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Physiological comfort and flame retardancy of fabrics with electrostatic self-assembled coatings

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ABSTRACT

Simultaneous improvement of flame retardancy and physiological comfort of clothing fabrics has not been studied before. One of the probable reasons for this is the complexity of dynamic processes involved. This work is a preliminary effort to understand various parameters involved in combining these two facets of fabrics. For this purpose, polyester fabrics are coated with branched polyethylenimine (BPEI) and sodium montmorillonite (smectite clay) via electrostatic self-assembly approach. The effect of their concurrent presence in different concentrations (variation of number of bilayers) on thermo-oxidative properties and flame retardancy behavior as well as physiological comfort (in terms of wicking, moisture management, and air permeability) of polyester has been assessed. The obtained results have shown the efficiency of the electrostatic self-assembly process in improving both facets. This work provides the foundation and knowledge for further development of effective coating systems with a multi-functional approach in the textile industry.

KEYWORDS:

Flame retardant textiles; electrostatic self-assembly; moisture management; montmorillonite.

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INTRODUCTION

Flame resistant textiles are important not just for fire fighters, laboratory, police or military personnel, but also in the sports industry (for example, car/motor bike racing). In these applications, a major concern during fire incidents is the associated thermal injury. It is shown that exposure to a radiant heat flux of 4 kW/m^2 , which is quite common in room corner and small-scale fires, causes second-degree burns to bare skin in 30 s [1,2]. However, most serious burns are often related to ignition of clothing than if no clothing had been worn, particularly when the initial fire is small or of short duration [3]. Also, ignition of the clothing results in a higher total body surface area burn, which increases third degree burns. Apart from clothing, other factors that influence the severity of burn injury include intensity of incident heat flux, exposure time, and combustion/pyrolysis products of fabrics [4].

Similar to bulk polymeric materials, textile fibers and fabrics require flame retardants (FR) like halogen- or to some extent phosphorous-based compounds to achieve satisfactory flame resistance. Their usage is often linked to eco-concerns as many of them ultimately yield persistent organic pollutants and generate corrosive/toxic combustion products [5]. Textiles, as they are often washed, flame retardant additives can leach out of the fabric and into the environment increasing the risks associated [6,7]. This is another reason why even some of the non-toxic flame-retardants cannot be used in these applications. For instance, lack of durability of boron-based flame-retardants restricts them to non-aqueous washing [8].

Further, personnel handling work involving risk of fire hazards are expected to put on fire resistant clothing as long as they are on duty. Therefore, a key performance criterion of protective clothing is physiological comfort of the wearer. This will significantly influence the efficiency at which he or she operates [9-13]. Considering that temperature changes in a (hygroscopic) fabric due to water vapor sorption can be as high as $15 \text{ }^\circ\text{C}$ [1], the differences in perceived comfort are expected to be significant. Temperature rise and higher body sweat can cause discomfort and heat stress to the wearer as well as skin damage from chafing. It is well known that in hot and humid conditions, trapped moisture may heat up and lead to diminished performance; while in cold conditions, trapped moisture results in temperature drop and cause hypothermia. In summary, air permeability, surface texture and moisture management of fire resistant fabrics are important. Moisture management indicates the ability of a garment to

transport moisture away from the skin to the garment's outer surface and subsequently to the environment. That is, it involves wettability, spreading ability and imbibition of moisture/sweat on/through the fabric.

Although modification of textile fibers have been reported [14], coating approach at fabric level remain a prominent strategy been explored to achieve flame retardancy in textiles. Different types of coatings have been used to impart flame retardant properties to textiles [15,16]. Some of these are based on intumescent systems [17,18], sol-gel based silica [19,20], polyphosphazenes [21], and phosphoramidate nanoparticles [22]. Very few studies used polymer nanocomposite coatings as flame retardant compositions on fabrics, which is the focus of the current work. For this process, a facile electrostatic self-assembly process is used [23-25]. In a typical process, fabric is alternatively dipped into positively and negatively charged (dilute) aqueous solutions. Electrostatic interactions between the charged layers drive the adsorption and assembly process. For more details on this process, please refer to Li *et al* [26]. Nonetheless, to-date, there are no reports discussing how the modifications to a fabric affect its moisture management and breathability properties. This is in spite of considerable efforts to develop smart fabrics [27]. From an application viewpoint, both these aspects (physiological comfort and flame retardancy) are equally important. Hence, this work is a first attempt in that direction.

EXPERIMENTAL SECTION

Materials

Polyester fabric of mass, 174 g/m², was locally purchased in Singapore and rinsed with deionized (DI) water (18.2 Ωcm^{-1}) prior to use. It has a circular knitting and single jersey structure along with stitch density of 18.1 wales/cm and 24.8 courses/cm. Cloisite® NaMMT clay with formula unit $\text{Na}_{0.65}[\text{Al,Fe}_4\text{Si}_8\text{O}_{20}(\text{OH})_2]$ was supplied by BYK Additives & Instruments, Singapore. NaMMT was added to DI water and mechanically stirred for a minimum of 12 h to produce 1 wt.% of exfoliated anionic deposition suspension. Base pH 6 for NaMMT suspension was adjusted to pH 10 through addition of 1 wt.% of NaOH solution. Cationic deposition solution was prepared by dissolving BPEI (M_w , 25 000 g/mol and M_n , 10,000 g/mol) in deionized water and magnetically stirring the solution for at least 12 h. BPEI was purchased from Sigma-Aldrich, Singapore. Base pH 9 for BPEI solution was adjusted to pH 7 using 0.1

wt.% hydrochloric acid prior to coating on polyester fabric. In another set of experiments, polyester fabric was pre-treated with alkali solution (10 wt.% NaOH). This was carried out by immersing the fabric in alkali solution for ~15 min at room temperature. This was followed by thorough washing to remove excess NaOH (as monitored by pH of DI water used for washing), rinsing and overnight air drying at room temperature.

Electrostatic self-assembly procedure and characterization

Polyester fabrics (neat and NaOH pre-treated) were alternatively immersed in 0.1 wt.% BPEI suspension and 1 wt.% NaMMT suspension. After each immersion step, substrates were washed with deionized water for 1 min to remove poorly adsorbed (and sometimes, excess) nanoparticles. Immersion duration for the first 5 bilayers was kept at 5 min to ensure stability and uniformity of the assembly. For subsequent bilayers, substrates were immersed only for 1 min. Every immersion cycle corresponds to one bilayer of assembly. Washing solutions were replaced after every 5 bilayers, while the suspensions were manually stirred and pH was checked to ensure invariability throughout the deposition process. Subsequently, fabrics were oven dried at 60 °C for 5 h.

Wettability of neat and coated polyester fabrics was characterized using goniometer (Data Physics Contact Angle System, OCA 15 Pro). Vertical wicking tests were carried out on fabric strips of 20 cm x 2.5 cm suspended in distilled water according to American Association of Textile Chemists and Colorists (AATCC) test method 197-2013. Wicking distance of water is taken over a period of 30 min. Moisture management measurements were carried out on Moisture Management Tester M290 according to AATCC test method 195-2009 to assess liquid moisture transportation through fabrics. Further, air permeability measurements of neat and coated fabrics were carried out by using ASIAN Air Permeability Tester and based on ASTM D737-04(2012).

Morphology of fabrics was analyzed using JEOL 5410 scanning electron microscope (SEM) and JEOL 6340 F field emission scanning electron microscope (FESEM). Structural chemistry of fabric surface was also assessed using attenuated total reflectance (ATR) mode of Spectrum GX (Perkin Elmer) Fourier Transform Infrared spectroscopy (FTIR). All spectra were acquired using 32 scans and 4 cm⁻¹ resolution. Pore sizes and their distribution in different fabrics were measured using PMI Capillary Flow Porometer CFP-1500A. Galwick (propene, 1,1,2,3,3,3-

hexafluoro, oxidized and polymerized) with surface tension of 15.9 dynes/cm was used as the wetting agent. All test samples were conditioned at a temperature of 21 ± 1 °C and relative humidity of 65 ± 2 % for 24 hours in accordance to ASTM D1776 / D1776M-15.

Thermo-oxidative stability of coated and uncoated fabric samples was investigated using thermogravimetric analysis (TGA), Q500 (TA Instruments). All samples were pre-dried at 110 °C for 24 hours in a convection oven. Tests were carried out from room temperature to 750 °C employing a heating rate of 20 °C/min. Flammability was evaluated according to Method A in ASTM D7309-11 using pyrolysis combustion flow calorimetry (PCFC) from Fire Testing Technology, UK. Testing conditions were as follows: initial sample quantities ~8-10 mg, combustion chamber temperature was held constant at 900 °C and the load temperature ~125 °C, heating rate 60 °C/min, and finally, nitrogen and oxygen flows were maintained at 80 mL/min and 20 mL/min, respectively.

To understand the durability of coatings, coated fabrics were washed according to in-house protocol (under aggressive conditions). Washing was carried out using Vortex stirrer, Scientific Industries, Model No. G560E Vortex-Genie 2. Two pieces (3 x 3 cm) of each fabric placed in 50 mL centrifuge tube were stirred in 25 mL water or hexane at ~1300 rpm. Five washing cycles were implemented where each washing cycle included 15 min of washing followed by forced drying at 70 °C using convection oven for 30 min. Washed fabrics were further evaluated for changes in surface chemistry and morphology, if any.

RESULTS AND DISCUSSION

Surface characterization

Static contact angle measurements on neat polyester fabric reveal that it is hydrophobic, as expected (Figure 1A, contact angle ~130°). However, after pre-treating polyester fabric with alkali solution, fabric became hydrophilic. As sodium hydroxide treatment involves nucleophilic substitution and the generation of negatively charged hydrophilic surface [28,29], it is rather not surprising to see the hydrophilic nature of the NaOH pre-treated fabric. Due to this hydrophilic nature, rapid spreading/sinking of water droplet on/into fabric is observed (within 0.5 s), thus making it impossible to determine the exact contact angle (see Figure 1B). Even all coated fabrics via electrostatic self-assembly process show a similar behavior.

Figure 1. Representative water contact angle images for (A) neat fabric and (B) NaOH pre-treated and all coated fabrics.

In general, inner surface of fabric (in contact with human body) is expected to be hydrophilic for achieving lower wetting times. This is essential as perspiration produced should be wicked through the fabric to outside and avoid fabric saturation near the skin [30]. This in turn is one of the major factors determining the overall physiological comfort of the wearer. In the current work, irrespective of fabric pre-treatment, based on contact angle results for coated fabrics, it is clear that surface coating with NaMMT can effectively induce hydrophilicity. To further analyze the surface chemical nature of fabrics, FTIR is carried out. Figure 2 shows the FTIR spectra of neat and untreated-coated fabrics along with BPEI and NaMMT as reference. Neat fabric shows strong peaks at 1710 cm^{-1} , 1250 cm^{-1} and $1115\text{--}1095\text{ cm}^{-1}$ (split peaks) corresponding to C=O , $\text{--CH}_2\text{--}$ and C--O--C , respectively. NaMMT displays strong characteristic Si--O peak at 1045 cm^{-1} and small water bending peak at 1640 cm^{-1} , while BPEI shows peaks at 1650 cm^{-1} , 1460 cm^{-1} and $1040\text{--}1380\text{ cm}^{-1}$ pointing to primary N--H , methylene C--H /secondary N--H and aliphatic C--N , respectively [31]. However, BPEI peaks are not evident in any of the coated samples regardless of the number of bilayers. This suggests either overshadowing of its peaks by those of neat fabric in similar bands or presence of lower concentrations on the surface. Additionally, only 20 bilayer fabric displays Si--O peak, which can be associated to its relative concentration in coated fabrics. FTIR spectra of pretreated-coated fabrics show similar pattern (Figure S1, Supplementary Information).

Figure 2. FTIR spectra of neat fabric, BPEI, NaMMT and untreated-coated fabrics (10 and 20 bilayers). BL in the figure indicates bilayers.

Further, SEM micrographs of neat fabric (Figure 3) and BPEI/NaMMT coated fabrics (Figure 4) at different magnifications show the effect of self-assembly process on surface morphology of fabrics. Uniform coating is seen on fiber surface. Increasing deposition layers from 10 to 20 resulted in thicker coatings and obvious bridging between fibers. This in fact seems to bind the fibers in a yarn more closely than neat fabric, and in turn significantly affecting inter-yarn porosity (Figure 5).

Figure 3. SEM micrographs of neat fabric at different magnifications.

Figure 4. SEM micrographs of untreated-coated fabrics (A, C) and NaOH pretreated-coated fabrics (B, D). BL points to bilayers and P for pre-treatment.

Figure 5. Pore size distribution for neat fabric and coated fabrics. An obvious increase in inter-yarn porosity for coated fabrics (in the range of 80 to 200 μm) is evident (inset).

Physiological properties

Vertical wicking: Figure 6 shows the measured wicking distance after 30 min for course- and wales- wise directions for all fabrics. Neat fabric do not show vertical wicking ability, as expected, because of its hydrophobic nature that prevents wetting, thereby wicking. All coated fabrics show superior wicking and capability improves with number of bilayers. Interestingly, NaOH pretreated-coated fabrics display significantly higher wicking distances than their untreated-coated counterparts. There might be two possible reasons for this behavior:

- Higher surface charge significantly improves the distribution of first monolayer of BPEI. As a consequence, higher surface uniformity will be developed creating a more uniform path for water-front migration.
- Contribution of hydrophilic nature of NaOH pretreated fabric in vertical wicking.

Exact involvement of these facets are currently further deliberated with Quartz Crystal Microbalance (QCM) measurements and is out of scope of the present manuscript. Comparing

vertical wicking results for NaOH pretreated-coated fabrics with those previously reported by Sampath *et al* [32], the advantages of electrostatic self-assembly process are quite evident. In their study, fabrics were pretreated with a wetting agent (blend of ethoxylated alcohol) and finished with combination of amino silicone polyether copolymer and a hydrophilic polymer. They reported vertical wicking distances of 14.7 cm (course-wise) and 16.2 cm (wales-wise) in 30 min compared to 18.3 cm (course-wise) and 19.2 cm (wales-wise) for 20 bilayer fabric in the current study.

Figure 6. Wicking distance for all fabrics after 30 minutes. 10 BL (P) and 20 BL (P) indicate the pre-treatment of fabric before electrostatic self-assembly process. BL and P are defined earlier.

Moisture management: Amongst many properties that a typical moisture management tester provides, some useful parameters for current analysis are chosen and the values are listed in Table 1 for neat and coated fabrics. These parameters include wetting time and maximum wetted radius for the top surface, one-way transport capacity (OWTC) across the thickness of fabric and overall moisture management capacity (OMMC). Even here, all coated fabrics performs better improving OWTC and OMMC as compared to neat fabric. Obviously, for neat fabric, its hydrophobic nature is a major disadvantage. Reduction in water transport across the fabric thickness for 20 bilayer fabric is hypothesized to be associated with torturous path presented by higher number of clay layers in coating. This indicates that after an optimal number of bilayers

(in this case, 10), subsequent addition of layers negatively affect water transport. Apart from surface characteristics, changes in filament shape and gradient effect are other approaches that are commonly used in sportswear to expedite water intake of outer layer and improve one-way transport capacity. Manshabia *et al* [33] investigated the effect of using a combination of filament shapes (flat, tetra-channel and circular) for inner and outer layers of polyester fabrics on moisture transport. Multichannel filaments were found to be effective as they had higher specific surface area, increasing the capillary pressure and wicking ability. Even with circular shaped filaments (shape of the filament in the current study as well), they reported superior OWTC value of 106.2% as compared to 41.2% obtained in the current study with 10 bilayer (pre-treated) fabric. Nonetheless, the latter shows better values in other moisture management parameters as summarized in Table 2.

In another study, Troynikov *et al* [34] investigated the influence of blends of various materials in knitted fabrics on moisture management. The fabric used in their study was intended for base layer of active sportswear, which can constitute a datum to gauge the efficiency of NaMMT/BPEI coating used in current study. Their results and comparison with 10 bilayer pre-treated fabric is also summarized in Table 2. Although they reported much superior OWTC for their base fabric, 10 bilayer fabric from current work displays better results for other moisture management parameters, in particular, top wetting time and maximum wetted radius. This indicates the potential of fire retardant coatings in achieving superior moisture management properties.

Table 1. Moisture management results of all fabrics.

Sample	Top wetting time (sec)	Top max. wetted radius (mm)	OWTC* (%)	OMMC
Neat fabric	120 ± 0.0	5.0 ± 0.0	- 1090 ± 10.3	0.0 ± 0.0
10 BL	15.1 ± 6.3	11.0 ± 4.8	199.0 ± 143 [#]	0.43 ± 0.16
20 BL	16.9 ± 2.3	5.0 ± 0.0	- 366.5 ± 604 [#]	0.15 ± 0.20
10 BL (P)	4.6 ± 0.9	23.3 ± 2.9	41.2 ± 5.8	0.50 ± 0.02
20 BL (P)	3.9 ± 2.0	25.0 ± 5.0	- 11.5 ± 0.6	0.39 ± 0.08

* Moisture management tester calculates OWTC based on the cumulative differences in moisture content between the bottom and top layers with respect to time. The water droplet travels from

the top to the bottom layer. The provided values from the equipment are used directly without any further modification.

[#] For 10 BL & 20 BL fabrics, severe inconsistency in OWTC resulted in rather large standard deviation values. This is attributed to lack of pre-treatment that resulted in lower surface uniformity, as discussed previously.

Table 2. Comparison between 10 BL (P) and other reported fabrics for moisture management.

Study	Top wetting time (sec)	Top max. wetted radius (mm)	OWTC (%)	OMMC
Current work, 10 BL (P)	4.6 ± 0.9	23.3 ± 2.9	41.2 ± 5.8	0.50 ± 0.02
Ref [31]	13.5	16	106.2	0.39
Ref [32]	5.6	14	328.5	0.64

Air permeability: Air permeability values for all fabrics are given in Figure 7. Drop in air permeability is seen with increase in number of bilayers. This is attributed to the effect of coating (binding the fibers together in a yarn) on the inter-fiber and intra-yarn porosity (as visualized in Figures 4 and 5). NaOH pretreated-coated fabrics displayed lowest air permeability consistent with SEM micrographs. Additionally, non-uniformly distributed lumps of clay deposited on yarns in untreated-coated fabrics might as well influence permeability results. Thus, it is argued that air permeability can be altered based on coating concentration (number of bilayers) and coating uniformity (fabric pre-treatment).

Figure 7. Air permeability values and corresponding percentage reductions (shown in brackets) are reported for all fabrics.

Thermal and Flammability properties

Thermo-oxidation stability of neat polyester and coated fabrics are evaluated using TGA and the data (Figure 8A) reveals the positive influence of coating. Table 3 also summarizes values of onset temperature at 10 % mass loss ($T_{10\%}$), peak temperature at first and second degradation steps (T_{P1} and T_{P2} , respectively) and residue mass at 700 °C as obtained from TGA under oxidative conditions. Although marginal, the drop in $T_{10\%}$ for coated fabric as compared to neat fabric is due to decomposition of adsorbed BPEI. Clay primarily acts like a protective ceramic shell over polyester fibers and its influence is seen from T_{P1} and T_{P2} , where T_{P1} corresponds to decomposition of base polyester fabric and T_{P2} oxidation of char as produced during thermo-oxidation. 10 bilayer fabric displays 16 °C increase in T_{P1} and 44 °C increase in T_{P2} compared to neat fabric. This is a confirmation of the barrier effect argument. Lack of any further improvement in $T_{10\%}$ or T_P temperature for 20 bilayer fabric suggests that 10 bilayer fabric already has optimal barrier effect with only 2.4 wt.% of add-on weight (considering maximum of 0.1 wt.% for clay dehydroxylation) as observed from residue at 700 °C. Further, it seems that thermo-oxidative decomposition is sparsely affected by enhanced coating uniformity (for

pretreated-coated fabrics) as observed by comparing TGA data for untreated-coated fabric (Table 3) and pre-treated coated fabric (Table S1).

Figure 8. Thermo-oxidative degradation of (A) neat and coated fabrics; and (B) specific heat release rate as observed from PCFC. BL as before indicates bilayer.

Table 3. TGA data obtained under oxidative conditions for neat fabric and untreated-coated fabrics.

Sample	T _{10%} (°C)	T _{P1} (°C)	T _{P2} (°C)	% residue
Neat fabric	402	432	553	0.0
10 bilayer fabric	399	447	597	2.2
20 bilayer fabric	399	446	578	3.4

Flammability properties of fabrics in terms of peak specific heat release rate (pHRR) and its corresponding temperature, total heat release (THR) and % char are summarized in Table 4. In Figure 8B, heat release rate curves for different fabrics are also shown. Figure 8B and Table 4 clearly point to the significant advantage of coated fabrics. For 10 bilayer fabric, pHRR and THR are reduced by 37% and 2%, respectively. However, only marginal improvements in these values are seen by increasing the number of bilayers to 20. This again suggests saturation of barrier effect on flammability properties. This is very similar to that observed even with bulk polymer/clay nanocomposites [5,35-37]. A huge reduction of 40-70% in the peak value of HRR is generally observed for exfoliated polymer/clay nanocomposites compared to their corresponding neat polymers. Despite this, the total heat release is generally the same for neat polymer and its nanocomposite; that is, nanocomposites burn evolving the same amount of heat but at a much lower rate. From a macroscopic viewpoint, even in the presence of nanoparticles, the combustion cycle is not interrupted but only delayed. Besides, once a critical composition was reached (typically around 7-10 wt.% of clay platelets), it is found that among the nanocomposites, differences in the reduction of HRR are not significant [36].

Temperature at pHRR is another factor that should be considered as this is a direct indicator of TBSA burns. 10 bilayer fabric shows 5 °C improvement compared to a 6 °C drop with 20 bilayer fabric. It should be noted that increasing the bilayers increases the concentration of BPEI, which has poor thermal stability, and will negatively affect the thermal and flammability properties. Also, alkali pre-treatment did not result in any further significant change in thermo-oxidative or combustion properties. Results for alkali pre-treated polyester fabrics are reported in Supplementary Information (Tables S1 and S2). Based on these results, it is argued that 10 bilayers can create enough tortuosity in free path length for gaseous decomposition products

(from fabric base material and BPEI) that coating uniformity becomes a minor factor and barrier effect dominates. Coating uniformity is also important and might play a dominant role when there are less than optimum number of bilayers. However, we will not be focusing on this issue in the current work as the main emphasis is to elaborate if it is possible to simultaneously improve both physiological and flammability properties. To sum up, 10 bilayer fabric shows optimum physiological and flammability properties. Further, taking into consideration the positive effect of fabric pre-treatment on physiological properties and with its neutral effect on flammability properties, it is easier to suggest the usage of pre-treatment on fabrics.

Table 4. PCFC data for neat fabric and untreated-coated fabrics.

Sample	pHRR (W/g)	Relative reduction in pHRR (%)	Peak temperature (°C)	THR (kJ/g)	Char (%)
Neat fabric	629 ± 32	-	457 ± 1	25.3 ± 0.79	12.1 ± 0.6
10 bilayer fabric	393 ± 10	37	462 ± 1	24.6 ± 0.35	16.0 ± 0.3
20 bilayer fabric	368 ± 15	41	451 ± 3	23.9 ± 0.34	16.7 ± 0.9

Wash fastness of coatings

Preliminary analysis of the durability of coatings (wash fastness) is carried out in terms of interaction of coatings with base fabric. Representative SEM micrographs of 10 bilayer fabric after subjecting to 5 washing cycles with DI water and hexane along with their respective FTIR spectra and static contact angle information are shown in Figure 9. Hexane is used to simulate a dry-cleaning condition where the cleaning agent typically used is tetrachloroethylene (perchloroethylene), which is non-polar and non-aqueous. Comparing Figure 9 with Figures 2 and 4A-B, clearly, the persistence of coating on fabric is obvious (even without the use of a binder) and the morphology remains unchanged irrespective of the washing liquid. Moreover, static contact angle information of water washed fabrics show increase in spreading time and sinking of water droplet (>60 sec), whereas hexane washed fabrics still displays rapid spreading and sinking of water droplet (within 4 s). This suggests persistent hydrophilic nature for hexane washed fabrics compared to water washed fabrics. However, irrespective of this minor difference the data points to the employability of this facile layer-by-layer electrostatic process even at an

industrial scale. Due to similarity in data, results for other fabrics are shown in Supporting Information (Figures S2-S7).

Figure 9. SEM images of 10 BL (P) fabric washed for 5 cycles in (A) water and (B) hexane. Insets provides FTIR spectra and instantaneous images of water sinking (steady sinking of water droplet limited contact angle measurement).

SUMMARY

This is the first preliminary study to understand the effect of electrostatic self-assembled coating on both flame retardancy and physiological comfort for clothing fabrics. NaOH pre-treatment improved the uniformity of coating without increasing the uptake of first monolayer, thus forming the basis for subsequent electro-static deposition. Presence of hydrophilic NaMMT significantly improved the wetting and wicking characteristics.

Increase in thermo-oxidative decomposition temperatures for coated fabrics established the barrier effect of clay layers. Significant improvements in flammability properties like reduction in HRR and temperature at pHRR confirmed the barrier effect imparted by clay layers. Similar to physiological comfort, thermal decomposition is influenced by number of bilayers. 10 bilayer fabric showed optimum physiological and flammability properties. Finally, preliminary wash fastness data indicated the binding of coating to base fabric.

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Physiological comfort and flame retardancy of fabrics with electrostatic self-assembled coatings

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Supplementary Information:

Figure S1. FTIR spectra taken on the surface of neat fabric and NaOH pretreated-coated fabrics. BL in the figure indicates bilayers.

Table S1. TGA data as obtained under oxidative conditions for pretreated-coated fabrics.

Sample	T _{10%} (°C)	T _{P1} (°C)	T _{P2} (°C)	% Residue
Neat fabric	402	432	553	0.0
10 BL (P)	401	447	604	1.8
20 BL (P)	397	446	571	3.5

Table S2. PCFC data for neat and pretreated-coated fabrics.

Sample	pHRR (W/g)	Reduction (%)	Peak Temp. (°C)	THR (kJ/g)	Char (%)
Neat fabric	629 ± 32	-	457 ± 1	25.3 ± 0.79	12.1 ± 0.6
10 BL (P)	395 ± 4	37	462 ± 1	24.8 ± 0.5	15.8 ± 0.2
20 BL (P)	366 ± 11	41	450 ± 6	23.2 ± 0.4	16.3 ± 0.7

Figure S2. SEM images of water washed fabrics, 3 wash cycles, for 10 and 20 bilayer coated fabrics.

Figure S3. SEM images of water washed fabrics, 5 wash cycles, for 10 and 20 bilayer coated fabrics.

Figure S4. SEM images of hexane washed fabrics, 5 wash cycles, for 10 and 20 bilayer coated fabrics.

Figure S5. FTIR Spectra for water washed fabrics, 3 wash cycles, for 10 and 20 bilayer coated fabrics.

Figure S6. FTIR Spectra for water washed fabrics, 5 wash cycles, for 10 and 20 bilayer coated fabrics.

Figure S7. FTIR Spectra for hexane washed fabrics, 5 wash cycles, for 10 and 20 bilayer coated fabrics.