Supporting information for

In-Situ Phosphine Oxide Physical Networks: A facile Strategy to Achieve Durable Flame Retardant and Antimicrobial Treatments of Cellulose

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SI-1. Materials and Methods

SI-1.2: NMR analysis

Solid-state ^{13}C and ^{31}P CP-MAS NMR spectra were measured at ambient conditions on a Bruker Avance III 400 NMR spectrometer (Bruker BioSpin AG, Fällanden, Switzerland) with a 4 mm CP-MAS probe. Approximately 30-50 mg of material was thoroughly packed into a 4 mm zirconia rotor. The ^{13}C and ^{31}P CP-MAS NMR spectra were recorded at 100.6 and 162.0 MHz, respectively, using the following parameters: 3.5 μs 90° excitation pulse on ^{1}H channel, 2 ms contact time with a ramp from 100 to 50% of power level on the proton channel, sample rotation of 10 or 13 kHz, 2 s relaxation delays, 71 kHz SPINAL 64 proton decoupling was applied during acquisition, and appropriate numbers of scans were recorded to yield reasonable signal-to-noise ratios. The ^{13}C and ^{31}P chemical shifts (δ) were referenced to the external resonances of adamantane at 38.5 ppm and solid $NH_4H_2PO_4$ at 0.0 ppm, respectively.

SI-2. Synthesis of phosphine oxide polymers

SI-2.1. Synthesis of Polymer-A (Poly-A)

TVPO   pip   Poly-A
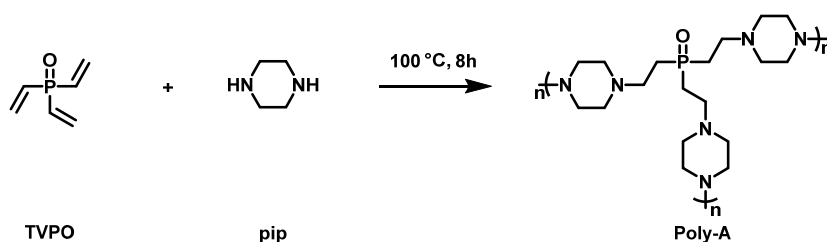
Scheme SI-1. A mixture of TVPO (128.11mg, 1.0 mmol) and piperazine (129.21 mg, 1.50 mmol) (1:1 M ratio) was taken in a pressure glass tube (Ace pressure tube, volume ~15 mL) and heated (100 °C for 1 and 8 hours) using a heating block on a hot plate to obtain a transparent Polymer-A.
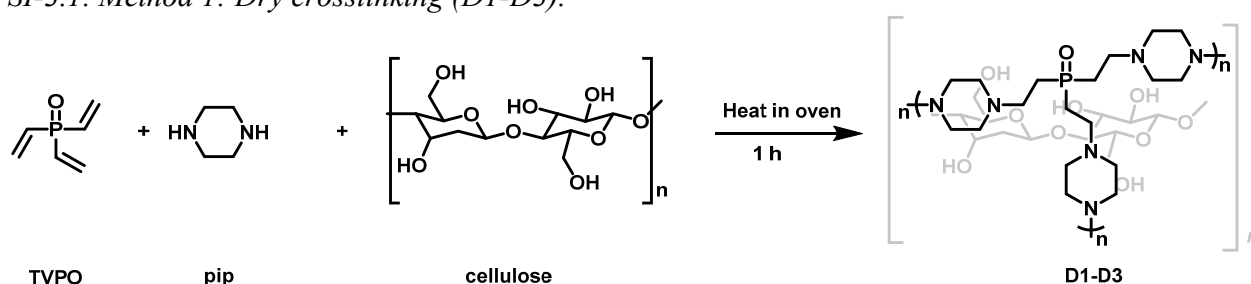
SI-2.2. Synthesis of Polymer-B (Poly-B)

TVPO   TPT   Poly-B
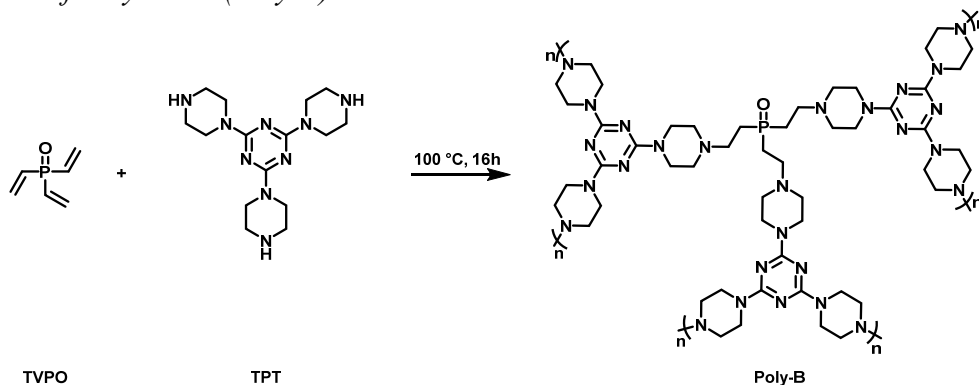
A mixture of TVPO (128.11mg, 1.0 mmol), TPT (333.44 mg, 1.0 mmol) (1:1 M ratio) in 1mL ethanol was taken in a pressure glass tube (Ace pressure tube, bushing type, back seal, volume ~15 mL, L×O.D. 10.2 cm× 25.4 mm) in heating blocks on a hot plate and heated to 100 °C for 16 hours to obtain a transparent Polymer-B.

SI-3. Synthesis of phosphine oxide modified cellulose fibers
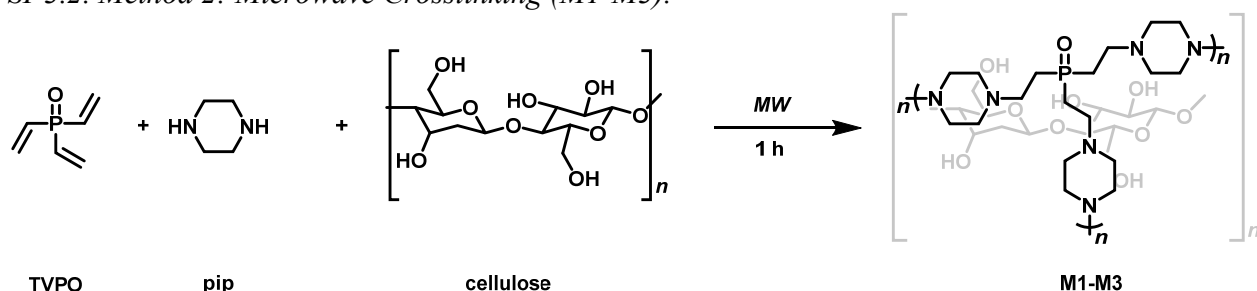
SI-3.1. Method 1: Dry crosslinking (D1-D3).

The conditioned cellulose fabric of the required dimension was taken in a flat petri dish and a mixture of TVPO and piperazine (1:1 molar ratio) dissolved in a specific amount of deionized water (volume = twice the weight of cellulose fabric) was applied evenly over the fabric with a syringe. To ensure uniformity in the application, both sides of the fabric surface were treated by applying half the solution to each side. As the cellulose fabrics are very hygroscopic, the solution spread quickly and evenly on them. The fabrics were left in the petri dish for 15 more mins to allow them to soak any excess solution left. The fabrics were then dried in the oven for 5 mins at 60 °C and were cured in a preheated hot air oven preheated oven at different temperatures (120 °C, 140 °C, 160 °C) for 1 hour. The phosphorus weight percent (P wt. %) of the treated cellulose fabrics was measured before and after washing, as shown in Table SI-1.

Table SI-1: Dry crosslinking curing conditions and % P content.

Sample name	Curing temp. (°C)	Time (hour)	P (%) before washing	*P (%) after washing	P retention (%)
D1	120	1	1.46 ± 0.11	0.88 ± 0.18	60
D2	140	1	1.26 ± 0.08	0.91 ± 0.29	73
D3	160	1	1.62 ± 0.34	1.29 ± 0.31	80

P: phosphorus, *P (%) after washing (5 laundry cycles)

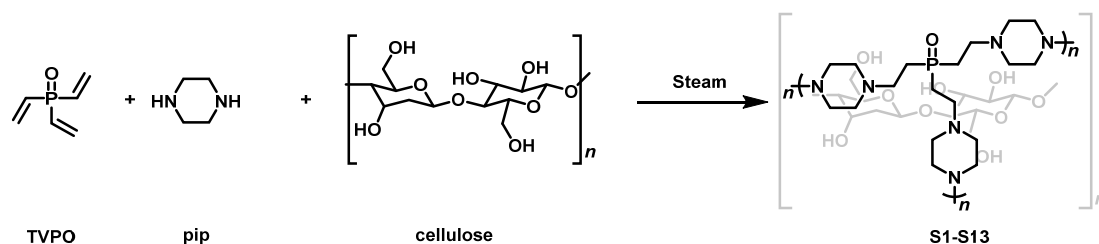*SI-3.2. Method 2: Microwave Crosslinking (M1-M3).*

The conditioned cellulose fabric of the required dimension was taken in a flat petri dish and a mixture of TVPO and piperazine (1:1 molar ratio) dissolved in a specific amount of deionized water (volume = twice the weight of cellulose fabric) was applied evenly over the fabric with a syringe. To ensure uniformity in the application, both sides of the fabric surface were treated by applying half the solution to each side. As the cellulose fabrics are very hygroscopic, the solution spread quickly and evenly on them. The fabrics were left in the petri dish for 15 more mins to allow them to soak any excess solution left. The fabrics were then dried in the oven for 5 mins at 60 °C and were placed in the glass tube, heated at different temperatures (120 °C, 140 °C, 160 °C) at 30 bar nitrogen pressure for 1 hour in a microwave reactor (Synthwave from MLS GmbH). The phosphorus weight percent (P. wt. %) of the treated cellulose fabrics was measured before and after washing, as shown in Table SI-2.

Table SI-2. Microwave Crosslinking conditions and % P content.

Sample	Curing temp. (°C)	Time (h)	P (%) before washing	*P (%) after washing	P retention (%)
M1	120	1	2.14 ± 0.29	2.08 ± 0.08	97
M2	140	1	2.14 ± 0.22	2.01 ± 0.18	94
M3	160	1	2.08 ± 0.19	1.97 ± 0.00	95

P: phosphorus, *P (%) after washing (5 laundry cycles)

SI-3.3. Method 3: Steam Crosslinking (S1-S13)

The conditioned fabric of the required dimension was taken in a petri dish and a mixture of TVPO and piperazine (1:1 molar ratio) dissolved in a specific amount of deionized water (volume = twice the weight of fabric) was applied evenly over the fabric. To ensure uniformity in the application, both sides of the fabric surface were treated by applying half the solution to each side. The fabrics were left in the petri dish for 15 more mins. The fabrics were then dried in the oven for 5 mins at 60 °C and mounted on a needle frame followed by steaming in an autoclave at 0.4 (110 °C) and 0.8 (117 °C) bar for varying durations (Fig. SI-1). The pressure in the autoclave was monitored and regulated. The phosphorus weight percent (P. wt. %) of the treated fabrics was measured before and after washing by ICP-OES (Table SI-3).

Table SI-3. Steam Crosslinking curing conditions and % P content.

Sample	*Curing temp. (°C)/ Pressure (bar)*	*Time (h)*	*P (%) before washing*	**P (%) after washing*	*P retention (%)*
S1	110 (0.4)	0.5	2.06±0.04	1.98±0.03	96
S2	110 (0.4)	1	2.05±0.02	2.03±0.01	99
S3	110 (0.4)	2	2.12±0.01	2.11±0.00	100
S4	110 (0.4)	4	1.91±0.01	1.88±0.03	98
S5	117 (0.8)	0.5	2.07±0.03	2.01±0.02	97
S6	117 (0.8)	1	2.12±0.04	2.06±0.03	97
S7	117 (0.8)	2	2.30±0.04	2.27±0.02	99
S8	117 (0.8)	4	2.50±0.01	2.50±0.04	100
S9	110 (0.4)	1	1.11±0.04	1.11±0.06	100
S10	110 (0.4)	1	1.56±0.03	1.56±0.04	100
S11	110 (0.4)	1	2.23±0.05	2.22±0.09	100
S12	110 (0.4)	1	2.67±0.08	2.66±0.14	100
S13[Δ]	110 (0.4)	1	2.16±0.02	2.06±0.02[Δ]	95

P: phosphorus, *****P (%) after washing (5 laundry cycles) and Δ P (%) after washing (50 laundry cycles)
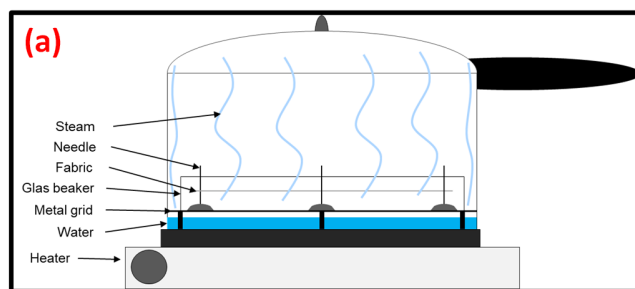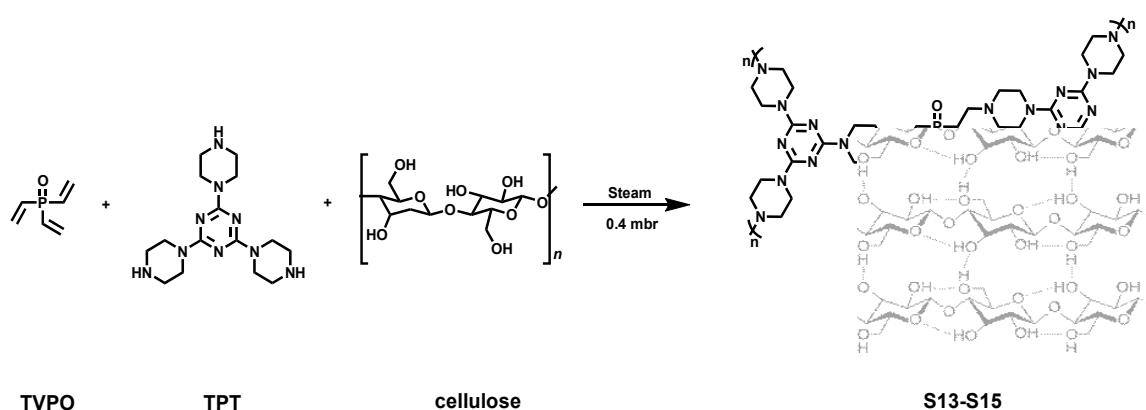
Fig. SI-1. Setup for steam crosslinking experiments.

SI-3.4. Steam Crosslinking using TVPO and TPT (S14 and S15).

The conditioned cellulose fabric of the required dimension was taken in a flat petri dish and a mixture of TVPO and TPT (1:1 molar ratio) dissolved in a specific amount of absolute ethanol (volume = twice the weight of cellulose fabric) was applied evenly over the fabric with a syringe. The fabrics were then let to soak for 15 mins and dried in the oven at 60 °C for 5 mins. The fabrics were then steam crosslinked in an autoclave (simple pressure cooker that was filled with 350 ml of deionized water) as shown in Fig. SI-1, at 0.4 bar (110 °C) for 1 hour. The phosphorus weight percent (P. wt. %) of the treated cellulose fabrics was measured before and after washing, as shown in Table 1.
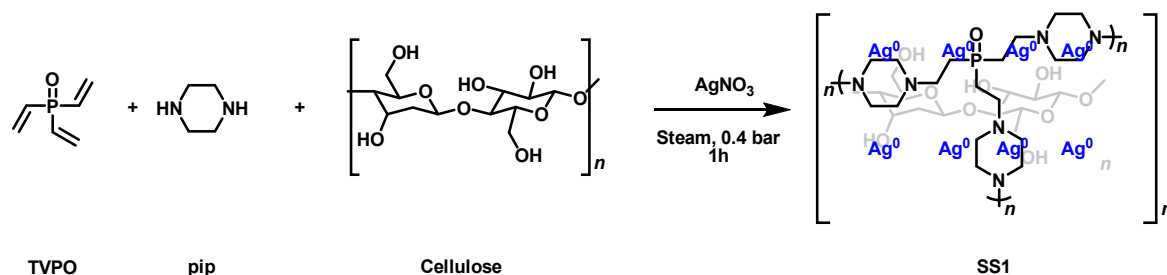
TVPO   pip   Cellulose   SS1

The conditioned fabric of the required dimension was taken in a petri dish and a mixture of TVPO and piperazine (1:1 molar ratio) dissolved in a specific amount of deionized water (volume = twice the weight of cellulose fabric) was applied evenly over the fabric with a syringe. The fabrics were then let to soak for 15 minutes and dried in the oven at 60 °C for 5 minutes. Subsequently, the required amount of AgNO3 dissolved in deionized water on cellulose in dark. The fabrics were then steam treated in the autoclave as shown in Fig. SI-1, at 0.4 bar (110 °C) for 1 hour. The Silver and phosphorus content in the treated fabrics before and after washing were determined by ICP-OES analysis (Table SI-4).

Table SI-4. Steam Crosslinking curing conditions and % P content.

Sample	Time	Temp.(°C)/ Pressure (bar)	P (%)		Ag (%)		Ag retention (%)
			before wash	after wash*	before wash	after wash*	
SS1	1	110 (0.4)	2.14 ± 0.29	2.08 ± 0.08	0.08 ± 0.01	0.08 ± 0.01	100
50WSS1$^\Delta$	1	110 (0.4)	2.14 ± 0.22	2.01 ± 0.18	0.08 ± 0.01	0.08 ± 0.01	100
SS2	1	110 (0.4)	2.08 ± 0.1	1.99 ± 0.05	0.75 ± 0.03	0.75 ± 0.10	100

P: phosphorus, *P (%) after washing (5 laundry cycles), Δ P (%) after washing (50 laundry cycles), Ag: Silver, *Ag^0 (%) after washing (5 laundry cycles), Δ Ag^0 (%) after washing (50 laundry cycles)
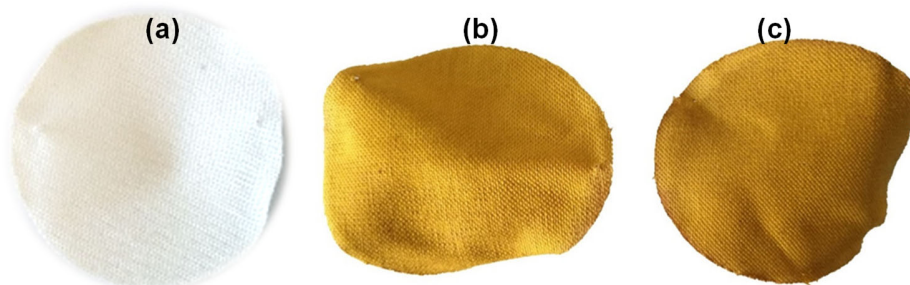

Fig. SI-2. (a) Cotton fabric containing TVPO, piperazine, and AgNO3 (0.1 % Ag, after drying at 60 °C for 5 min.). Cotton fabric after in-situ polymerization and reduction by steaming for 1 h with **(b)** 0.08% and **(c)** 0.75% AgNPs in the final fabric.

SI-4. Laundering of treated cellulose fabric (AATCC 61-1996)

The AATCC test method-61-2013 was followed to simulate five home laundering cycles to assess the durability of the treatment. Typically, a 152.4 × 50.8 mm sample was sandwiched between two multi-fiber test fabric and was stitched along the edges (Fig.S1). For each sample, three specimens were prepared for washing. For one specimen, 0.225g of detergent 98 (ECE 98), 150 mL of demineralized water, and 50 steel balls were added to the steel washing container. Then the container was sealed and transferred into an Atlas Launder-O-Meter Model LEF. The washing was carried out for 45 min at 49 °C to simulate five home laundering. After 45 min, washing containers were removed from the Launder-O-Meter and the specimens were rinsed thoroughly with demineralized water three times. The sample was then dried in the oven at 60 °C for 2h followed by conditioning in standard atmosphere for 24 h before other characterization and analysis.
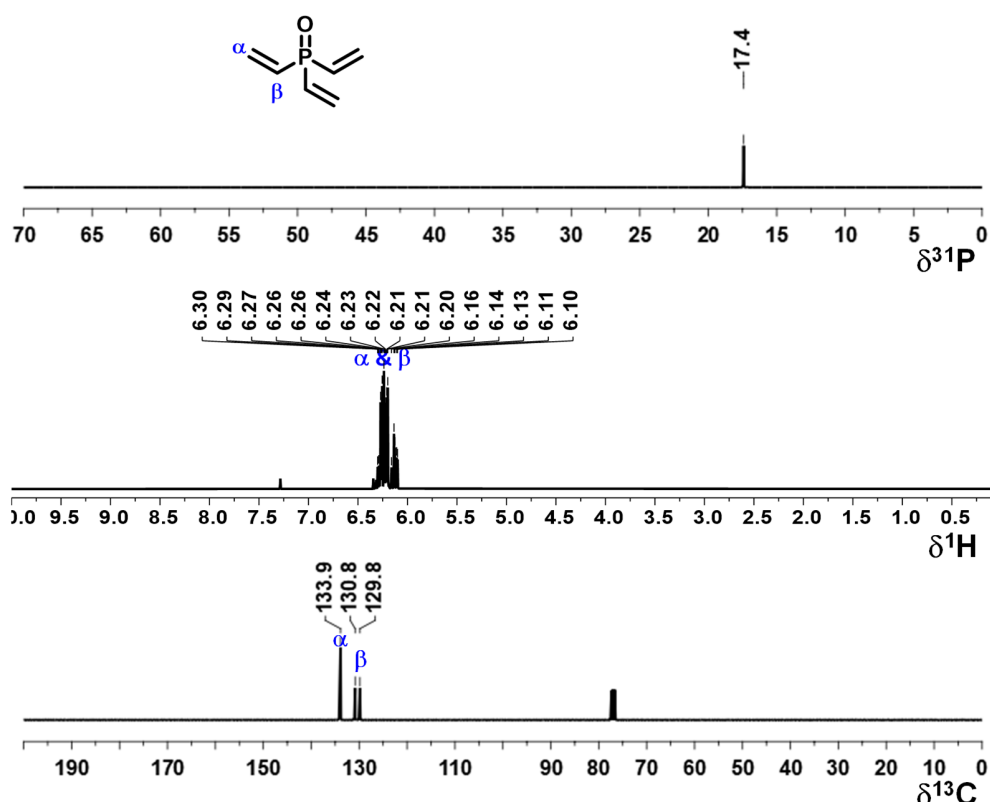
SI-5. NMR characterizations

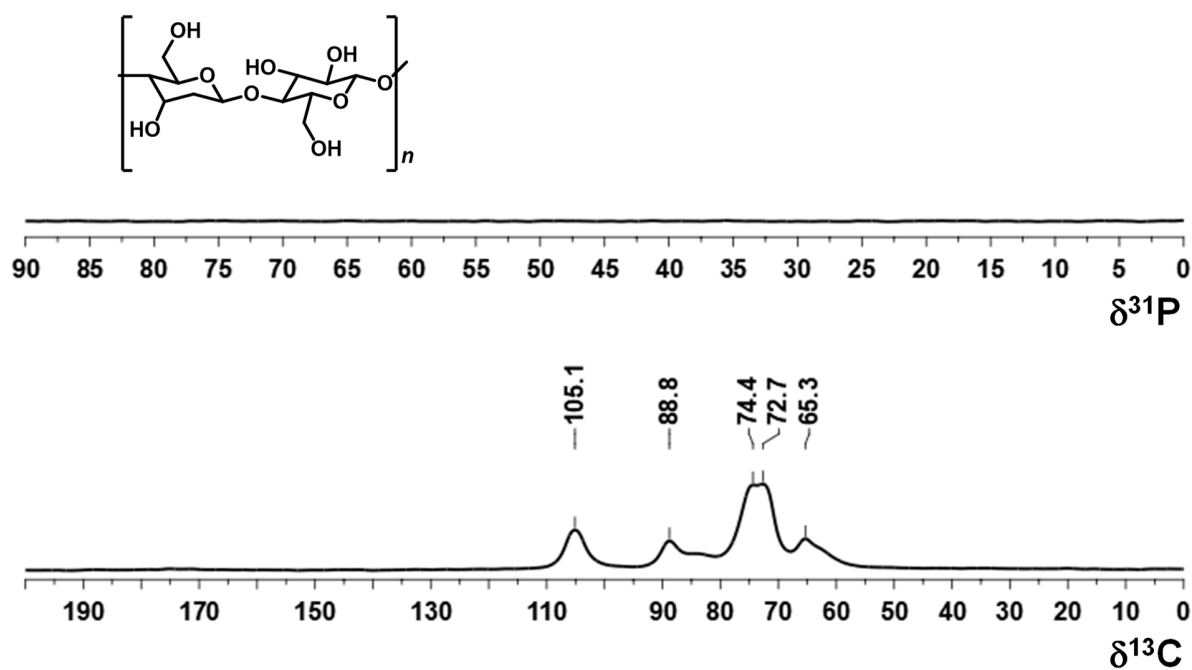**Fig. SI-2:** ^{1}H and ^{13}C NMR spectra with expanded regions of interest and with resonance assignments of **TVPO** (CDCl$_3$).[1]

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Fig. SI-3.

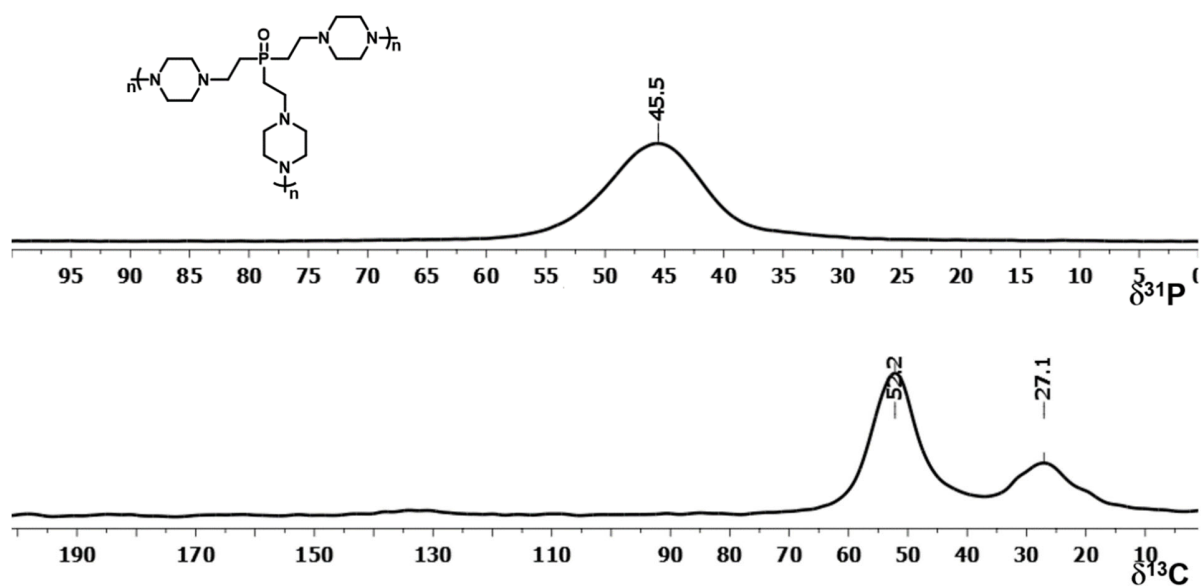^{13}C and ^{31}P CP-MAS NMR spectra of **Cellulose blank**.

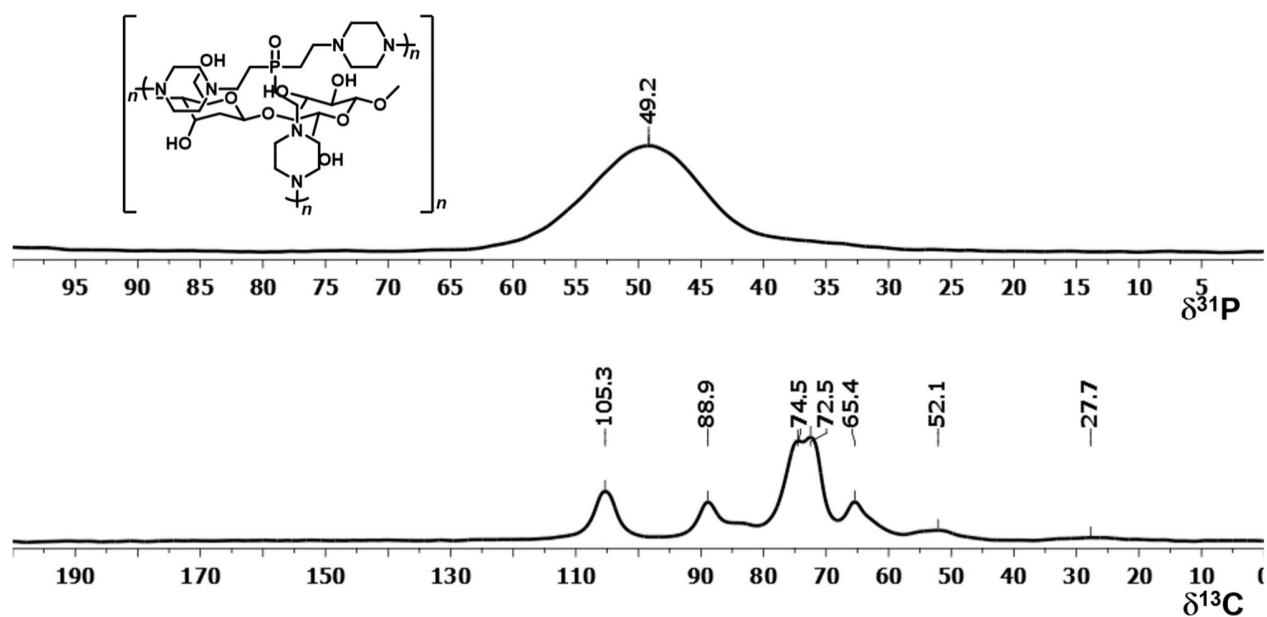**Fig. SI-4.** ^{13}C and ^{31}P CP-MAS NMR spectra of **Poly-A**.

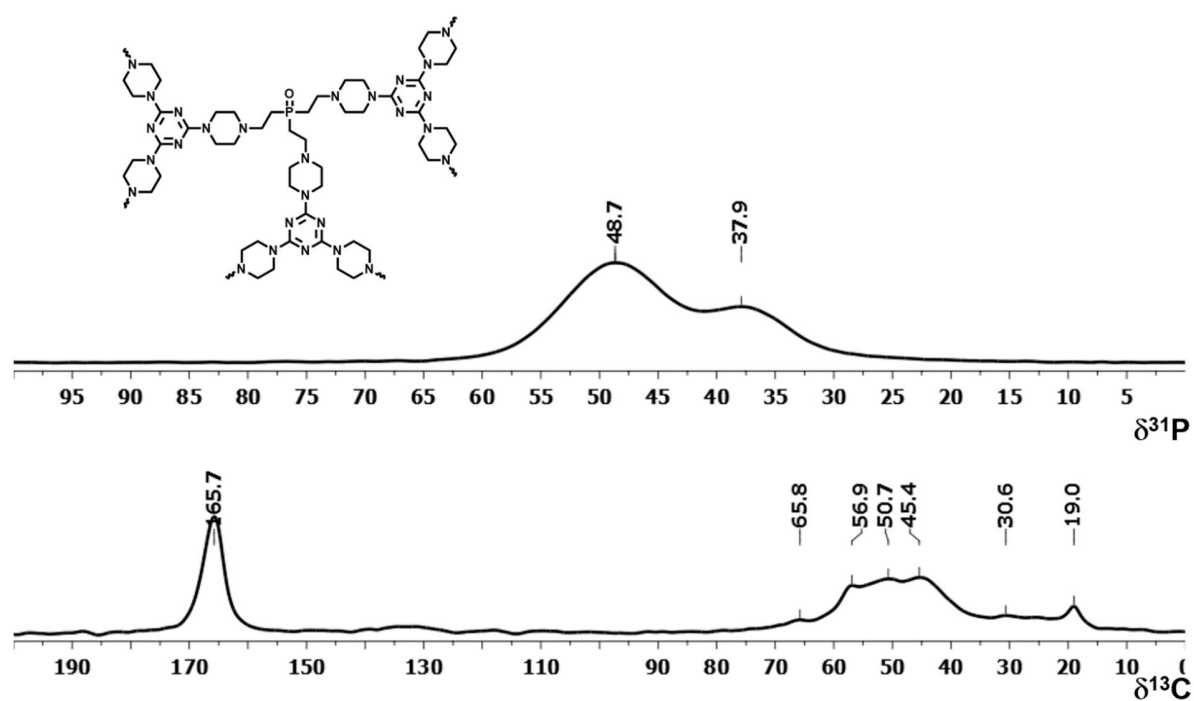**Fig. SI-5.** ^{13}C and ^{31}P CP-MAS NMR spectra of treated cellulose fabrics **(S12)**.

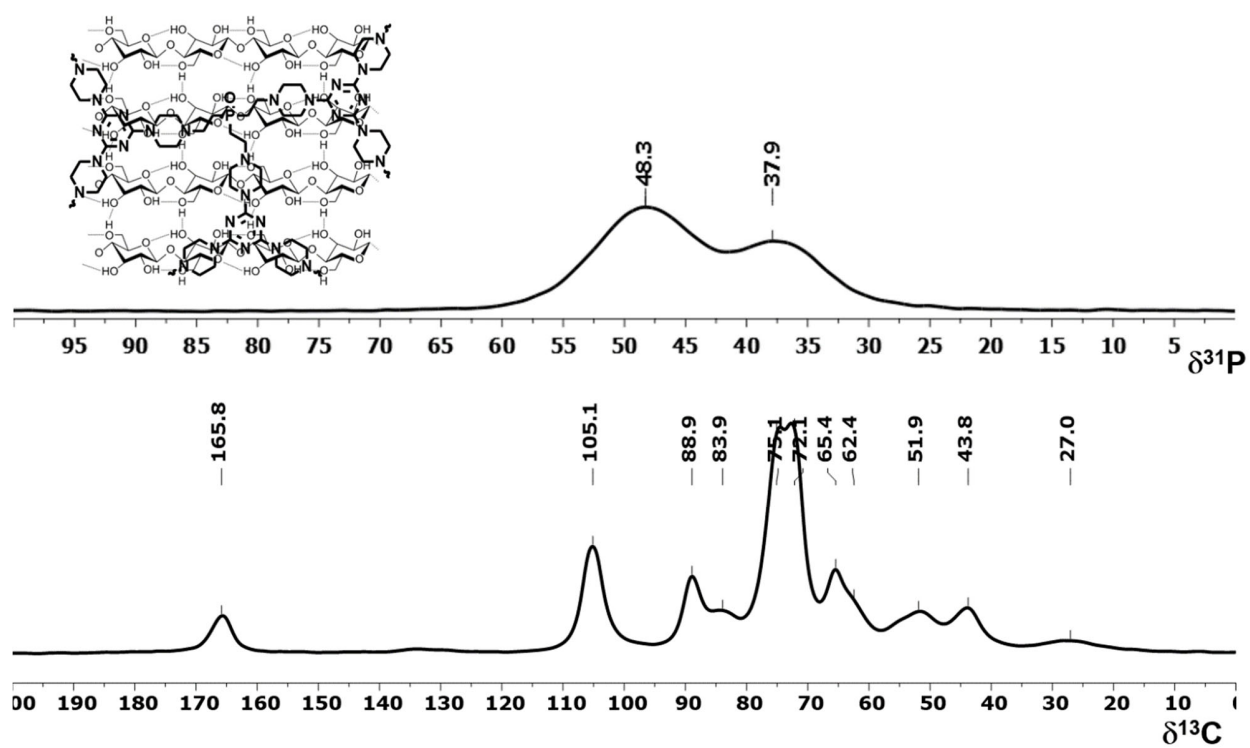**Fig. SI-6.** ^{13}C and ^{31}P CP-MAS NMR spectra for **Poly-B.**

SI-7. ^{13}C and ^{31}P CP-MAS NMR spectra for treated cellulose fabrics **(S14).**

The additional resonances observed at 37.9 ppm in the ^{31}P MAS NMR spectra of samples **Poly-B** and **S14** are assignable to terminal phosphorous groups bearing only two instead of three triazine ligands [1].

SI-6. Cellulose digital pics after burning
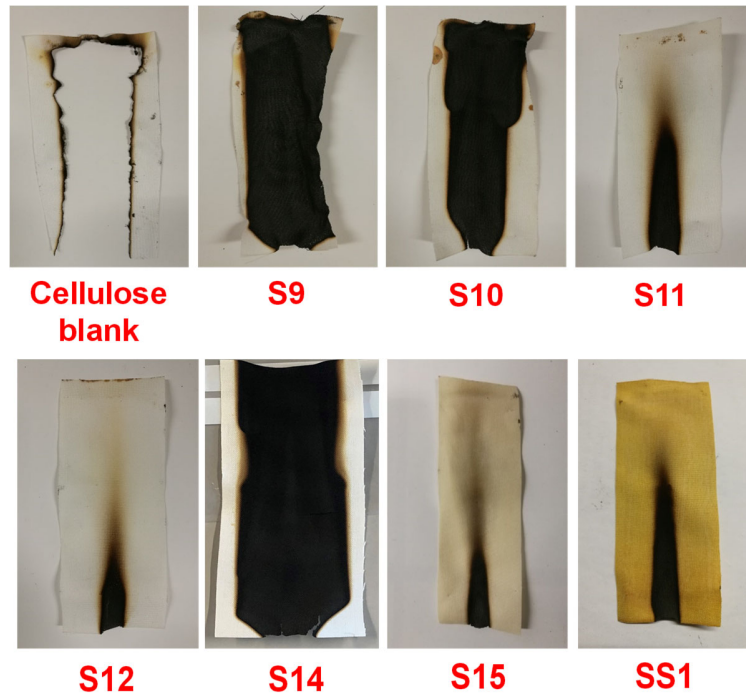

Fig. SI-9. Photographs of Cellulose fabrics with sample numbers after testing.

SI-7. Microscale Combustion Calorimeter (MCC)
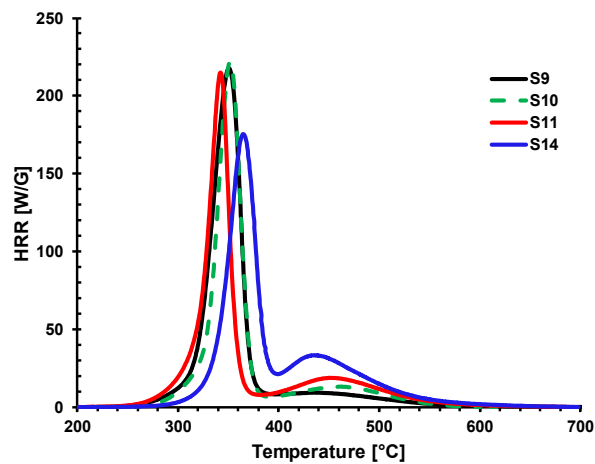
Fig. SI-10. Heat release rate (HRR) of **S9**, **S10**, **S11,** and **S14** measured using MCC.

SI-8. Thermogravimetric analysis (TGA)

(a)

(b)

(c)

(d)
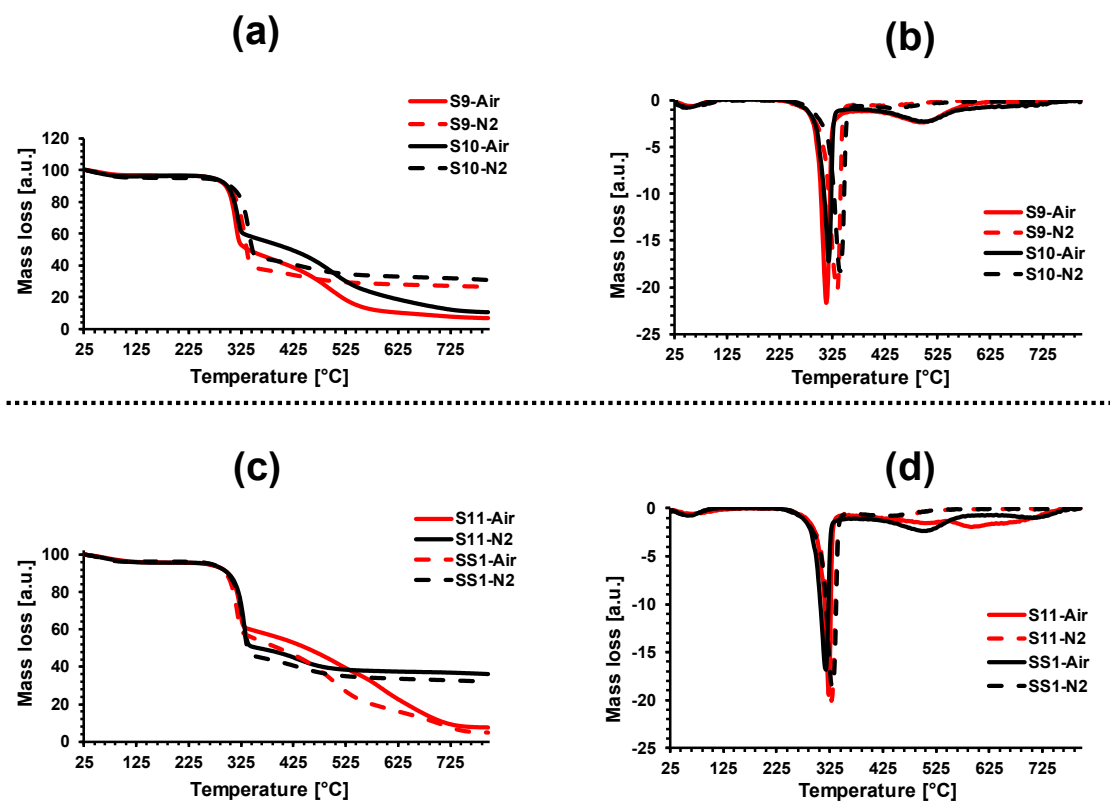
Fig. SI-11. (a) TGA **(b)** DTG curves of S9 and S10 under Air/N$_2$ **(c)** TGA **(d)** DTG curves of S11 and SS1 under Air/N$_2$.
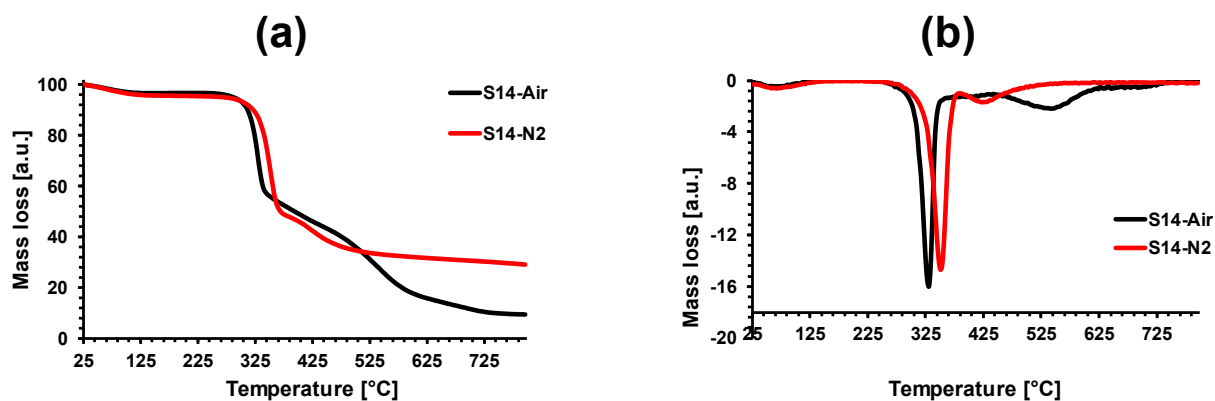
(a)

(b)

Fig. SI-12. (a) TGA **(b)** DTG curves of S14.

Table SI-5: TGA data of treated cellulose T_{donset} (°C): the temperature of 97% excluding moisture. $\mathbf{T}_{dmax}$ (°C): the temperature of the maximum mass loss rate is measured as the DTG peak maximum.

| Sample	P (%)	N₂			air		
		T_{donset} (°C)	T_{dmax} (°C)	Residue 800°C/(wt. %)	T_{donset} (°C)	T_{dmax} (°C)	Residue 800°C/(wt. %)
Blank	---	331	358	12.2	318	334	2.4
Poly-A	---	361	408	3.4	345	355	2.4
S9	1.11 ± 0.06	312	334	26.7	300	315	6.4
S10	1.56 ± 0.04	315	330	30.0	305	320	5.1
S11	2.22 ± 0.09	312	329	36.2	310	324	7.4
S12	2.66 ± 0.14	311	327	34.2	313	324	5.8
Poly-B	---	401	421	28.9	398	407	8.9
S14	1.00±0.02	331	350	28.8	313	331	6.4
S15	1.98 ± 0.03	322	336	31.4	322	330	7.3
SS1	2.08 ± 0.08	311	331	32.1	301	317	4.8

SI-9. EDX analysis of char
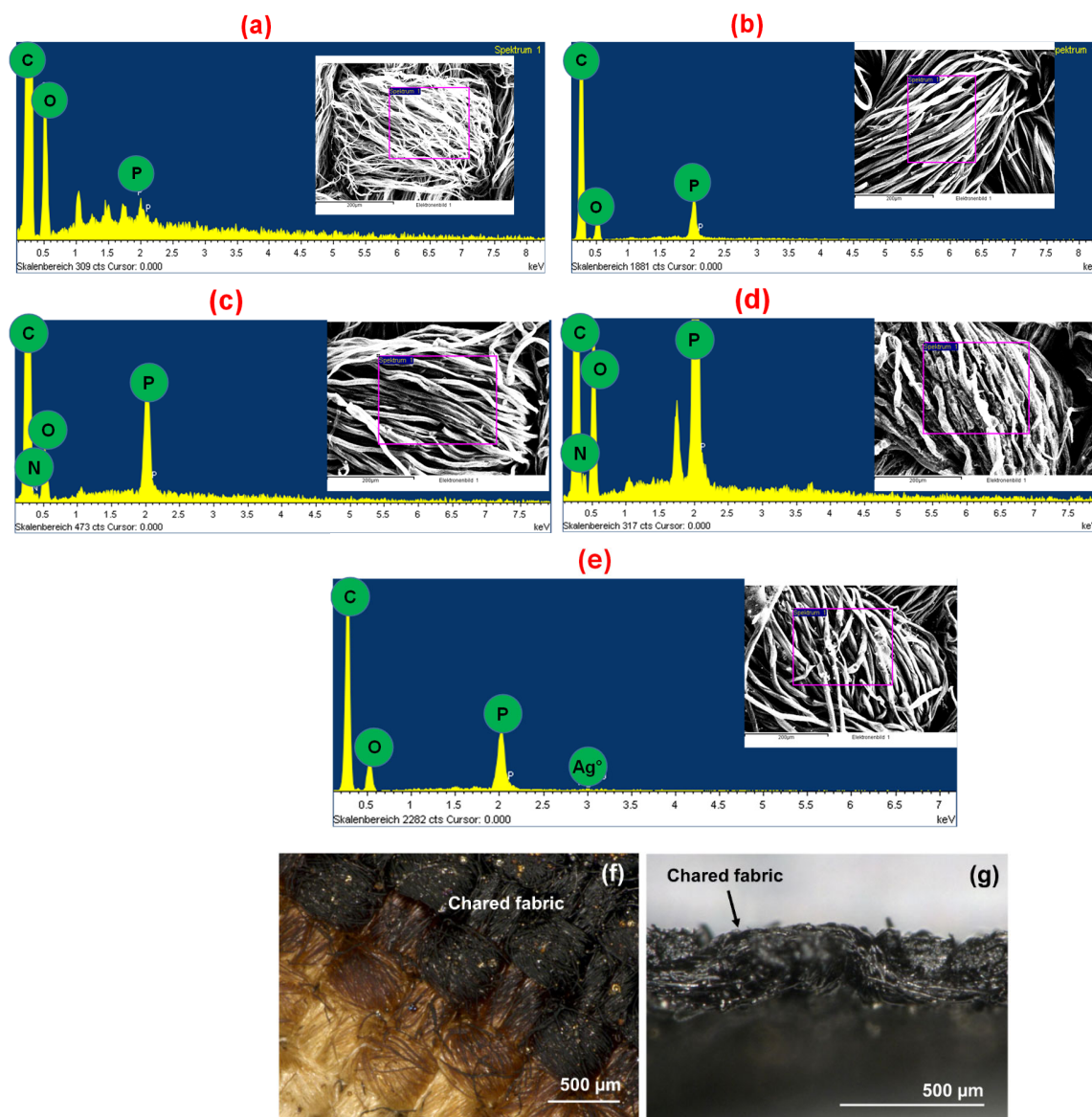
Fig. SI-13. EDX spectra of chars obtained after burning test of (a) **S9**, (b) **S12**, (c) **S14**, (d) **S15** and (e) **SS1**. (f and g) Microscopic images of char residue after burning test of **S12.** Images were recorded using a KEYENCE VHX-1000 Digital microscope.

Table SI-6: EDX (weight %) of S9, S12, S14, S15 and SS1 cotton fabrics residue.

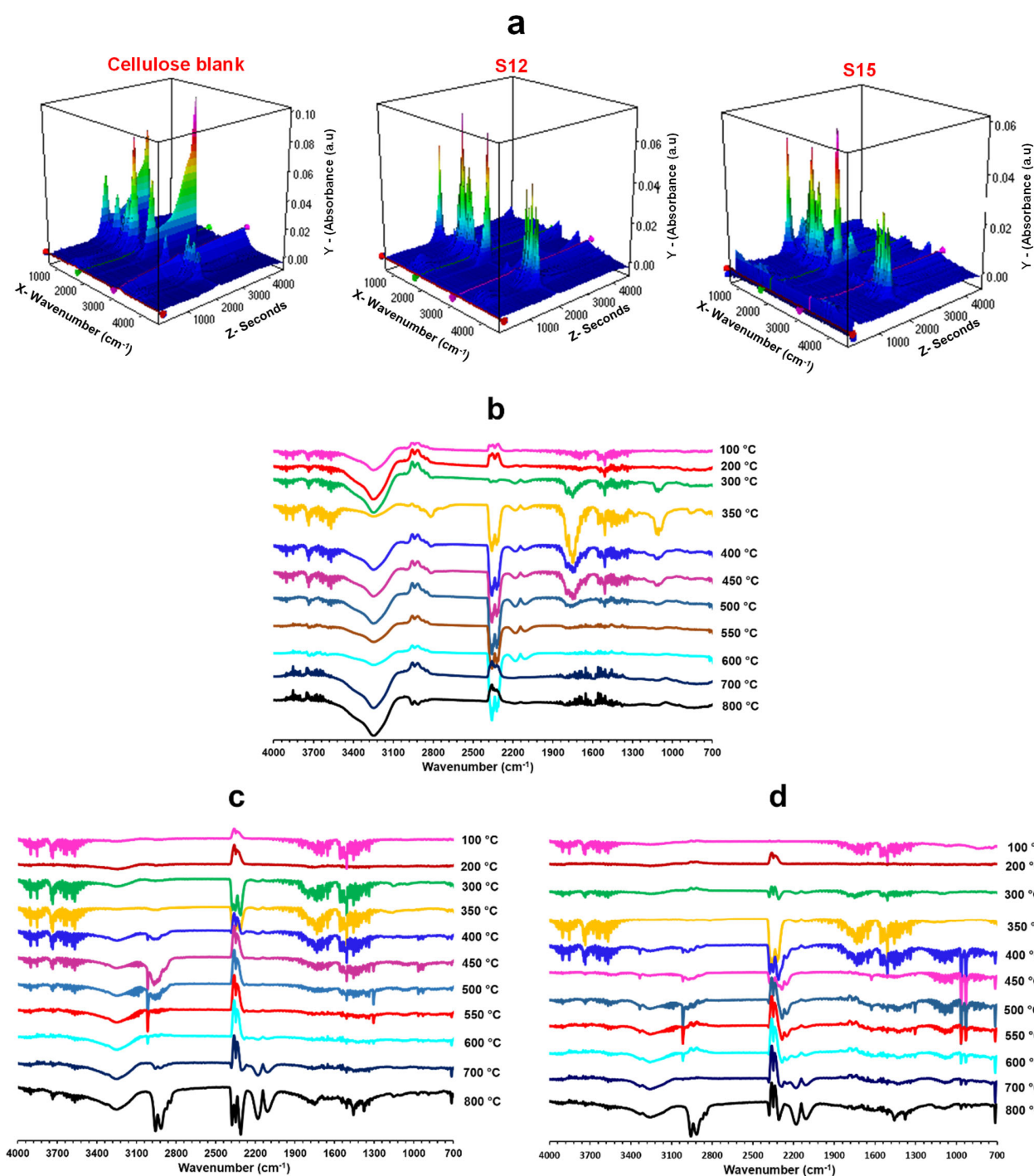| Samples	P.(%)	C.(%)	O.(%)	N.(%)	Ag°. (%)
S9	0.22	81.04	18.74	---	---
S12	3.67	75.74	20.59	---	---
S14	3.08	81.31	14.72	0.89	---
S15	5.40	59.56	25.31	9.73	---
SS1	5.47	71.88	22.39	---	0.25

SI-10. TGA-FTIR analysis

Fig. SI-14. The 3D TG-FTIR spectra of evolved volatiles and the corresponding FTIR spectra under different temperature for the (a) pristine (b) S12 and (c) S15 cotton fabric.

A time profile of volatiles produced during the thermal decomposition process of treated cellulose can give an understanding of the change in volatile composition with temperature. Fig. SI-14a represents the 3D plot of the TG-FTIR spectra of volatiles formed during the decomposition of treated cellulose. The blank cellulose starts to decompose at 300 °C, which is confirmed by TGA results. The appearance of the –OH (peak at 3228 cm^{-1}), C=O (peaks at 1743 cm^{-1}) and C-O-C (peak at1105 cm^{-1}) after 350°C shows the dehydration reactions of cellulose, yielding carbonyls derivatives[2]. For **S12** and **S15** (Fig. SI-12c, d), new peaks at 3234 cm^{-1} (-NH), 3014 cm^{-1} (-CH), 2129 cm^{-1} (CO), 1268 cm^{-1} (P=O), 1068 cm^{-1} (P-OH) and NH$_3$ (933cm^{-1}) around 300 °C corresponds to the decomposition of the crosslinked phosphine oxide polymer. The relation between the relative intensity of selected pyrolysis products (H$_2$O, CO$_2$, CO and carbonyl compounds) formed during the entire pyrolysis process as a function of temperature for cellulose are displayed in Fig. SI-SI-15. The CO and CO$_2$ release after 500 °C and 600 °C and beyond corresponds well with weight loss at this temperature in the TGA analysis (**Fig. 4**) and results have also been reported in the literature [3, 4].
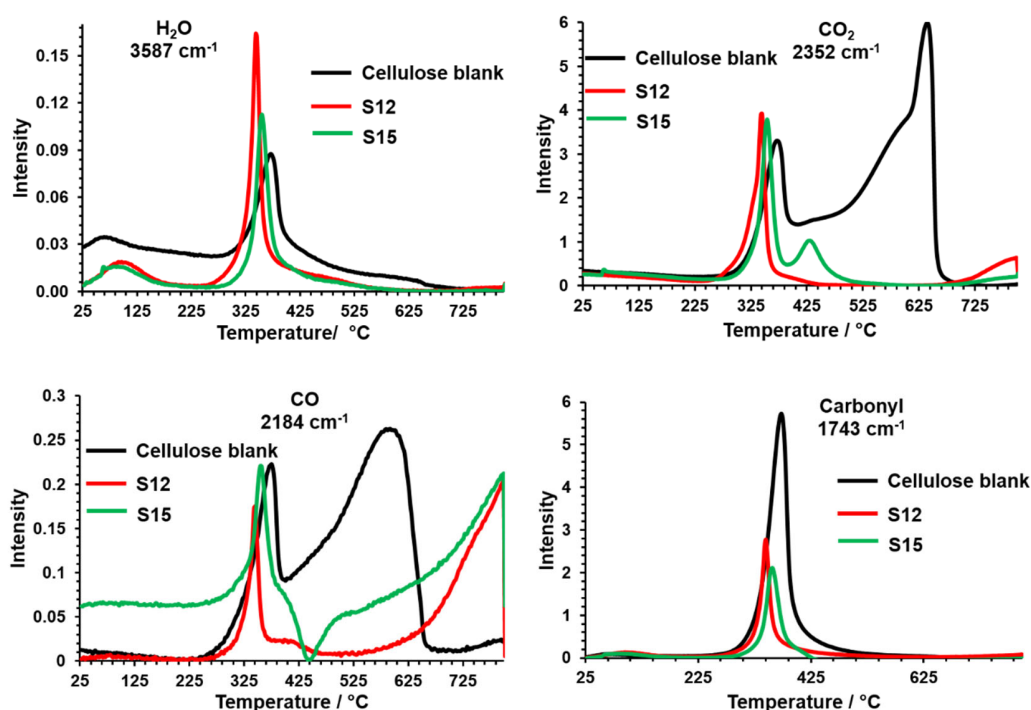

Fig. SI-15. TGA-FTIR spectra of the total pyrolysis products and intensity of characteristic peaks for selected pyrolysis products of cellulose blank and coated fabrics.

It can be seen that the maximum absorbance intensities of all selected pyrolysis products of treated cellulose appear earlier than the blank cellulose. The higher amount of nonflammable gases (such as H$_2$O

and CO_2) formed in the case of treated cellulose could help to cool down the system, dilute the flammable volatiles and restrict the oxygen access to the decomposing polymers (Fig. SI-15). Additionally, the release of flammable volatiles like an alkane, CO, aliphatic ether, and carbonyl compounds are comparably lower for treated cellulose. A reduced amount of flammable species (CO, carbonyl compounds) can lower the fuel response to underlying material and improve the treated cellulose's fire resistance.
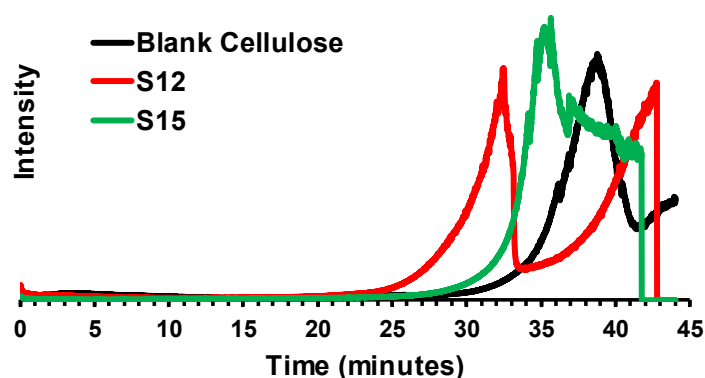
SI-11. DIP-MS data

Fig. SI-16. DIP-MS data of **Cellulose blank**, **PP**, **S12, and S14**: (total ion chromatogram).

From the TGA data (Table SI-5), it can be seen that there is a significant increase in char formation for the treated cellulose under N_2 compared to blank cellulose. However, under oxidative conditions, a considerably lower char was observed. The phosphine oxide macromolecules may likely be active in the gas phase. Therefore, DIP-MS analysis was performed to evaluate the chemistry of volatiles produced during the thermal decomposition of the fabrics (Fig. SI-16). From the total ion chromatogram (TIC) shown in Fig.SI-16, it can be noticed that, during decomposition, the treated cellulose shows the formation of volatile components earlier than the blank cellulose. Blank cellulose decomposes in one step at temperatures above 350 °C, characterized by the presence of a single peak in the TIC (Fig. SI-16). Extracted ion chromatograms of **S12** and **S14** are further shown in Fig. SI-17 and SI-18, respectively. For **S12** and **S15**, species corresponding to PO$^\bullet$ (*m/z* 47), piperazine (*m/z* 86), triethyl phosphine oxide (*m/z* 131) and TPT (*m/z* 333) were detected (Fig.SI-17 and 18).
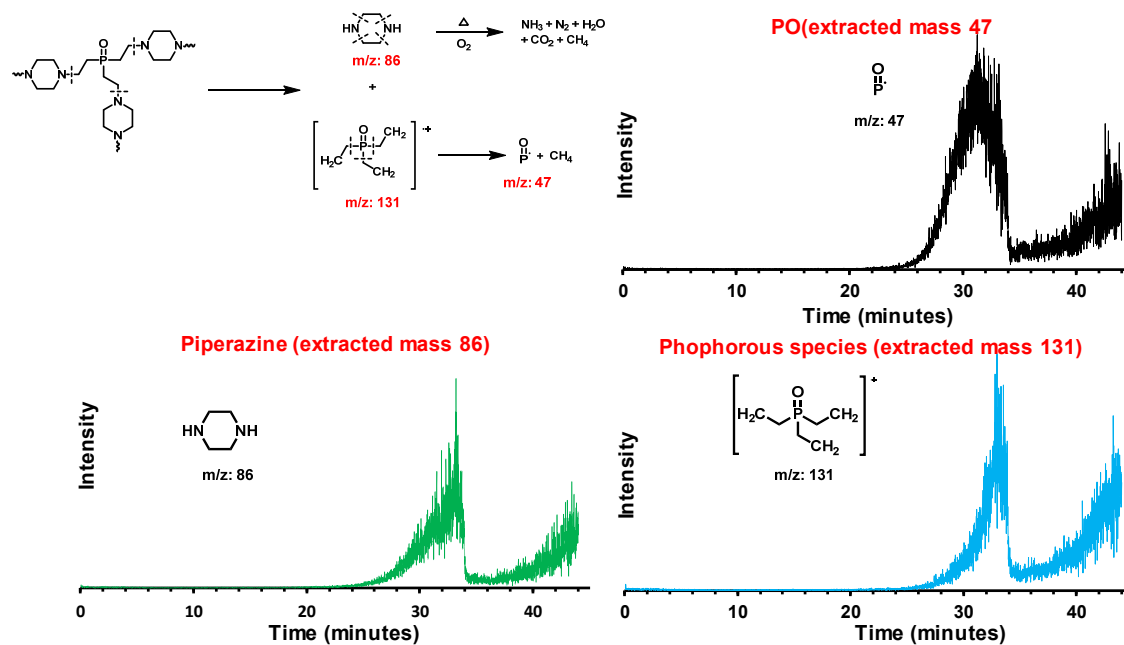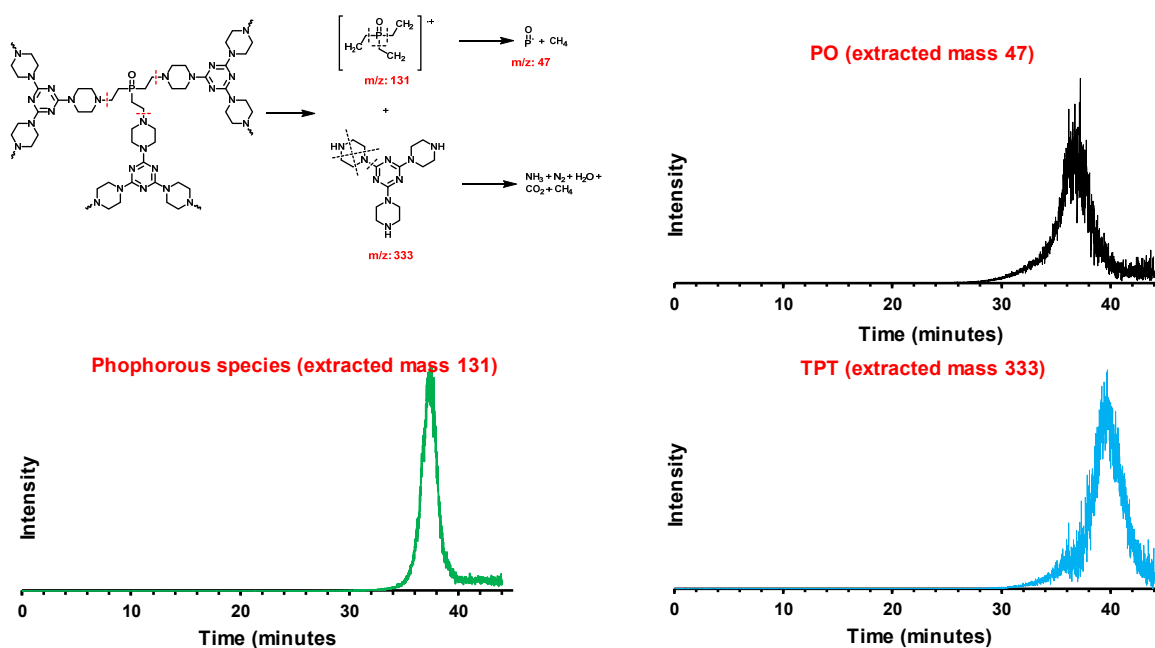
Fig. SI-17. DIP-MS data of **S12**.

Fig. SI-18. DIP-MS data of **S15**.

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SI-12. Fabric properties
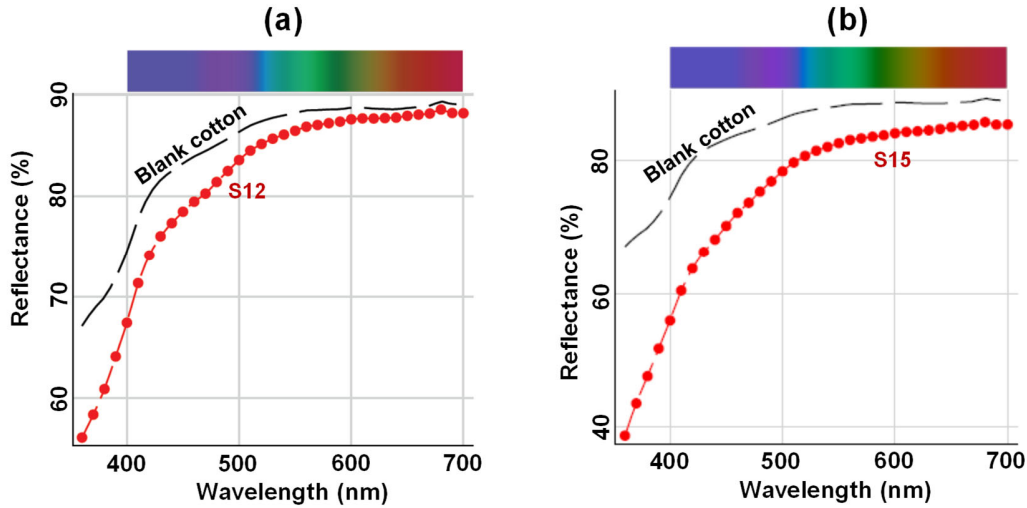
(a) appearance and comfort

Fig. SI-19. Comparison of reflectance between blank cotton fabric with (a) **S12** and (b) **S15**.

(b) Mechanical properties and bending length

Before the strength test, the blank fabric was steamed for 30 minutes at similar conditions used in the FR treatment. Then fabric samples were dried in an oven at 80 °C for 6 h and transferred to a conditioning room under standard atmosphere for 48 h. Similarly, **S12** was also washed, dried, and conditioned before the strength test. To measure the strength, warp and weft yarns (See Fig. SI.20 for warp and weft direction) were carefully unraveled from the fabric and tested separately in a Zwick/Roell Z100 tensile tester keeping the jaw distance of 5 cm (length of the sample tested). Ten samples from each yarn were tested and reported as average with standard deviation.
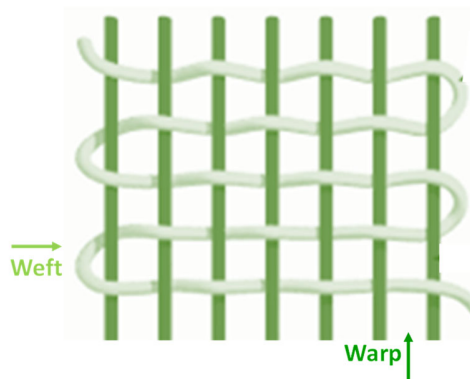

Fig. SI.20. Schematic representation of a plain-woven fabric showing warp and weft directions.

Table SI-7: Change in mechanical and fabric properties of the fabric after treatment.

Sample	Strength (N)		Bending length (cm)	
	Warp	Weft	Warp	Weft
Untreated	6.1 ± 0.16	7.13 ± 0.1	5.4	4.6
S12	6.3 ± 0.18	7.49 ± 0.2	7.3	7.0

To determine the FR treatment's change in flexibility on the fabric, the bending length of the untreated cellulose fabric and S12 was determined as per ASTM 3188 standard. 15×2.5 cm fabric strips were prepared in both warp and weft direction to determine the bending length. Typically, one strip of the sample was transferred to the platform and underneath the template bar. Then both template and sample were slowly pushed forward and the strip of the fabric dropped over the edge of the platform until the tip of the specimen was viewed in the mirror of the bending length tester. The movement was stopped and the length of the fabric strip bending over the edge was noted down as bending length. For each warp and weft direction, 3 samples were prepared and the average bending length is reported in Table SI7.

References

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