds to phosphate group in phytic acid, and higher binding energy peak P2 corresponds to phosphoramide group (Wang et al. 2013, 2015a, b; Wu et al. 2015). In overall, the XPS spectrum of treated fabric further evidenced the functionalization to the surface resulted through carbamate and phosphoramide bonding.

Tensile test and Laundry performance

Tensile test was performed to determine the breaking strength of the phytic acid treated and untreated cotton and Nyco fabrics using Instron universal testing machine. The breaking strength values of the fabrics are shown in Fig. 10. Breaking strength of the phytic acid treated cotton fabric (95 N) was reduced by around 40% to that of cotton control (165 N). The reduction in strength can be due to the increased loading of the flame retardant onto the fabric and reaction conditions for its treatment. Besides, phytic acid treated Nyco fabric also followed a similar trend for breaking strength.

The treated fabrics were subjected to home laundry procedure to evaluate the flame retardant performance after washing. For durability studies, five normal home laundry cycles were performed for phytic acid functionalized cotton fabric according to the AATCC 135, and the flame retardant performance was evaluated through the vertical flame test. No significant change was observed in the flame retardant behavior of treated cotton even after five home laundry cycles in terms of char length. Char lengths for PA treated cotton fabric after one and five laundry cycles were found to be 4.5 and 4.75 inches, which are similar to the unlaundered PA treated cotton fabric. However, PA treated Nyco fabric was burnt completely in the vertical flame test after one home laundry cycle. The Post VFT images after laundry are shown in Fig. 11.

Conclusions

In conclusion, for the first time, cotton and Nyco fabric have been successfully functionalized covalently using phytic acid. The functionalized fabric was characterized using various techniques, and the fire-retardant behavior was evaluated. The new chemical functionalization of fabric through CDI chemistry successfully incorporated phytic acid, which acted as a flame retardant molecule to the fabric. Phytic acid functionalized fabrics showed better thermal and flame-retardant properties than the control samples. We are currently working on improving the durability and commercial viability of this covalent functionalization strategy towards durable flame-retardant cotton and Nyco fabrics. This unique functionalization method also opens up a way to attach molecules of interest on these fabrics for multifunctional properties such as anti-microbial, insect repellency, etc.

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References

Cheng XW, Guan JP, Chen G, Yang XH, Tang RC (2016a) Adsorption and flame retardant properties of bio-based phytic acid on wool fabric. Polymers 8:122

Cheng XW, Guan JP, Tang RC, Liu KQ (2016b) Phytic acid as a bio-based phosphorus flame retardant for poly (lactic acid) nonwoven fabric. J Clean Prod 124:114–119

Edwards B, El-Shafei A, Hauser P, Malshe P (2012) Toward flame retardant cotton fabric by atmospheric pressure plasma-induced graft polymerization: synthesis and application of novel phosphoramidate monomers. Surf Coat Technol 209:73–79

Feng Y, Zhou Y, Li D, He S, Zhang F, Zhang G (2017) A plant-based reactive ammonium phytate for use as a flame-retardant for cotton fabric. Carbohyd Polym 175:636–644

Galina L, Cristopher K, Alexander BM, Jaime CG (2013) Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame retardant cotton. Biomacromol 13:2843–2848

Gao WW, Zhang GX, Zhang FX (2015) Enhancement of flame retardancy of cotton fabrics by grafting a novel organic phosphorous-based flame retardant. Cellulose 22:2787–2796

Ireni NG, Narayan R, Basak P, Raju KVS (2016) Functional polyurethane–urea coatings from sulfur rich hyperbranched polymers and an evaluation of their anticorrosion and optical properties. N J Chem 40:8081–8092

Jia Y, Hu Y, Zheng D, Zhang G, Zhang F, Liang Y (2017a) Synthesis and evaluation of an efficient, durable, and environmentally friendly flame retardant for cotton. Cellulose 24:1159–1170

Jia Y, Lu Y, Zhang G, Liang Y, Zhang F (2017b) Facile synthesis of an eco-friendly nitrogen–phosphorus ammonium salt to enhance the durability and flame retardancy of cotton. J Mater Chem A 5:9970–9981

Kadla JF, Gilbert RD (2000) Cellulose structure: a review. Cell Chem Technol 34:197–216

Klemm D, Heublein B, Fink HF, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. Angew Chem 44:3358–3393

Lam YL, Kan CW, Yuen CW (2011) Effect of oxygen plasma pretreatment and titanium dioxide overlay coating on flame retardant finished cotton fabric. BioResources 6:1454–1474

Laufer G, Kirkland C, Morgan AB, Grunlan JC (2012) Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton. Biomacromol 13:2843–2848

Li YC, Schulz J, Mannen S, Delhom C, Condon B, Chang S, Zammarano M, Grunlan JC (2010) Flame retardant behavior of polyelectrolyte—clay thin film assemblies on cotton fabric. ACS Nano 4:3325–3337

Li R, Wei Z-D, Gou X-L, Xu W (2013) Phosphorus-doped graphene nanosheets as efficient metal-free oxygen reduction electrocatalysts. RSC Adv 3:9978–9984

Liu Z, Nie H-G, Yang Z, Zhang J, Jin Z-P, Lu Y-Q, Xiao Z-B, Huang S-M (2013) Sulfur nitrogen co-doped three-dimensional carbon foams with hierarchical pore structures as efficient metal-free electrocatalysts for oxygen reduction reactions. Nanoscale 5:3283–3289

Liu XH, Zhang QY, Cheng BW, Ren YL, Zhang YG, Ding C (2018) Durable flame retardant cellulosic fibers modified with novel, facile and efficient phytic acid-based finishing agent. Cellulose 25:799–811

Narkhade M, Thota S, Mosurkal R, Muller W, Kumar J (2016) Layer-by-layer assembly of halogen-free polymeric materials on nylon/cotton blend for flame retardant applications. Fire Mater 40:206–218

Schartel B (2010) Phosphorus-based flame retardancy mechanisms—old hat or a starting point for future development? Materials 3:4710–4745

Soares S, Camino G, Levchik S (1995) Comparative study of the thermal decomposition of pure cellulose and pulp paper. Polym Degrad Stab 49:275–283

Tsafack MJ, Levalois-Grützmacher J (2007) Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: flame and waterproof cotton textiles. Surf Coat Technol 201:5789–5795

Wang C, Sun L, Zhou Y, Wan P, Zhang X, Qiu J (2013) P/N co-doped microporous carbons from H3PO4-doped polyaniline by in situ activation for supercapacitors. Carbon 59:537–546

Wang X, Romero MQ, Zhang XQ, Wang R, Wang DY (2015a) Intumescent multilayer hybrid coating for flame retardant cotton fabrics based on layer-by-layer assembly and sol–gel process. RSC Adv 5:10647–10655

Wang Y, Zhang B, Xu M, He X (2015b) Tunable ternary (P, S, N)-doped graphene as an efficient electrocatalyst for oxygen reduction reaction in an alkaline medium. RSC Adv 5:86746–86753

Wu J, Zheng X, Jin C, Tian J, Yang R (2015) Ternary doping of phosphorus, nitrogen, and sulfur into porous carbon for enhancing electrocatalytic oxygen reduction. Carbon 92:327–338

Yu B, Wang X, Qian X, Xing W, Yang H, Ma L, Lin Y, Jiang S, Song L, Hu Y, Lo S (2014) Functionalized graphene oxide/phosphoramide oligomer hybrids flame retardant prepared via in situ polymerization for improving the fire safety of polypropylene. RSC Adv 4:31782–31794

Yu-Chin L, Sarah M, Alexander BM, SeChin C, You-Hao Y, Brian C, Jaime CG (2011) Intumescent all-polymer multilayer nanocoating capable of extinguishing flame on fabric. Adv Mater 23:3926–3931

Zhao CX, Liu Y, Wang DY, Wang DL, Wang YZ (2008) Synergistic effect of ammonium polyphosphate and layered double hydroxide on flame retardant properties of poly (vinyl alcohol). Polym Degrad Stab 93:1323–1331

Zheng Z, Liu S, Wang B, Yang T, Cui X, Wang H (2015) Preparation of a novel phosphorus-and nitrogen-containing flame retardant and its synergistic effect in the intumescent flame-retarding polypropylene system. Polym Compos 36:1606–1619

Zhou Y, Ding C, Qian X, An X (2015) Further improvement of flame retardancy of polyaniline-deposited paper composite through using phytic acid as dopant or co-dopant. Carbohyd Polym 115:670–676