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Cone calorimeter evaluation of two flame retardant cotton fabrics

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SUMMARY

Unbleached (gray) cotton needle-punched nonwoven (NW) fabrics with 12.5% polypropylene scrim were treated with two phosphate–nitrogen-based flame retardant (FR) formulations, Southern Regional Research Center (SRRC)-1 and SRRC-2. The SRRC-1 formulation contains diammonium phosphate as the FR chemical along with urea and dimethyloldihydroxyethyleneurea. Because a trace amount of formaldehyde was still expected to be released from SRRC-1-treated FR cotton under high heat, it was preferable to eliminate the dimethyloldihydroxyethyleneurea, leading to the revised formulation SRRC-2. It has a higher content of diammonium phosphate and did not use the polyethylene emulsion that was in SRRC-1. Both formulations were of low cost as they were developed at SRRC using industrial grade chemicals. The fabrics were evaluated with a cone calorimeter using three heat flux levels, 20, 30, and 50 kW/m^2. On the basis of the overall cone calorimeter results for heat released and ignition times, FR NW fabrics that were treated with SRRC-2 were found to be slightly superior in flammability properties to those treated with the earlier SRRC-1 formulation, but the differences were statistically insignificant. Both preparations were much less flammable than the untreated control cotton NW fabrics. Compared with the untreated NW fabrics, the FR fabrics had higher visible smoke production. Copyright © 2012 John Wiley & Sons, Ltd.

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1. INTRODUCTION

The US mattress business is large with the wholesale value of mattresses being estimated at $5.6bn in 2009 [1]. In North America, nearly 95% of the residential mattresses are built with polyurethane foam with innerspring and natural or synthetic fiber nonwovens (NWs) underneath the ticking. The high load of combustible polyurethane foam burns with melting and dripping and contributes to the spreading of a fire [2]. To pass the dual burner test of Federal Regulation 16 CFR 1633, these mattresses need a flame retardant (FR) barrier fabric. Cotton NW barrier fabrics are attractive because they are natural, biodegradable, economical, and soft to the touch [3]. To date, the industrial development of FR cotton barrier NW fabric/highloft for mattresses has employed either boric acid or phosphates [4]. As a result, cotton continues to be very cost-effective for manufacturers of low to medium price mattresses. Nonwovens used as flame-blocker fabrics for mattresses that meet required flammability tests have been developed. Our focus has been on gray (greige), that is, unbleached, cotton NWs as an economical fabric that can be treated to meet the FR tests. Bleaching is an unnecessary step, adding cost (cost of bleaching is approximately $1.50/kg of cotton) and pollution problems, for

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fabric that will not be a visible part of the mattress. The gray fabric contains 12.5% of polypropylene scrim needed during needle punching to give necessary sturdiness to the NW fabric.

In the present manuscript, fire barrier is defined as follows: an NW fabric that wholly or partially protects combustible materials from specified fire insults, which inhibits penetration of the fire source to the combustible components and which significantly reduces the heat release of the protected mattress. For any FR barrier fabric to be successful, it must meet the required standard along with a reasonable cost. High-cost barrier will not be acceptable for use in low-cost mattresses. The present manuscript describes a barrier for low-cost to medium-cost residential mattresses. Expensive mattresses can afford the use of expensive FR barrier fibers such as aramid (~$44/kg) and modarcrylic (~$15/kg) or use specialized FR barrier NW/knit/woven materials that will protect the mattresses from the open-flame dual burner test.

The Southern Regional Research Center (SRRC)-1 formulation contains diammonium phosphate (DAP) as an FR chemical along with urea and dimethyloldihydroxyethyleneurea having ultra-low formaldehyde (Table I). The original hypothesis was that formaldehyde would not be a problem because several layers of other fabrics would separate the sleeper from this barrier fabric, and there would be no direct contact with the skin. Also, a review of toxicological literature on formaldehyde by Karen Haneke [5] concluded that there is no proven adverse effect on humans. However, because formaldehyde is an International Agency for Research on Cancer Group I carcinogen and a trace amount was expected to be released from SRRC-1-treated FR cotton under high heat, it was preferable to eliminate dimethyloldihydroxyethyleneurea from the formulation. That was a motivation to improve on the SRRC-1 formulation. The SRRC-2 formulation was developed with a higher content of DAP (15% vs 10% in the SRRC-1 formulation). Also, it did not use the polyethylene emulsion of SRRC-1 (Table I). The need to possess zero formaldehyde-releasing properties is discussed in the literature review of Horrocks [6].

Diammonium phosphate has often been used as an FR chemical to produce nondurable or semidurable finishes on cotton. According to the literature, the treatment of DAP and urea, which are main components for SRRC-1 and SRRC-2, onto cotton is semidurable. Upon curing, DAP reacts with the hydroxyl groups of cellulose to produce cellulose phosphate, and this reaction yield is above 90% in the presence of urea [7]. The durability test showed that the cotton treated with DAP and urea bore 10 laundering cycles [7]. However, because the same study showed that its durability was influenced by hard water launderings, we considered them as nondurable. In Standard 16 CFR 1633 [8], it was noted that National Institute of Standards and Technology examined the fire performance of two mattress designs that used different barrier materials/systems made with water-soluble flame retardants. National Institute of Standards and Technology fire tests were conducted after the mattress sets were exposed to 10 localized, wetting and drying cycles. It was concluded that the effects of this severe wetting exposure scenario did not change the overall flammability performance of the mattress sets.

Diammonium phosphate lowers the combustion temperature of the material, decreases maximum rates of weight loss, and causes a higher amount of char [9]. In earlier research [10–15], better flammability resistance resulted from synergism of phosphorus and nitrogen and from urea or certain urea derivative compounds.

Table I. Formulations SRRC-1 and SRRC-2.

Chemicals	SRRC-1 (%)	SRRC-2 (%)
DMDHEU	5.0	—
Diammonium phosphate	10.0	15.0
Urea	5.0	5.0
Polyethylene emulsion	1.5	—
$MgCl_2$, $6H_2O$	1.0	—
Citric acid	1.0	1.0
Triton X-100	0.7	0.7
Water	75.8	78.3
Total	100.0	100.0

DMDHEU, dimethyloldihydroxyethyleneurea; SRRC, Southern Regional Research Center.

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Standard 16 CFR 1633, effective since July 1, 2007, requires new residential mattresses sold in the USA to resist ignition during open-flame dual burner testing [8]. The standard establishes two test criteria: The peak heat release rate (PHRR) must not exceed 200 kW during a 30-minute test of a whole mattress, and the total heat released for the first 10 min of the test of the whole mattress must not exceed 15 MJ [16]. The Federal Regulation 16 CFR 1633 requires that the whole mattress be constructed and full-scale fire tests be performed per the standard dual burner test. For the manufacturers, evaluating the mattress by the standard test and recording of results are important to verify that mattresses comply with the regulation. It has been shown that a mattress with an effective FR barrier can have PHRR of less than 50 kW in the test of a whole mattress and thereby show greater resistance to burning [17].

This study was one of a series of separate projects to evaluate the effectiveness of the FR treatments and the use of the FR fabrics as a flame-blocker fabric for mattresses [13]. Briefly, the goal was to compare the two FR fabrics and determine which formulation imparts higher flame resistance to gray cotton NW fabrics in this small-scale test as a precursor to possible future bench-scale testing of fabric/foam composite specimens and the more expensive whole mattress fire tests. Such an FR NW fabric would have high potential for use as an FR barrier fabric, even in the manufacture of the lowest-cost mattresses. The importance of the cone calorimeter test is its ability to produce flammability characteristics of ignition times, heat release rate, smoke production, and mass loss rate.

The limited objective of this study was to determine the flammability performance of the two FR gray cotton blend NW fabrics in a cone calorimeter. The cone calorimeter was used to test the specimens in accordance with the procedures in ASTM International Standard method E 1354, standard test method for heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. The test methodology is also following the International Organization for Standardization (ISO) standards 5660-1/ISO 5660–2. In the cone calorimeter test, a small 100 mm by 100 mm specimen is exposed to a constant external heat flux by a conical radiant electric heater. Measurements of the depletion of oxygen levels in the exhaust are used to calculate the rate of heat released because of combustion. A load cell provides measurements of the weight loss, and a laser in the exhaust duct provides measurements of the visible smoke in the exhaust. The cone calorimeter is a cost-effective bench-scale test for obtaining data on the heat release rate characteristics of materials, a major indicator of the effectiveness of an FR treatment.

2. EXPERIMENTAL

2.1. Materials and flame retardant treatments

Gray cotton blend NW fabric: Gray cotton needle-punched NW fabric (87.5% cotton with 12.5% polymer scrim of polypropylene), 1.3 mm thick, 150 g/m^2 (5 oz/yd^2) was donated by the Warm Company, Lynnwood, Washington.

Flame retardant formulations: The nondurable FR formulations were the phosphate–nitrogen-based formulations SRRC-1 and SRRC-2 (Table I). Diammonium phosphate and urea were purchased from Magnolia Chemical and Solvent Inc., New Orleans, LA and Triton X-100, a wetting agent, was purchased from Fisher Scientific, Pittsburgh, PA. All chemicals were commercial grade and were not further purified. The wetting agent improved the wetting ability of the formulation to wet gray cotton fiber/NW fabric. Flame retardant formulations were applied at the SRRC to the fabrics with two immersions and two nips on a laboratory padder (Werner Mathis USA Inc., Concord, NC). The thoroughly wetted and saturated fabrics were passed through the first padding at a nip pressure of 621 kPa (90 psi) at a speed of 2 m/min to obtain a low wet pick-up of about 60%. Fabrics were again saturated in the formulation and passed through a nip pressure of 68.9 kPa (10 psi) at 2 m/min to obtain a wet pick-up of 95–100%. The samples were placed on a pin frame and dried in a laboratory dryer (Werner Mathis USA Inc., Concord, NC) at 135 °C for 2 min 45 s. The technique of double immersion and double padding was used to obtain good penetration of FR chemicals into the fiber and uniform saturation of FR chemicals in gray fabrics. The add-on of FR chemicals was 20% on weight of the fiber for SRRC-1 and 18% for SRRC-2.

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2.2. Methods

The cone calorimeter at the Forest Service Forest Products Laboratory (FPL) was used to test the 100 mm by 100 mm specimens in accordance with the procedures in ASTM International test method E 1354-10a. The Forest Service FPL cone calorimeter is a Model No. Cone 2A, Combustion Analysis System (AutoCal) manufactured by Atlas Electric Devices Company of Chicago, IL, USA. Specimens were tested in the horizontal orientation, and the data were collected every second. The specimens were tested using heat flux intensities of 20, 30, and 50 kW/m^2 (Tables II–V). Three replicates of each sample type (untreated, SRRC-1, and SRRC-2) and heat flux levels were tested. The initial sample masses of specimens were approximately 2 g (Table III). Prior to testing, the specimens were conditioned at 50% relative humidity and 23 °C. Because the intended application was as a barrier fabric on mattresses, specimens were tested on the standard 13 mm thick low-density refractory blanket with the backside of the specimen wrapped in aluminum foil. The standard frame was used but no grid. With frame, the exposed surface area of the specimen was 0.008836 m^2, which was used to express the results per unit surface area.

The data recorded included those specified in the ASTM standard E1354 or the corresponding ISO 5660–1 and ISO 5660–2 standards. The data reported in this paper include the following measurements: *heat release rate* (kW/m^2) including the *PHRR* (kW/m^2); *time to PHRR* (s); *total heat released* for test duration (MJ/m^2); *average effective heat of combustion* (MJ/kg); *average mass loss rate* for the period of 10%–90% mass loss ($g/s\text{-}m^2$); *mass at sustained ignition* (g); *sample mass*

Table II. Ignition-related results.

Test series no.	Treatment	Flux level	Time for sustained ignition[a]	Time of peak heat release rate[a]	Mass at sustained ignition[a]	FPL test ID
		(kW/m^2)	(s)	(s)	(g)	
1	Untreated	20	13.9 (2.4)	26.0 (1.0)	1.49 (0.21)	1747
2	SRRC-1	20	22.9 (10.0)	33.3 (9.2)	1.66 (0.27)	1753
3	SRRC-2	20	27.6 (7.1)	41.7 (12.0)	1.59 (0.39)	1819
4	Untreated	30	8.8 (1.7)	20.7 (1.2)	1.48 (0.08)	1776
5	SRRC-1	30	9.8 (0.2)	20.7 (1.5)	1.45 (0.10)	1820
6	SRRC-2	30	11.7 (0.8)	21.3 (0.6)	2.03 (0.05)	1777
7	Untreated	50	4.7 (0.5)	16.3 (1.2)	1.58 (0.12)	1754
8	SRRC-1	50	8.4 (6.0)	20.0 (6.9)	1.64 (0.48)	1756
9	SRRC-2	50	11.6 (1.3)	21.0 (2.6)	1.16 (0.10)	1757

SRRC, Southern Regional Research Center; FPL, Forest Products Laboratory; ID, identity document.
[a]Means (standard deviation) for three replicates.

Table III. Heat released-related results.

Test series no.	Treatment	Flux level	Peak heat release rate[a]	Total heat released[a]	Average effective heat of combustion[a]
		(kW/m^2)	(kW/m^2)	(MJ/m^2)	(MJ/kg)
1	Untreated	20	137 (18)	3.29 (0.27)	15.9 (1.2)
2	SRRC-1	20	57 (14)	1.77 (0.11)	10.4 (0.8)
3	SRRC-2	20	48 (16)	1.37 (0.15)	8.2 (1.4)
4	Untreated	30	152 (24)	3.53 (0.06)	16.5 (0.6)
5	SRRC-1	30	86 (14)	2.57 (0.25)	13.2 (1.8)
6	SRRC-2	30	86 (2)	2.50 (0.17)	10.9 (0.2)
7	Untreated	50	196 (5)	4.23 (0.50)	17.7 (1.4)
8	SRRC-1	50	102 (30)	3.53 (0.23)	13.5 (0.2)
9	SRRC-2	50	83 (11)	2.80 (0.26)	11.6 (1.0)

SRRC, Southern Regional Research Center.
[a]Means (standard deviation) for three replicates.

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Table IV. Mass loss-related results.

Test series no.	Treatment	Flux level	Initial mass[a]	Residual mass fraction[a]	Sample mass loss[a]	Average mass loss rate (10%–90%)[a]
		(kW/m^2)	(g)	(−)	(kg/m^2)	(g/m^2s)
1	Untreated	20	1.8 (0.1)	−0.1 (0.2)	0.21 (0.02)	3.7 (1.9)
2	SRRC-1	20	2.3 (0.1)	0.27 (0.01)	0.18 (0.01)	2.6 (0.3)
3	SRRC-2	20	2.3 (0.1)	0.30 (0.04)	0.18 (0.01)	2.7 (0.5)
4	Untreated	30	1.8 (0.04)	−0.08 (0.06)	0.22 (0.02)	4.7 (0.4)
5	SRRC-1	30	1.9 (0.1)	0.02 (0.08)	0.21 (0.02)	2.6 (0.6)
6	SRRC-2	30	2.5 (0.1)	0.17 (0.05)	0.24 (0.02)	3.4 (0.3)
7	Untreated	50	1.9 (0.2)	−0.17 (0.04)	0.25 (0.02)	4.4 (0.6)
8	SRRC-1	50	2.3 (0.04)	−0.13 (0.14)	0.29 (0.03)	3.1 (0.2)
9	SRRC-2	50	2.2 (0.1)	−0.09 (0.1)	0.27 (0.02)	2.9 (0.2)

SRRC, Southern Regional Research Center.
[a]Means (standard deviation) for three replicates.

Table V. Smoke-related results.

					Smoke production	
Test series no.	Treatment	Flux level	Average SEA[a]	Time of peak SEA[a]	Total[a]	Percentage post-ignition[a]
		(kW/m^2)	(m^2/kg)	(s)	(m^2/m^2)	(%)
1	Untreated	20	63 (11)	52 (18)	13 (2)	88 (2)
2	SRRC-1	20	146 (47)	23 (11)	27 (8)	62 (13)
3	SRRC-2	20	170 (35)	47 (16)	32 (8)	64 (1)
4	Untreated	30	73 (20)	16 (8)	16 (4)	85 (4)
5	SRRC-1	30	88 (24)	28 (9)	19 (7)	60 (9)
6	SRRC-2	30	144 (39)	50 (37)	34 (11)	66 (6)
7	Untreated	50	98 (21)	23 (16)	24 (6)	96 (2)
8	SRRC-1	50	72 (36)	62 (38)	20 (9)	61 (23)
9	SRRC-2	50	183 (57)	76 (40)	49 (13)	31 (7)

SRRC, Southern Regional Research Center; SEA, specific extinction area.
[a]Means (standard deviation) for three replicates.

loss for test duration (kg/m^2); *residual mass fraction* (residual mass as fraction of the initial mass); *average specific extinction area* (average SEA, m^2/kg); *time for peak SEA* (s); *total smoke production* (m^2/m^2) and percentage of total for the period after specimen ignition (%); and *time for sustained ignition* (4 s criterion for sustained ignition, s). As noted by the cited units, the heat release results from the cone calorimeter test are reported on a per unit area basis.

Statistical analysis was performed with SAS for Windows, SAS 9.2, of SAS Institute, Cary, NC, USA. The general linear model procedure was used to evaluate the significance of differences between the means (*t*-test (least significant difference) option, alpha equal to 0.05). The *t*-test option performs pair-wise tests, equivalent to Fisher's least significant difference test in the case of equal cell sizes for all main-effect means.

3. RESULTS AND DISCUSSION

The results from the cone calorimeter tests included data related to ignition (Table II), heat release rates (Table III, Figures 1–3), mass loss (Table IV), and smoke (Table V).The cone calorimeter tests were conducted using three different heat flux levels for the external exposure to the test specimens, 20, 30, and 50 kW/m^2. In practice, the selection of heat flux level depends on the expected fire scenario.

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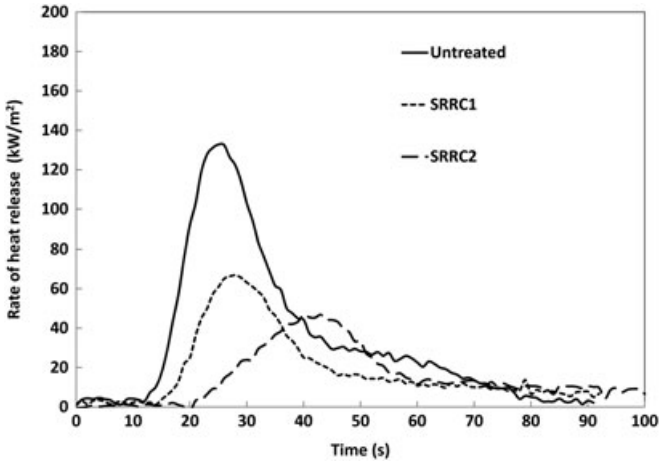

Figure 1. Examples of heat release curves for untreated and treated samples tested at 20 kW/m^2 heat flux level. SRRC, Southern Regional Research Center.

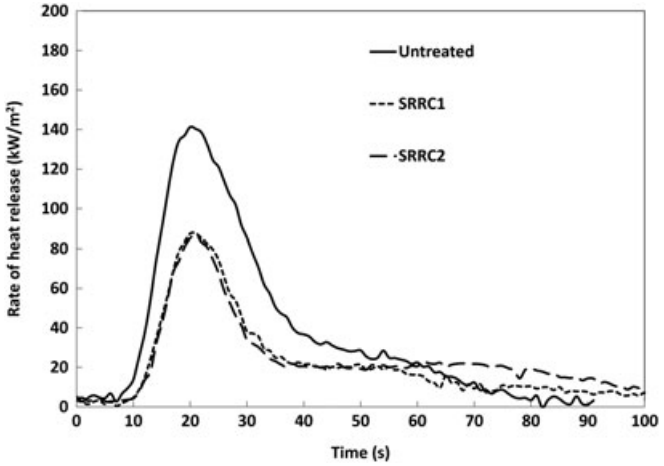

Figure 2. Examples of heat release curves for untreated and treated samples tested at 30 kW/m^2 heat flux level. SRRC, Southern Regional Research Center.

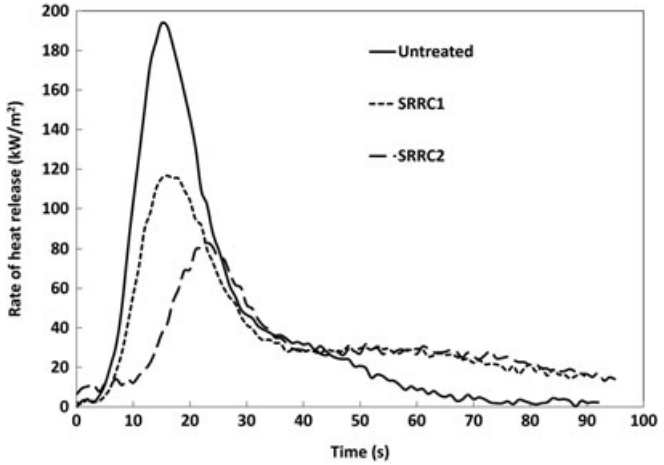

Figure 3. Examples of heat release curves for untreated and treated samples tested at 50 kW/m^2 heat flux level. SRRC, Southern Regional Research Center.

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In terms of the test, too low of a heat flux level can result in problems with sustained flaming ignition of FR-treated specimens, whereas too high of a heat flux can make it difficult to distinguish between materials as the specimens undergo rapid combustion. The 35 kW/m^2 level is often associated with a mild fire exposure, and the 50 kW/m^2 level is likewise associated with a well-developed fire. In other studies in which the cone calorimeter was used to evaluate specimens of fabric/foam mattress composites, a heat flux level of 35 kW/m^2 is typically used [18,19]. The 35 kW/m^2 level is also the flux level specified in ASTM E 1474, standard test method for determining the heat release rate of upholstered furniture and mattress components or composites using a bench-scale oxygen consumption calorimeter. The 50 kW/m^2 heat flux level has also been used in tests of fabric/foam composites [20].

Plots of the various results (Tables II–V) from the cone calorimeter tests generally indicated a linear relationship with heat flux level in the tests of the untreated cotton samples but often significant nonlinear relationships (as indicated by low R^2 in a linear regression of data) in the tests of the FR-treated cotton samples. The data for the PHRR is shown in Figure 4 as an example. Other data that exhibited similar behavior included times for sustained ignition, times for PHRR, total heat released, and average effective heat of combustion. When observed, the nonlinear effect had a greater rate of change in the test results when the flux level was increased from 20 to 30 kW/m^2 than that observed when the flux level was increased from 30 to 50 kW/m^2. This reduction in the effect of higher heat flux exposure at the higher heat flux levels suggests that the mechanisms of the FR treatments required some initial heating/combustion to become effective. This would be consistent with the mechanism for a DAP treatment being one of causing a higher char yield.

3.1. Ignition

The observed length of time before sustained ignition was increased by the FR treatments, particularly for the tests conducted using 20 kW/m^2 heat flux level (Table II). For the 20 kW/m^2 heat flux level, the untreated specimens ignited at 14 s, whereas the treatments increased the times to 23 s and 28 s for treatments SRRC-1 and SRRC-2, respectively. For all three heat flux levels, the order of increased sustained ignition times was as follows: untreated < SRRC-1 < SRRC-2. For the tests at 30 and 50 kW/m^2, the differences in ignition times between specimen types were greatly reduced (Table II) and not statistically significant. The times for sustained ignition were significantly less for the higher heat flux level. Similar behavior was observed for the time for the PHRR (Table II) except that the differences between the three types of specimens for the 30 kW/m^2 heat flux level were even smaller than was the case for the times for sustained ignition at that heat flux level. As discussed later in the section on testing fabrics in the cone calorimeter, we had difficulties with the value used to time

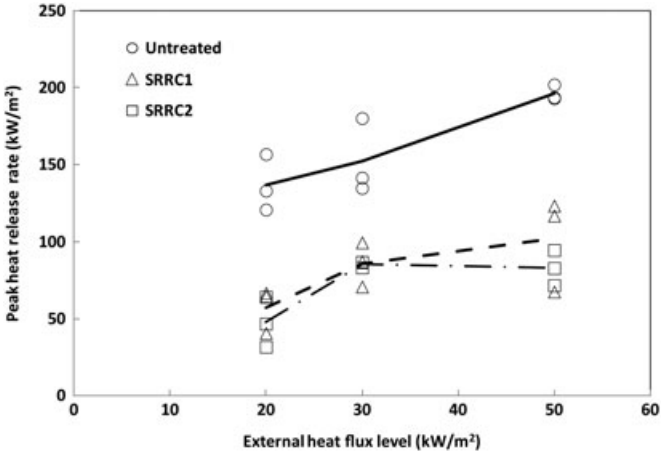

Figure 4. Graph of the peak heat release rate data plotted against the external heat flux level used in the tests. Lines are for the averages of the data for given treatment and heat flux level. SRRC, Southern Regional Research Center.

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shift the oxygen consumption data (i.e., heat release rate) to account for the time delay in the analyzer response to the change in oxygen level, which has a direct impact on the absolute values for the times for PHRR and their relative values to the times for sustained ignition based on visual observations. Differences for the mass at sustained ignition followed no consistent pattern in terms of treatment or heat flux level (Table II). But, if the mass values at sustained ignition are expressed as mass loss at sustained ignition, the smallest mass losses were recorded for the ignition of the untreated specimens, and the SRRC-2-treated specimens had greater mass loss at the time of observed ignition than the SRRC-1 specimens at each heat flux level. However, the differences between the mean values were not statistically significant. The greater mass loss at ignition may reflect the DAP causing the lowering of the degradation temperature of the material. The SRRC-2 treatment had a higher level of DAP. Results for mass loss are based on mass of the specimen as tested including any mass loss due to the add-on FR chemicals (Table I) that added to the initial mass of the specimens (Table IV).

3.2. Heat released

The treatments significantly reduced the heat release rate as exhibited in reductions in the PHRR and total heat released (Table III, Figures 1–3). The means for PHRR and total heat released were slightly less for SRRC-2 treatment than those for SRRC-1 treatment (Table III). However, the difference between the two treatments was only statistically significant for the total heat released in the 50 kW/m^2 tests. As previously discussed, the PHRR increased with heat flux level, and the increase in PHRR was considerably smaller for the FR-treated specimens when the heat flux was increased from 30 to 50 kW/m^2 than for untreated specimens or when the heat flux was increased from 20 to 30 kW/m^2 (Figure 4). The drop in heat release rate for the first peak is normally associated with the development of a char layer that provides some protection to the underlying material. The DAP in the treatments is understood to increase the amount of char produced. At 30 kW/m^2, any differences between the two treatments were less evident in comparison with the data for 20 and 50 kW/m^2 (Figures 1–4, Table III). Although the small number of replicates (three) makes it risky to conclude too much from the data, the data suggests the nonlinear relationships between heat release rates, and heat flux level (Figure 4) may be an additional factor in the smaller observed differences between the two treatments at 30 kW/m^2 compared with the other two heat flux levels.

The FR treatments also reduced the average effective heat of combustion (Table III). Differences in average effective heat of combustion between each of the three samples (untreated, SRRC-1, and SRRC-2) were statistically significant. The means for the average effective heat of combustion for the SRRC-2 specimens were less than the means for SRRC-1 or untreated. The average effective heat of combustion increased with increased heat flux level. As with other results, the increase in average effective heat of combustion was small for the FR-treated specimens when the heat flux was increased from 30 to 50 kW/m^2. Values for effective heat of combustion in the cone calorimeter are MJ/kg of mass loss. If the effect of the add-on chemicals was merely to add noncombustible volatiles, an add-on of 19% (i.e., corresponding increase in mass loss) would have reduced the heat of combustion values from 15.9, 16.5, and 17.7 MJ/kg (values for untreated at three flux levels, Table III) to 13.4, 13.8, and 14.8 MJ/kg, respectively. The reported effective heat of combustion values for the SRRC-1 and SRRC-2 are lower (Table III). These results are consistent with the FR treatments causing a higher char yield and the higher heat flux levels reducing the char yield.

In the cone calorimeter tests of the untreated gray cotton NW fabric, the average effective heat of combustion values were 15.9, 16.5, and 17.7 MJ/kg for the heat flux levels of 20, 30, and 50 kW/m^2, respectively (Table III). In an oxygen bomb calorimeter/adiabatic bomb calorimeter test (Parr 1266 Isoperibol Bomb Calorimeter following the ISO 1928 standard and using a fixed value for fuse and nitric acid corrections) of the untreated gray cotton NW fabric, the gross heat of combustion value was 20.6 MJ/kg. In a bomb calorimeter, a specimen is inserted in a steel cylinder (i.e., the bomb) that is pressurized with excess pure oxygen. The cylinder is inserted in a bucket with water. The surrounding calorimeter jacket is held at a constant temperature while heat from the burning specimen causes temperature of the bomb and the water in bucket to rise. An ignition circuit is used to ignite the very small specimen. With appropriate corrections, the temperature rise of the water in the bucket is measured to determine the gross calorific value for the specimen. There is no residual

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combustible char in an oxygen bomb calorimeter test. For a material with no residual char, the heat of combustion in a cone calorimeter test corresponds to the net heat of combustion, which is the gross heat of combustion minus the latent heat of water evaporation. Using an equation of Dietenberger [21] for cellulosic fuels, it is estimated that the 20.6 MJ/kg value for the gross heat of combustion corresponds to a value of 19.3 MJ/kg for the net heat of combustion.

The gray cotton NW fabric was 87.5% cotton and 12.5% polypropylene scrim. Because the polypropylene scrim contributed to the heat released in the cone calorimeter test, some additional testing was conducted to help identify the potential contribution of the polypropylene scrim. Two tests of untreated samples of *s*punlaced (hydroentangled) bleached cotton NW fabric (1.7 mm thick:220 g/m^2) in the cone calorimeter using a heat flux of 30 kW/m^2 resulted in a slightly lower average effective heat of combustion of 16.0 MJ/kg. The fabric was developed at SRRC from bleached cotton fiber: bleached cotton comber noil fiber, 50%:50%, w/w. The mean value for the untreated gray cotton NW fabric tested at 30 kW/m^2 was 16.5 kW/m^2.

An oxygen bomb calorimeter/adiabatic bomb calorimeter test of cotton fiber resulted in a gross heat of combustion value of 17.0 MJ/kg. Thus, the corresponding value for the untreated gray cotton NW fabric of 20.6 MJ/kg was 21% greater. A literature value for the heat of combustion of polypropylene is 43.3 MJ/kg [22]. A linear combination of the 17 MJ/kg value for cotton and 43.3 MJ/kg value for polypropylene in proportion to the 0.875/0.125 composition of the blended fabric produced an estimate for the heat of combustion of the blended fabric of 20.3 MJ/kg, which was consistent with the 20.6 MJ/kg value obtained in the test of the blended fabric. Thus, about 27% of the total heat content of the untreated gray cotton NW fabric was the polypropylene scrim.

In the micro-scale combustion calorimetry (MCC)/pyrolysis combustion flow calorimetry test [22] (ASTM D7309), the sample undergoes thermal degradation in a nitrogen/anaerobic environment, and only the volatile pyrolysis gases are combusted in the determination of the total heat release. In literature MCC tests of untreated cotton fabric [23], the reported total heat released was 10.6 MJ/kg for a char yield of 5.8%. In MCC tests conducted as part of a companion study of the untreated gray cotton NW fabric, the total heat release was 9.5 MJ/kg, and the char yield was 16.8%. Using the char yield value to convert the 9.5 MJ/kg value based on initial specimen mass to a mass loss basis, the total heat release in the MCC test was 11.4 MJ/kg of mass loss. The values obtained in the cone calorimeter for effective heat of combustion of the untreated gray cotton NW fabric (16–18 MJ/kg) are consistent with these results for the oxygen bomb calorimeter (20.6 MJ/kg gross/19.3 MJ/kg net) and the MCC test (11.4 MJ/kg), particularly given the very low residual mass in the cone calorimeter tests of the untreated fabric (Table IV).

A linear regression of the average effective heat of combustion results (Table III) with the residual mass fraction (Table IV) resulted in a predictive model ($R^2 = 0.71$). Using this linear model and the char yield of the untreated, SRRC-1, and SRRC-2 specimens in the MCC tests (16.8%, 31.7%, and 37.6%, respectively) resulted in estimates of 10.9, 7.9, and 7.8 MJ/kg, respectively. The corresponding MCC results for total heat released on a per mass loss basis were similar, 11.4, 6.3, and 6.4 KJ/kg. The similar results support the reasoning that the effectiveness of the treatments in the cone calorimeter tests was largely because of the shifts of the degradation process to greater residual char and less volatile gas. It should be noted that a correlation between the total heat released in the MCC and the total heat released in the cone calorimeter can be poor for other FR-treated materials [24], particularly for halogenated FR-treated products [25].

The slightly lower heat released results for the SRRC-2-treated fabric likely reflected the increased amount of DAP. It also is possibly due to the elimination of the high-density polyethylene emulsion in the SRRC-1 formulation (Table I), which has higher heat content than cotton. The elimination of the emulsion may have permitted better FR coating and penetration of the cotton.

3.3. Mass loss

The FR treatments reduced the average mass loss rate compared with the untreated specimens (Table IV). As will be discussed later in the section on testing fabrics in the cone calorimeter, the determination of mass loss had considerable variability because of the small initial mass of approximately 2 g. Negative final mass values were recorded in some tests. In the 20 kW/m^2 tests, the residual mass fractions (Table IV) of the treated samples were 0.27 and 0.30 for SRRC-1 and

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SRRC-2, respectively, compared with −0.1 for the untreated samples. However, there were small differences in the results for the sample mass loss (Table IV). In thermogravimetric analysis (TGA) tests at a heat ramping rate of 10 °C/minute conducted in an companion study of the gray cotton NW fabric, the SRRC-1 [13] and SRRC-2 treatments increased the residual mass fraction at 600 °C from less than 0.02 for the untreated in either air or nitrogen to 0.07 and 0.13, respectively, for tests in air and 0.21 and 0.28, respectively, for tests in nitrogen. As with the other results, these results are consistent with the higher DAP levels in the SRRC-2 treatment causing increased char yield.

3.4. Smoke

More visible smoke was produced in the tests of the FR-treated specimens (Table V). At each heat flux level, the average SEA and total smoke production were greatest for the SRRC-2-treated specimens. The differences between the means for the SRRC-2-treated specimens and the untreated specimens were statistically significant. In the tests of an untreated specimen, almost all (>85%) of the smoke production occurred after sustained ignition of the specimen (Table V). In tests of FR-treated specimens, at least 34% of the smoke production occurred before the observation of flaming ignition (Table V). Thus, the increased smoke production for the FR-treated specimens was likely because of the delayed ignition of the treated specimens. Legislative requirement of CFR 1633 does not address smoke generation. In a full-scale mattress test, the delayed ignition characteristics of the treated specimens would also reduce the surface burn area and thereby result in lower total smoke generation.

3.5. Testing fabrics in cone calorimeter

As noted by others [26–29], there are challenges to the testing of cotton fabrics with a cone calorimeter. One challenge is the selection of incident heat flux intensity. The selection of the heat flux level affects the results with regard to the behavior of the material and the ability of the equipment to record the behavior. The use of the fastest available scan rate is needed. Because data is collected at specified time intervals, the PHRR is a function of the scan rate. For this reason, heat release rate data is also often reported as averages for 60, 180, and 300 s after sustained ignition of the specimen. The short durations of these cotton fabric tests were not conducive to such averaging of the data. The use of lower heat flux levels can address some of these difficulties, but low heat flux levels reduce the repeatability of the results. This may be because of erratic response of the materials to low heat flux levels. Pottel [28] noted that the presence of the spark igniter immediately above the specimen and the resulting rapid flash ignition of the flammable pyrolysis gases may explain differences in behavior of some fabric/foam composites in the cone calorimeter and the large-scale furniture test.

Another issue often discussed in the literature [27,29] for testing of fabrics is the use of a grid to keep the specimen from deforming during the tests. Grids are recommended to reduce variability in the results [29]. We conducted a limited number of tests with various types of grids. As reported by others, the use of a grid tends to reduce the PHRR and prolong the duration of the test. Visual observations suggested that the flaming cotton NW fabrics were not dramatically deformed until significant combustion of the specimen had occurred. The simplest condition of testing without a grid was used for all the reported experiments. We did use the frame to provide some initial restraint of the specimen. The deformation of the specimen did often prevent re-insertion of the spark igniter when the initial flaming ceased.

There is a time delay for the response and recording by the oxygen analyzer of the changes in the oxygen concentrations in the exhaust. Thus, a time shift of the heat release rate data is made relative to the times recorded for other data such as the mass loss from the load cell, smoke production data from the laser, and the visual observation of sustained ignition. With the very rapid combustion of the fabric, the results were more sensitive to possible variations in the actual delays compared with the specified time shift used to analyze the data. The time delay directly affects the times for PHRR and its comparison with the observed times for sustained ignition (Table II). In these tests, we initially had the time shift for the oxygen analyzer set for 12 s longer than what was ultimately used in the data reported in this paper. In the tests with the 50 kW/m^2 heat flux level (Figure 3), this initial longer time shift resulted in the loss of the initial portion of the heat release rate curves because the time shift of the oxygen data was performed during the initial data acquisition. Calibration of the time shift resulted in the adjustment to a value 12 s shorter. This adjustment

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resulted in observed times for sustained ignition closer to the start of the heat release rate curve rather than closer to the times for the PHRR.

Another problem with testing the fabric alone was the relatively small initial mass of the samples. The design of the cone calorimeter is based on heavier samples. The weighing system of the FPL cone calorimeter is described as having an active measuring range of 0–500 g with a 0.01 g resolution. The ASTM E1354-10a standard specifies a weigh scale accuracy of 0.1 g. The initial mass of the fabric samples was approximately 2 g.

Because the intended application was as a barrier fabric on mattresses, specimens were tested on the standard 13 mm thick low-density refractory blanket with the back side of the specimen wrapped in aluminum foil. For materials less than 6 mm thick that are intended to be used with an air space adjacent to unexposed surface, ASTM E1354 discussed the use of a metal frame to provide spacing greater than 12 mm behind the test specimen.

3.6. Application of the cone calorimeter test results to full-scale mattress tests

This project to evaluate the gray cotton blend NW fabric treated with two FR formulations in the cone calorimeter was one of a series of projects to evaluate the effectiveness of the FR treatments and the use of the FR fabrics as a flame-blocker fabric for mattresses. Cone calorimeter results likely applicable to an effective flame-blocker fabric include ignition times, peak heat release, and char yield. Treatment SRRC-2 had the longest times for sustained ignition at each of the heat flux levels used in this study. It also had the lowest PHRR and lowest total heat released at each of the heat flux levels. The residual mass fraction was the highest for the SRRC-2 treatment at each of the heat flux levels. In ASTM E 1474 and in studies reported in the literature [18–20], the specimen tested in the cone calorimeter is a fabric/foam composite, which is intended to represent the use of the fabric with a mattress. Various specimen configurations of the fabric/foam composites were investigated by Fritz and Hunsberger [18]. Such fabric/foam composite tests are recommended as a suitable follow-up to this study. Models have been developed to use results from cone calorimeter tests of fabric/foam composites to predict results in full-scale furniture tests [30].

4. SUMMARY

This ‘green’ cotton barrier NW fabric (with 12.5% polypropylene scrim) is unique in the sense that it is from a renewable resource, biodegradable and economical, and it employs gray cotton suitable for low-cost residential mattresses. Gray cotton blend NW fabric treated with two phosphate–nitrogen-based FR formulations, SRRC-1 and SRRC-2, were evaluated with a cone calorimeter. Both formulations produced effective FR cotton NW fabrics. They showed significantly reduced PHRR and low total heat released with delayed ignition time. On the basis of the test results of their flammability properties, FR NW fabrics that were treated with SRRC-2 were found to be slightly superior to those treated with the SRRC-1 formulation. Both formulations produce more smoke than the untreated control; however, legislative requirement of CFR 1633 does not comment on the smoke generation.

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