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Smoldering and Flame Resistant Textiles *via* Conformal Barrier Formation

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Abstract

A durable and flexible silicone-based backcoating (halogen free) is applied to the backside of an otherwise smoldering-prone and flammable fabric. When exposed to fire, cyclic siloxanes

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Supporting Information

Supporting Information is available online from Wiley InterScience or from the author.

(produced by thermal decomposition of the backcoating) diffuse through the fabric in the gas phase. The following oxidation of the cyclic siloxanes forms a highly conformal and thermally stable coating that fully embeds all individual fibers and shields them from heat and oxidation. As a result, the combustion of the fabric is prevented. This is a novel fire retardant mechanism that discloses a powerful approach towards textiles and multifunctional flexible materials with combined smoldering/flaming ignition resistance and fire-barrier properties.

Graphical Abstract

Keywords

textile; backcoating; smoldering; fire; flame-retardant

Worldwide, the costs from fire losses are estimated at approximately 1% of the global gross domestic product.^[1] In the U.S., home fires are the most frequent and deadly type of fire (84 % of civilian deaths occurred in home building fires).^[2] Residential upholstered furniture (RUF) fires are the single largest cause of civilian deaths in home fires (about 24%) with a yearly estimated average of 610 deaths, 8900 fires, 1120 injuries and \$566 million in direct damage.^[3] The filling material (typically a polyurethane foam) is the major fuel source in RUF. The ignition of the filling material is mediated by the upholstery fabric (directly exposed to the ignition source) and can occur *via* an open-flame source (*e.g.*, candle-like-flames) or a smoldering source (*e.g.*, cigarettes). The fire hazard of RUF can be mitigated by using upholstery fabrics that meet the three following requirements: (1) inhibit smoldering ignition, (2) inhibit flaming ignition and (3) act as fire barriers (*i.e.*, prevent flame-breakthrough and decrease the heat release rate generated by the filling material). This is a problematic task because carbon-based polymers (used for the large majority of textiles) show a trade-off between smoldering and flammability: the more carbon stays trapped as char, the lower the flammability (less fuel available for the flame in the gas phase) and the higher the smoldering propensity (more fuel available for heterogeneous oxidation in condensed phase).^[4] Addressing this challenge would not only significantly decrease the number of fire deaths worldwide, but also provide a technical solution for other textile

applications (e.g., draping, bedding, carpeting, protective clothing, flexible barrier materials).

There are several strategies implemented to make textiles flame-retardant (inherently flame resistant fibers, flame-retardants, surface modifications, back-coatings and emerging nanotechnologies such as layer-by-layer)^[5–7]. However, flame-retardant textiles often have limited durability (e.g., do not pass the U.K. soak test at 40 °C for 30 min),^[9] and do not generally provide concomitant resistance to smoldering, flaming (see aforementioned trade-off) and flame-breakthrough. Additionally, textiles need to comply with subjective requirements that are customer dependent (color, general appearance, material selection, “hand and feel”, etc.) and are not generally met by inherently flame resistant fibers.

Backcoating (BC) is a technique by which the flame-retardant is mixed in a binder and uniformly applied to the back surface of an otherwise flammable fabric. The most common BC solution for imparting flame retardancy to upholstery fabrics is the combination of halogen-based flame retardants in vinyl-copolymeric or acrylate-based systems.^[5] However, environmental, health and safety concerns for halogenated flame retardants have caused the market and the community to look for alternative approaches to improve fire safety.^[7, 8] Fabric manufacturers need to consider these additional aspects and balance factors of ecotoxicity, durability, performance, aesthetics, comfort, process adaptability and cost in the selection of a flame-retardant solution. Horrocks *et al.* demonstrated that it is possible to meet the U.K. match ignition resistance requirement for RUF with halogen-free BC formulations by using phosphorous-based flame-retardants.^[9, 10] However, the durability of these formulations was limited by the hydrolytic stability and water solubility of the flame retardants. Moreover, the smoldering resistance and fire barrier properties of the backcoated fabrics in a forced combustion scenario were not investigated.

In the present communication, a halogen-free BC is demonstrated using vinyl-modified aluminum-hydroxide (65 % by mass) and vinyl-modified nanosilica (13 % by mass) as reactive fillers, and a silicone elastomer (crosslinked by Pt-catalyzed hydrosilation) as binder. Such a BC is durable (no significant mass loss is measured in the aforementioned U.K. soak test), has a benign toxicological profile (silicone elastomers are largely used for medical device applications)^[11], and is durable, thanks to the intrinsic properties of the silicon elastomer (excellent chemical, UV, temperature resistance and adhesion strength)^[12] and the reactive fillers (negligible water solubility and leaching). The BC is applied by knife coating to the back side of a cotton fabric. The color or general appearance of the fabric’s face is not affected (see Figure S1 and S2, Supporting Information). After coating, the fabric shows a negligible increase in thickness but almost a 2-fold increase in area density due to the high content of high-density fillers (aluminum hydroxide and silica represent approximately 78% of the mass of the coating) and the capability of the silicon binder to penetrate and fill the gaps between the fibers (see Table 1).

Aluminum-hydroxide is replaced by vinyl-modified aluminum-hydroxide in the BC formulation to reduce flexural rigidity, thereby improving drape and comfort properties of the backcoated fabric (BCF). The flexural rigidity is approximately 82 μJ for the pristine fabric (Fabric), 751 μJ for the BCF with standard aluminum-hydroxide (ATH-Fabric) and

291 μJ for the BCF with vinyl-modified aluminum-hydroxide (vATH-Fabric) (see Table 1). As a benchmark, the flexural rigidity measured for a commercial backcoated fire-barrier for upholstered furniture (knitted fabric made from glass core spun yarn with cotton fibers sheath; area density of $284 \text{ g} \cdot \text{m}^{-2} \pm 5 \text{ g} \cdot \text{m}^{-2}$, thickness of $1.5 \text{ mm} \pm 0.1 \text{ mm}$, negligible air permeability) is about $840 \mu\text{J}$. This indicates that both ATH-Fabric and vATH-Fabric retain sufficient flexibility for their intended use. Moreover, vATH-Fabric shows a reduction in stiffness by a factor of about 2.6 as compared to ATH-Fabric. The vinyl based surface modifier in vATH-Fabric can likely reduce the stiffness of the BC by disrupting the hydrogen bonding at the interface between aluminum hydroxide and the silicone binder,^[13] and by introducing an excess vinyl groups (not consumed by hydrosilylation) that are available to crosslink at fire temperatures.^[14] Noticeably, such increase in flexibility is achieved without affecting the fire performance (see Table S1, Supplemental Information). For the remainder of this study, only BCF vATH-Fabric is further investigated due to its superior flexibility.

The smoldering ignition resistance of BCF and pristine fabric were investigated according to ASTM E1353-08a with a mockup assembly of fabric and foam. The pristine cotton fabric mockup is extremely smolder prone and failed the test, *i.e.*, the specimen continued to smolder after the 45-minute test duration (see Figure 1a). The BCF did not smolder and completely suppressed charring in the foam substrate. Remarkably, the BC also extinguished smoldering of the cigarette ignition source in less than 30 s, by limiting the oxygen supply (air diffusion and convection through the fabric is prevented and water vapor is released *via* endothermic decomposition of aluminum hydroxide) (see Figure 1b).^[15]

The flaming ignition resistance was assessed by a simulated match-flame ignition test on a fabric/foam mockup that conveniently indicates the ignition behavior of RUF when tested in accordance with source 1 ignition condition of BS5852.^[9,16] The mockup with pristine fabric (see Figure 2a) showed ignition after the first application of the ignition flame, followed by rapid flame propagation, flame breakthrough into the foam and flaming drips. The mockup with BCF (see Figure 2b) easily passed the test (no ignition after the application of the ignition flame for 20 s) and ignition was not observed even after multiple applications of the ignition flame (3 flame applications of 20 s each, not a test requirement). Noteworthy, halogen based BCs or flame retardant fabrics, containing halogens and/or formaldehyde, are typically required to pass this test and meet durability requirements. ^[5, 7, 10]

The fire barrier properties were investigated by cone calorimetry (ASTM E 1354) on a fabric/foam mockup in a forced combustion scenario with an external incident heat flux of 35 kW/m^2 . In the pristine fabric/foam mockup, the fabric ignited after $\sim 20 \text{ s}$ and formed a char layer that temporarily shielded the underlying foam (Figure 3a). After $\sim 180 \text{ s}$, flaming stopped and smoldering started oxidizing and disrupting the char barrier. At this stage, the rate of pyrolysis of the foam gradually increased with the extent of disruption of the charred fabric.

After $\sim 240 \text{ s}$, smoldering char piloted the ignition of the pyrolyzing foam (now largely exposed to the cone heater) and transition to flaming occurred. This observation clearly

shows the deleterious effects of sustained smoldering on subsequent flammability. In the BCF/foam mockup, the BCF ignited after ~ 30 s and flame-out occurred after ~ 90 s (Figure 3b). During the combustion process, the BCF first turned black after ~ 60 s due to charring, and then gradually turned to a tan/white color due to the formation of a thermally stable coating that prevented fabric smoldering and foam ignition. Figure 3c compares the dynamic heat release rates (HRR) for the two mockups. For the pristine fabric/foam mockup, the first peak in HRR is attributed to fabric combustion, the second broad and smaller peak to fabric smoldering, and the third one to foam combustion. For the BCF/foam mockup, there is only a single peak due to the partial combustion of the fabric. Table 2 summarizes the cone calorimetry data in terms of ignition time, peak of heat release rate (PHRR), total heat release rate (THR), and percentage foam residue. The BC increases ignition time by 55 % and reduces PHRR by ~48 %, THR by 85 % and mass loss of the foam (main fuel source in RUF) by ~94 %.

After cone calorimetry, the thermally stable residue generated on the face-side of the BCF was analyzed by energy-dispersive X-ray spectroscopy (EDX) (Figure 3d). The data show atomic concentrations of about 5 % C, 61 % O and 32 % Si, which are consistent with the formation of silica (possibly together with silicon oxycarbide)^[17] and the white color of the residue shown in Figure 3b at 90s. Silica is generated by the oxidation of the cyclic siloxanes, which are a main product of decomposition of silicones.^[18] EDX data for the face side of the BCF before cone calorimetry indicate atomic concentrations of 84 % C, 16 % O and 0 % Si. Thus, the Si atomic concentration increases from 0 % up to 32 % during combustion. Scanning electron microscopy (SEM) and optical stereo-microscopy (see Figure 3d and 3f) reveal the morphology of the residues. The yarn shape and structure of the fabric are well preserved during combustion and each single fiber is encapsulated and protected by a conformal coating (*i.e.*, a coating that ‘conforms’ to the surface of the substrate). This is clearly indicated by the individual loose fibers that protrude from the yarns and show an increase in diameter from about 10–20 μm in the pristine fabric (Figure 3e) to 30–60 μm in the BCF after fire exposure (Figure 3f).

It has been reported that silica can be generated during the thermal degradation of silicones in the gas plume and fall back onto the fabric or can be directly generated on the silicone surface and transported by the convective flow.^[18–19] However, these mechanisms by themselves do not justify the observed morphology of the residue, *i.e.*, the formation of a highly conformal coating and the lack of silica accumulation around the sample. We postulate three possible mechanisms for the formation of the conformal coating during combustion: (a) liquefaction of the silicone backcoating followed by transport to the fabric face through wicking (promoted by the low surface energy of siloxane)^[19b] and consequent *in-situ* (*i.e.*, on the fiber surface) oxidation to silica; (b) adsorption on the fabric surface of volatile cyclic siloxanes, generated by the decomposition of the silicone backcoating, and consequent *in-situ* oxidation, and; (c) *ex-situ* oxidation of the volatile cyclic siloxanes followed by transport and adhesion to the fiber surface. For the backcoating formulation used here, there was no macroscopic sign of liquefaction (*e.g.*, dripping or shape variation of the sample throughout testing) (see Figure S3, Supporting Information). Indeed, about 90 % of cyclic siloxanes (trimer, tetramer, pentamer and hexamer) will vaporize rather than liquefy as soon as they are generated, typically at temperature above 300 °C.^[19c] In addition,

there is experimental evidence that silica accumulates on the cellulose fabric even when fabric wicking is not possible (e.g., without direct contact between the fabric and the silicone) (see Figure S4, Supporting Information). These observations suggest that mechanism (a) is not very likely to occur, nevertheless it cannot be completely excluded based on the limited data available. Irrespectively of the specific mechanism, mass transfer from the back to the face side of the fabric enables a novel flame retardant mechanism by generating a thermally stable and highly conformal coating that prevent the combustion of the fibers. Hydrogen-bonding interactions at the fiber interface promote the growth of the conformal coating by: (1) stabilizing the siloxanes through adsorption (both in gas phase and liquid phase) and promoting *in-situ* oxidation, or; (2) promoting the adhesion of silica generated *ex-situ*.^[19d,19e] In the fabric used here, high-surface-area cotton char generates a substrate with hydrogen-bonding capability, eventually enhanced by oxidation. Once an initial silica layer is formed, more silica will accumulate on the surface due to strong silica-siloxane or silica-silica hydrogen bonding. Noticeably, a proper engineering of the fabric surface to increase the hydrogen-bonding capability or surface area would likely promote the growth of the conformal barrier.

In conclusion, a durable halogen-free BC formulation with a benign toxicological profile has been successfully developed. The flexibility of BC (critical for drape, formability and comfort of the BCF) is enhanced by vinylsilane modification of aluminum hydroxide without increasing flammability (as shown by microscale combustion calorimetry). This BC provides the fabric with an unusual combination of flaming/smoldering ignition resistance and barrier properties without affecting color or general appearance of the fabric's face. The requirements of both the simulated match-flame ignition and smoldering tests for upholstered furnishings fabrics are easily met. Cone calorimetry shows that the BCF has excellent fire barrier properties. In foam/fabric mockups, BCF reduces the peak heat release by ~48 % and the total heat release by ~85 % as compared to the pristine fabric. When exposed to an intense heat source, water vapor is released and mass transfer phenomena enable the formation of a thermally stable conformal coating on the face-side of the fabric. As a result, flame penetration and ignition of the flammable foam substrate are prevented. This novel flame retardant technology, developed and discussed here for reducing the fire hazard of upholstery furniture (single largest cause of fire deaths in U.S.), can be easily extended to textiles for different applications like protective clothing, draping, bedding, carpeting, transportation and other multifunctional barrier materials (paper, leather, etc.) requiring flexible structures. Furthermore, the mass transfer mechanisms and interface interactions that are specifically exploited here for flame retardant applications, might have other important applications like, for example, in silica based template fabrication, coating for scratch resistant materials and silica reinforced composites.

Experimental Section

The uncertainties reported in this paper represent one standard deviation.

Chemicals, backcoating preparation and characterization

Two-part component (base and curing agent) silicone Sylgard 184 (Dow Corning). Aluminum-hydroxide (Apyral 40CD, Nabaltec) and vinyl-silane modified aluminum-hydroxide (Apyral 40VS1, Nabaltec). 20.43g of aluminum-hydroxide is dispersed into 10g Sylgard 184 base in a bladeless mixer (SpeedMixer, Flack Tek Inc) for 5 min. Thereafter, 1g of curing agent is added and mixed for 1 min. After application of the BC on the fabric by knife coating, curing was completed at 80°C in 5h. Zeiss Ultra 60 was used for field emission scanning electron microscope (at <5 kV accelerating voltage) and EDX spectroscopy (at <10 kV accelerating voltage) on samples sputter coated with Au/Pd (60 %/40 % by mass). EDX typical uncertainty for atom % was 0.5 %. Leica MZ16 stereomicroscope was used for optical imaging. FTIR spectra were collected in attenuated total reflectance mode using a Tensor 27 Bruker spectrophotometer and averaged over 128 scans at a resolution of 4 cm⁻¹. The flexural rigidity of the fabrics was measured by Peirce' cantilever test.^[20] The wash resistance test was performed according to U.K. SI1324.^[9]

Smoldering and Flaming Resistance

Microscale combustion calorimetry was run according to ASTM D7309 method A on 3 mg samples with an E factor of 15.21 kJ/g O₂ and a heating rate of 1 °C s⁻¹ up to 1000 °C. TB-117-2013 compliant foam was used in all composite tests.^[21] For cone calorimetry (ASTM E 1354), the foam (105 mm × 105 mm × 51 mm) and the fabric (105 mm × 105 mm) were held together with a standard retainer frame. For ASTM E1353-08a, the smoldering ignition source was a NIST SRM 1196 cigarette. The simulated match-flame ignition test, designed to simulate the UK fire and furnishing regulatory requirements as determined by BS5852: Source 1,^[9] has been described elsewhere.^[16]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Image of the whole mockup assembly at the end of the smoldering ignition test for the
pristine fabric mockup (a) and for the BCF mockup (b).

Figure 2. Images of foam/pristine fabric mockup (a) and foam/BCF fabric (vATH-Fabric) mockup (b) during the flame ignition test. Insets indicate the time t after removal of the ignition flame when the images were recorded and the flame impingement duration i of the ignition flame.

Figure 3.

Images of the pristine fabric/foam mockup (a) and the BCF/foam mockup (b) during cone calorimetry. Heat release rate as a function of time (c). SEM/EDX image of BCF residue (top face) after cone calorimetry (d). Optical microscopy of the BCF face before (e) and after (f) cone calorimetry.

Table 1

Flexural rigidity, thickness and area density of the fabrics.

Sample	Backcoating formulation	Area density [g m ⁻²]	Thickness [mm] ^[a]	Flexural rigidity [μJ]
Pristine fabric	NA (no backcoating)	448 ± 3	1 ± 0.2	82 ± 6
ATH-Fabric	aluminum hydroxide	900 ± 25	1 ± 0.1	751 ± 26
vATH-Fabric	vinylsilane-modified aluminum hydroxide	879 ± 10	1 ± 0.1	291 ± 52

^[a]
(data measured by cross sectional imaging)

Table 2

Cone calorimetry data for the fabric/foam mockups.

Sample	Ignition time [s]	PHRR [kW m ⁻²]	THR [MJ m ⁻²]	Foam Residue [%]
Fabric/foam	20±1	348±39	53±1	5.0±0.3
BCF/foam	31±2	180±18	8±1	89±1.1