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Research Article

Variation of flammability and smoke toxicity of upholstered furniture composites with fire retardant treatment

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ABSTRACT

Since the 1980s, mass market upholstered furniture sold in the United Kingdom has incorporated flame retardant chemicals to meet regulatory flammability requirements. However, UK fire deaths remain comparable with similar European countries which have no such regulations. Quantitative measures of the effect that different chemical flame retardants additives have on the flammability and smoke toxicity of UK regulatory-compliant upholstered furniture remain limited. It has been shown that most fatal fires involve upholstered furniture; most fire deaths result from toxic gas inhalation; gas phase flame retardants increase the toxicity of smoke; and the fall in fire deaths over the last 30 years is the same in countries with and without furniture flammability regulations. Moreover, the presence of certain flame retardants in furniture is a significant obstacle to any meaningful end-of-life processing.

The burning behaviour and smoke toxicity of nine upholstered furniture composites using a range of flame retardant technologies were assessed in the cone calorimeter. The total heat release (THR) varied from 46 MJ m^{-2} to 68 MJ m^{-2} , the time-to-ignition (tti) from 8 s to 105 s, and peak heat release rate (pHRR) from 230 kW m^{-2} to 430 kW m^{-2} . The composite filled with PET showed the longest tti while the expandable graphite fabric on the FR-foam showed the lowest pHRR. The composite with the Br-FR fabric and the FR-foam had the shortest tti, the greatest smoke, the second highest CO and the highest HCN yield. The composite with the non-FR fabric and the PET filling had the longest tti. For all the fabrics, the transition from non-FR to FR foam resulted in significant increases in the smoke, CO and HCN, except CO of Br-FR and FR-foam was slightly lower than non-FR foam.

Smoke toxicity predictions show that the use of gas phase flame retardants in both the fabrics and fillings of upholstered furniture contributes to the high proportion of smoke-related fire casualties. The work shows that the smoke toxicity of upholstered furniture can be reduced by using condensed phase FRs, such as expandable graphite, or less flammable materials, such as polyester wadding. The regulatory component tests which focus on ignitability have been shown to be ineffective at assessing the fire safety of composites representative of furniture as sold. The alternative approach of assessing heat release and smoke toxicity, as described here, would improve the fire safety of furniture while reducing reliance on additive flame retardants acting in the gas phase.

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1. Introduction

A recent statistical study [1] has shown that upholstered furniture fuels most of the domestic fires in England which result in fatalities. It goes on to show that most of those fire deaths result from inhalation of smoke and toxic gas. Since the 1980s the United Kingdom has had regulations limiting the flammability of domestic upholstered furniture. The current Furniture and Furnishings (Fire)

(Safety) Regulations (FFFSRs) originate from 1988 and are some of the most stringent in the world. They define the flammability limits of furniture at both a component level (separate tests for fillings and fabrics) and at a composite level (where fabric-filling combinations are tested). Some account is taken of the risks associated with end use, with different requirements for sleep surfaces, indoor and outdoor seating, etc. Although the regulations do not specify the use of fire-retardant chemicals their use has become ubiquitous in mass market upholstered furniture. The regulations are currently under review, with a consultation on their revision published in August 2023.

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Since the regulations were introduced in 1988, the UK's fire death rate has decreased at a comparable rate to similar European countries [2] as shown in Fig. 1. New Zealand has no furniture flammability regulations, mainland Europe has much less stringent regulations, but their fire death rates are similar to those of the UK. California also had stringent furniture flammability regulations until 2012, which in practice meant that most upholstered furniture in the US was compliant with the Californian standard, although California is only 25 % of the US market. When they were relaxed chemical flame retardants (CFRs) were no longer necessary. As Fig. 1 shows, this relaxation has not coincided with an increase in fire deaths.

However, the change has not been without controversy. It has been argued that the relaxation of the Californian regulations was misguided [3] and that furniture fires are still a problem in the US [4]. In particular, polyurethane foam in furniture and mattresses provides a large mass of easily ignited fuel, which may require additional fire protection, through barrier fabrics, fire protected covering materials, or flame retardants added to the foam [5]. These viewpoints are less focussed on the harmful effects of exposure to certain CFRs in current use, and the length of time after a CFR has been shown to be harmful that it continues to be released into homes and the wider environment. Elsewhere, it has been argued that the use of CFRs in Californian furniture was unnecessary and did not deliver a fire safety benefit [6].

A very large body of research has identified the releases of CFRs into the environment [7–9] their persistent, bioaccumulative and toxic (PBT) properties [10–12] and particularly their endocrine-disrupting effects on humans exposed to CFRs in household dust [13–16], etc. The key piece of research that is missing, and is urgently needed, is a reconciliation of the harm caused by upholstered furniture fires with the harm caused by life-altering changes brought about by endocrine-disrupting CFRs. Undoubtedly, fire deaths and injuries are much easier to quantify (Fig. 1 shows 5 to 10 lives lost per million of population per year from fire. Ahrens [4] estimates that around a third of fire fatalities were fuelled by upholstered furniture and mattresses, giving 1 to 3 deaths per million population per year). Hundreds of millions of people are exposed to endocrine-disrupting CFRs from furniture, and the num-

ber of life-altered victims may be hundreds to thousands of times greater than the fire fatalities.

Overall, the lack of correlation between the existence of furniture flammability regulations and fire death rates suggests that the reduction in fire death rate is largely due to other factors, such as changes in smoking locations, behaviours and products, a decrease in open-source heating and increased prevalence of affordable and effective smoke detectors. When trying to determine why the UK's furniture fire regulations have not lowered the UK fire deaths beyond other countries, the cause of fire injury or fatality must be considered. Fire statistics [17] for the UK show that the proportion of both non-fatal and fatal fire-related casualties caused by smoke inhalation has exceeded 50 % since the introduction of the 1988 FFSRs. It has been reported that gas-phase flame retardants increase smoke toxicity [18] and that the flame retardants in UK furniture increase the toxicity as they reduce the rate of burning [19].

Furniture and furnishing manufacturers have become reliant upon two families of fire-retardant chemicals to make furniture compliant with the regulations. These are brominated fire retardants (BrFRs) and chlorinated organophosphate flame retardants (OPFRs). Both inhibit flaming combustion by the production of hydrogen halides. These interfere with the free radical chain reactions of flaming combustion, by replacing the highly reactive OH· and H· with less reactive Br· or Cl·. This leads to an increase in the products of incomplete combustion, including carbon monoxide (CO), hydrogen cyanide (HCN), organic compounds and smoke [20].

Historically, brominated flame retardants have been used to make both foam and fabric compliant with the FFSRs. However, for the last 15 to 20 years, polyurethane foam formulations have used chlorinated organophosphate esters, particularly tris(chloroisopropyl) phosphate (TCIPP) (Fig. 2(a)) to make combustion modified high-resilience polyurethane foam (CMHR-PU) for the UK domestic furniture market [21]. In mainland Europe, flexible polyurethane foam used for furniture is routinely recycled at end-of-life, reclaiming polyols and isocyanates. In the UK, the presence of TCIPP in the foam prevents any meaningful form of end-of-life processing. Brominated flame retardants continue to be applied to upholstery fabrics by a process of blade back-coating. Typical

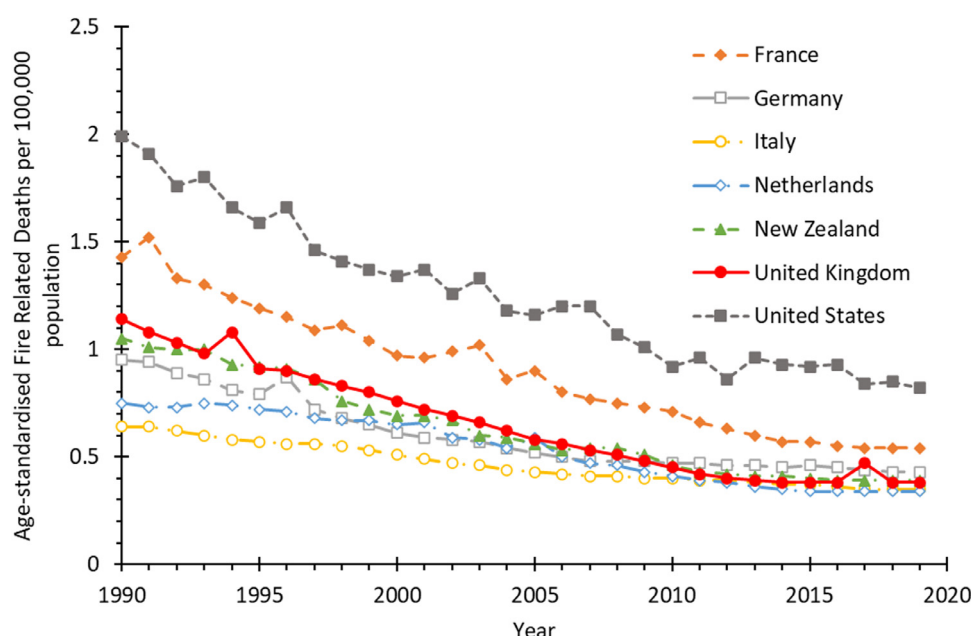


Fig. 1. Fire deaths per 100,000 population in UK (with the most stringent furniture flammability regulations) and in other developed countries (without or with limited domestic furniture flammability regulations).

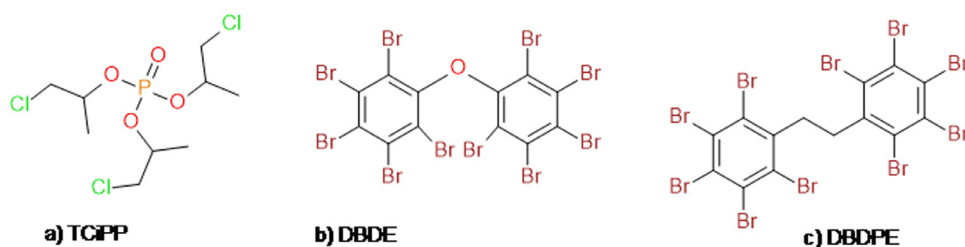


Fig. 2. Structures of flame retardants (a) tris(chloroisopropyl)phosphate (TGIPP), (b) decabromodiphenyl ether (DBDE), and (c) decabromodiphenylethane (DBDPE).

back-coating formulations contain 40 % to 60 % flame retardant, by weight, in an organic binder. The most common group of brominated flame retardants used were polybrominated diphenyl ethers (PBDEs). Unfortunately, as one member of the group was shown to be persistent, bioaccumulative and toxic [22] (PBT), it was replaced by another chemically similar analogue: a process described as “regrettable substitution”. The last remaining PBDE, decabromodiphenyl ether (deca-BDE) (Fig. 2(b)), continued to be widely used on upholstery fabrics until the Stockholm Convention identified it as a persistent organic pollutant (POP). Restriction came into effect in March 2019. Rather than causing a shift away from PBDEs in upholstery back-coating, deca-BDE was replaced by the chemically similar decabromodiphenyl ethane (DBDPE) (Fig. 2(c)). DBDPE has been commercially available as a flame retardant since the early 1990s [23]. In December 2022, another arm of the UK government, the Environment Agency specified that waste seating containing persistent organic pollutants must be incinerated in specialist facilities and was not suitable for either landfill or any recycling processes [24].

Therefore, the use of CFRs to meet the current UK furniture fire safety regulations prevents any meaningful end-of-life processing, while the data in Fig. 1 show the UK reduction in fire deaths mirrors that of similar European countries and New Zealand.

Barrier/interliner type fabrics can be employed to increase the fire safety of foams and foam furniture, as demonstrated by Nazare [25–28] and Kim [29]. However, the component testing focus of the current FFSRs means that foam must be tested without the interliner and shown to be compliant, even if an interliner is used in the final construction. One emerging alternative to brominated flame retardants for back-coating is expandable graphite (EG). Unlike either OPFRs or BrFRs, EG has a physical, blocking function as a fire retardant in the condensed phase as a barrier-forming intumescent. Typically, graphite flakes (0.5 mm across, 1–10 μm thick) are treated with sulphuric acid, which intercalates between individual graphene layers. On heating, the acid treatment volatilises, forcing the graphene plates apart. This results in the formation of graphite “worms” that increase the flake thickness [30] by factors up to 400. Entanglement of these worms and increased distance between the individual graphene layers results in an insulating char [31] which has anisotropic thermal conductivity: it conducts heat well across the graphene layers, but poorly from layer to layer [32]. This keeps the underlying fuel cooler, while conducting heat away from the ignition source. EGFR can be used to make both filling and fabrics compliant with the FFSRs.

Mass market furniture fillings are predominantly flexible polyurethane foam and natural and man-made fibres. One of the most widely used fibres is polyester (PET) in the form of “wadding”, a resilient layer of non-woven PET. PET wadding passes the UK’s regulatory test without the need to add flame retardants due to its relatively low melting point and high ignition temperature (220–268 $^{\circ}\text{C}$ and 432–488 $^{\circ}\text{C}$ respectively). On exposure to heat, the fine fibres of the wadding collapse and shrink away from the ignition source. If they do ignite, polyester tends to burn from a liquid pool. Its use in its unadulterated form facilitates both chem-

ical and mechanical recycling. The PET wadding may be used alone as a filling in thinner products such as headboards, or as a comfort layer between fabric and foam in larger products.

UK fire statistics [16] show that most fire deaths and most fire injuries result from inhalation of toxic smoke, and that this proportion is increasing, although overall fire deaths are decreasing. They also show that most domestic fires start in kitchens, but the most lethal fires start in living rooms and bedrooms [1]. The large amounts, and high fuel load of upholstered furniture and bedding suggests that building contents, particularly upholstered seating and beds, may be responsible for most of the smoke toxicity deaths.

1.1. Regulatory furniture flammability test procedures

The UK’s regulatory framework, the FFSRs, specify the ignitability and flammability using an L-shaped rig. In BS 5852 [33] for upholstered furniture, the fabric is placed directly over 75 mm thick pieces of a special formulation of standard, low density of flexible polyurethane foam, which does not contain any flame retardants. This foam cannot be used in any furniture products sold in the UK. To test the filling, it is covered with a standard polyester fabric. Ignition is tested with a cigarette (smouldering) and match (flaming) test. Special cigarettes, not available for purchase by consumers, which do not have reduced ignition propensity (RIP) properties, must be used. In the match test, similar test pieces are exposed to a 40 mm flame, to simulate ignition from a match for 20 s, designated as “ignition source 2”. These tests have the advantage that fabric or filling manufacturers can verify the compliance of the component they are selling, while upholstered furniture manufacturers can offer any fabric on any furniture design. However, for both fabrics and fillings, the test scenario is unrealistic, specifying foam or cigarettes which would not be present on UK furniture. In contrast, the corresponding European standard, EN 1021-1 [34] uses an RIP cigarette, representative of a readily available ignition source, and a match test (EN 1021-2 [35]) applied to the fabric over the actual filling, uses the same size of flame, but is only applied for 15 s. This approach has allowed manufacturers to reduce the CFR usage to that which is actually required for that fabric-filling combination. The complex interaction between the burning fabric and molten foam means there is no obvious correlation between the fire behaviour of fabrics and fillings, when tested as components, and their behaviour in combination, as composites [36].

In addition, the FFSRs also stipulate a composite test method for certain fabric-filling combinations for upholstered seating and bed headboards. The test method and ignition source vary depending on the nature of the product and filling, but frequently uses the more severe crib #5 test (a 17 g wood crib, ignited between the horizontal and vertical planes of the L-shaped rig). This ignition source was reported to have a maximum adjacent heat release rate of 13 kW m^{-2} and a maximum heat flux of 1.8 kW m^{-2} beneath it [37]. This additional requirement drives the widespread deployment of CFRs in UK furniture. The FFSRs relate to

Table 1

Fillings and fabrics used in this study with abbreviation and description. “Compliant” indicates that the component meets the test requirements of BS5852 for upholstery products, and is therefore compliant with the FFFSRs.

Material	Abbreviation	Description	Compliant
Non-fire retarded polyurethane foam	NoFR-PU	Hardness grade 130; density 22 kg m ⁻³ ; used in BS 5852–1 test of upholstery fabrics.	×
Combustion modified high resilience polyurethane foam	CMHR-PU	Hardness grade 190; density 33 kg m ⁻³ ; flame retardants tris(chloroisopropyl)phosphate (TCiPP) and melamine. Representative of typical PU foams used in headboards.	✓
Polyester wadding (polyethylene terephthalate) (PET)	PET 1	1200 g m ⁻² (30 kg m ⁻³) an alternative filling to PU foam.	✓
	PET 2	300 g m ⁻² (43 kg m ⁻³) a “comfort layer” used between the core filling and fabric.	✓
Non-fire retarded fabric	NoFR-Fab	Tweed textured polyester fabric (240 g m ⁻²) without flame retardant treatment.	×
Fabric with brominated flame retardant back coating	BrFR-Fab	Based on NoFR-Fab backcoated with a fire-retardant treatment containing decabromodiphenyl ethane (total area density 420 g m ⁻²).	✓
Fabric with expandable graphite flame retardant	EGFR-Fab	Based on NoFR-Fab with a thin layer of expandable graphite particles laminated between the fabric and a spunbond polyester backing fabric (total area density 340 g m ⁻²).	✓

upholstered furniture which they define as having a fabric cover and a soft filling. The sides of divan bed bases have a fabric cover, often matching other fabric on the bed, but no soft filling. Therefore, they are not upholstered, and hence not subject to regulation, and so any fabrics may be used, without flammability assessment.

Both the cigarette and match tests indicate pass or fail, but provide little understanding of the underlying fire behaviour. They give no information on the different fire retardant mechanisms operating, or how they affect the fire behaviour and smoke toxicity.

1.2. Scientific assessment of burning behaviour

Cone calorimetry provides a scientific assessment of a sample's burning behaviour under fairly realistic well-ventilated conditions. In addition to measuring the heat release rate (HRR) by oxygen depletion calorimetry, it also records sample mass, smoke opacity and carbon dioxide (CO₂) and carbon monoxide (CO) concentrations, each as a function of time during the test. It is essentially a 1-dimensional physical fire model which is well-suited to assessing the fire behaviour of layered composites, such as those used in upholstered furniture. However, care needs to be taken in preparing such composites to ensure that their heat transfer behaviour is comparable from one sample to another.

From 1993–1995 Sundström led a European Commission project [38,39] entitled “Combustion behaviour of upholstered furniture (CBUF) – fire safety of upholstered furniture – EUR 16477 EN” in response to upholstered furniture being a major contributor to European fire deaths. As part of this project Babrauskas and Wetterlund conducted 1270 individual tests on furniture composites (representative of real furniture pieces) in the cone calorimeter (ISO 5660) and compared them with the burning behaviour of upholstered furniture. This resulted in the development of “The CBUF Test Protocol”, a robust, repeatable protocol for assessing composite burning behaviour of fabric filling samples, using the cone calorimeter. The main advantages of this protocol are that it is a realistic test scenario, and it is capable of giving reproducible results. Initial experiments, using the cone calorimeter, made “cushions” for testing in a simpler, and more intuitive way. Unfortunately, the burning behaviour of these cushions could not be replicated from one test to the next. The additional reproducibility afforded by the CBUF protocol results from the compression of the fillings within the fabric shell being kept constant.

This work aims to investigate the effect of fire retardants in the fabric and filling of nine furniture composites using the CBUF protocol in the cone calorimeter. In addition to the HRR, the smoke toxicity of the nine furniture composites was measured during each test. Unlike the regulatory tests described above which

are valuable for ensuring compliance with the FFFSRs, the cone calorimeter has enabled us to undertake a scientific assessment of the various parameters quantifying the burning behaviour and toxic gas emissions.

2. Materials and methods

The fillings and fabrics used in this study are shown in Table 1. The components were selected so that a range of fabric-filling combinations used by the UK furniture and furnishings industry, had their fire behaviour investigated. Components were selected to be comparable to each other, and representative of typical composites used to construct headboards, and hence representative of typical upholstered furniture components which are compliant with the FFFSRs. The non-fire retarded polyurethane foam (NoFR-PU), which has a lower density than most upholstery foams, was the only CFR-free upholstery foam available in the UK. It is used as a filling when testing fabrics for compliance with the current furniture flammability regulations. The three fabrics were an untreated, and two fire retardant treated versions of the same material. All materials were provided by the Silentnight Group Ltd. (UK).

2.1. Sample preparation for cone calorimetry

Miniature cushioned pads consisting of a fabric, “comfort layer” (PET 2) and core filling were prepared in accordance with the CBUF Test Protocol [40] (Fig. 3). Core filling blocks of PU foam (both CMHR and No-FR), and PET 1, were nominally 40 mm thick. These fillings, along with PET 2 (18 mm uncompressed thickness), were cut square with 90° corners with face dimensions of 102.5 (± 0.5) mm × 102.5 (± 0.5) mm using a scalloped-blade knife. Fabrics were cut square to 200 (± 0.5) mm × 200 (± 0.5) mm. All fabrics and fillings were weighed to ensure that each piece was within 5 % of the mean weight of each sample type. Fabrics were then cut according to the pattern given in the protocol [38]. The masses of each component are shown in Table 2.

Forming blocks 98 mm × 98 mm × 50 mm, made from solid polyethylene, were used to ensure reproducibility of the fabric cover geometries. To form the fabric cover, the cut fabric (show-side of fabric facing up) was placed centrally under a forming block. A thin film of adhesive (Fabri-Tac; Abakhan Fabrics, UK) was applied to the 10 mm wide gluing area of the long-edged sides, then firmly pressed onto the short-edged sides. Two elastic bands were used to hold the glued edges in place under tension. The sample was then left for 24 h to allow the glue to dry. The bands were then removed and any fabric protruding from the bottom edge trimmed off with scissors. The forming block was removed

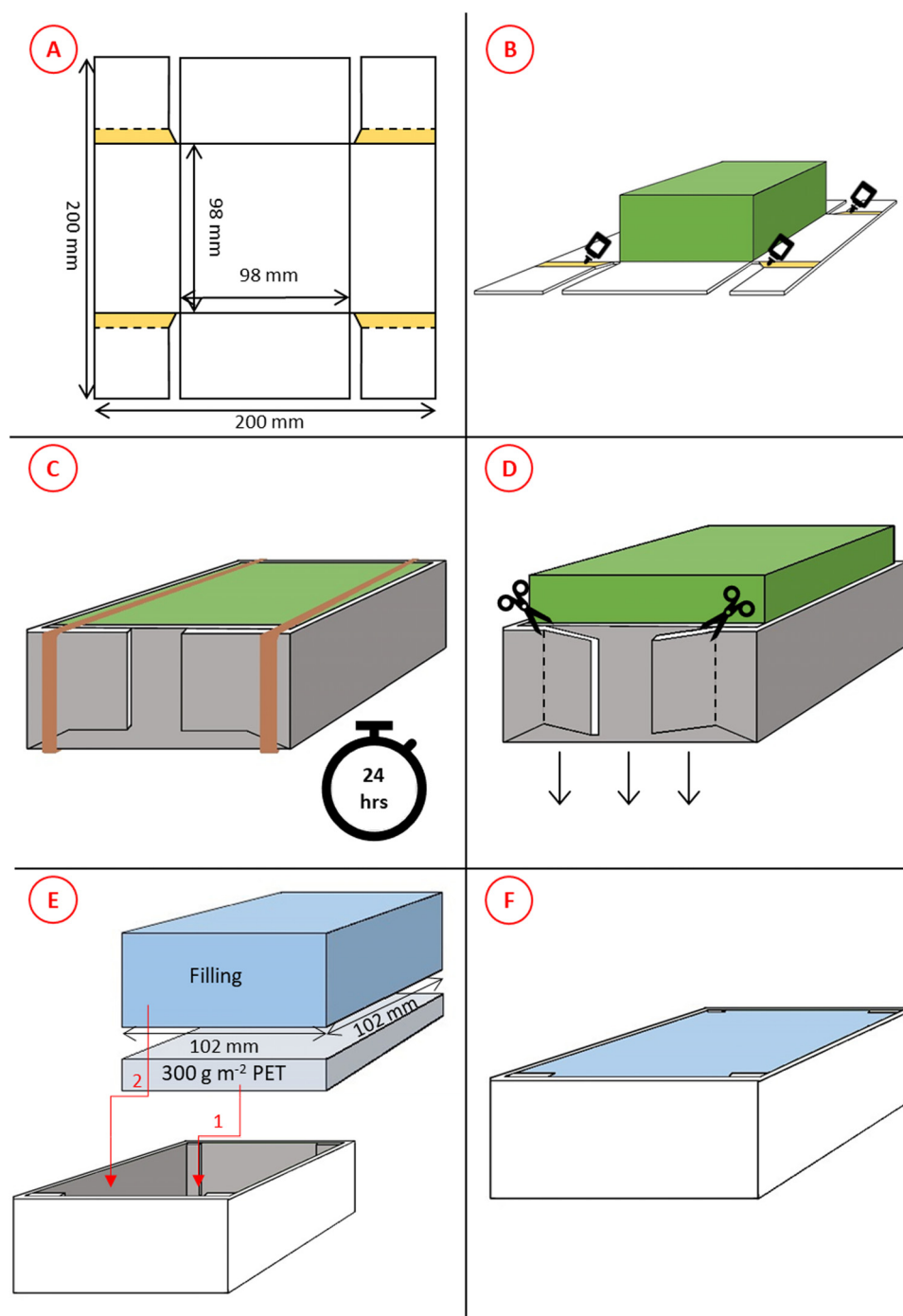


Fig. 3. Key stages of the sample preparation of fabric-filling composites for cone calorimetry. (A) Fabric is cut to a template. (B) Fabric is placed (show-side up) centrally under a forming block (green) and a thin film of adhesive is applied to the gluing area (yellow). (C) The short-edged sides of the fabric are folded up against the forming block followed by the long-edged sides, elastic bands are used to hold the glued edges in place and under tension. The sample is left for 24 h allowing the adhesive to dry. (D) The forming block is removed from the fabric cover, the loose tabs are removed from the fabric before the cover is turned out, so the show-side is facing out. (E) The fabric cover is filled with the comfort layer (PET 2) (light blue/grey) and core filling material (blue). (F) The 'cushion' (depicted upside down) is checked to ensure filling's corners align with the fabric covers, and the fabric is taut to the filling, without air pockets or twisting.

from the fabric shell, before cutting off the loose tabs and finally being turned inside out to hide the seam edges (Fig. 3(A–D)).

Fillings were placed within the fabric shell starting with the PET 2 “comfort layer”, followed by the core filling, ensuring that the corners of the fillings align with the fabric shells (Fig. 3(E)). Furthermore, care was taken to ensure that the shell was taut to the filling, without any twisting or air pockets. Finally, aluminium foil (thickness 0.03–0.04 mm) was used to wrap the samples such that only the square face of the specimen's fabric face was exposed.

2.2. Cone calorimetry

Cone calorimetry was carried out in triplicate and in accordance with ISO 5660, using an irradiance of 35 kW m^{-2} . The specimen was placed in the sample holder, without using the upper retaining frame, following the CBUF protocol. The end of the test was reached once all the following three criteria had been met; a minimum of 5 min had elapsed; flaming had stopped; the mass loss rate had dropped below $150 \text{ g m}^{-2} \text{ min}^{-1}$.

Table 2

Average sample masses of each material component as used in the cone calorimetry samples.

Component material	Component mass (g)
NoFR-PU	11.5 ± 0.2
CHMR-PU	17.4 ± 0.4
PET 1	14.8 ± 0.5
PET 2	3.3 ± 0.1
NoFR-Fab	12.1 ± 0.1
BrFR-Fab	16.8 ± 0.2
EGFR-Fab	14.4 ± 0.2

Additional gas sampling was carried out by drawing a metered volume of effluent gas collected at a depth of 450 mm below the mouth of the chimney stack during the test. The sampled gas was drawn through two sets of two bubblers, in sequence, to trap individual toxic components. Each set was pumped for 5 min at a flow of 1 L min⁻¹, once sustained flaming has commenced. The concentrations were determined using ion chromatography (HPIC) and a spectrophotometric technique for quantification of HCN [41], based on the methodology described in ISO 19701 [42].

2.3. Regulatory testing (BS 5852 and EN 1021)

In order to benchmark the fabric/filling combinations against the current British and European regulatory tests, each combination was tested for smouldering ignition and match ignition following the BS and EN standards. For compliance with EN1021-2, the actual composite was tested for 15 s with a 40 mm flame, in triplicate. For compliance with BS 5852, upholstery fabrics/fillings were tested in a composite using a defined “standard” filling/fabric (respectively). The “match” ignition flame of BS 5852 is also 40 mm, but it is kept in contact with the test piece for 20 s, and tested in duplicate.

3. Results and discussion

Table 3 shows the results of the benchmark testing. The NoFR fabric/noFR-PU foam combination was the only one which did not meet the current regulatory requirements. In every other case, the combinations tested resisted both cigarette and match ignition for 15 and 20 s.

3.1. Fire hazards: ignition and heat release

Initial cone calorimetry experiments on composites had shown poor reproducibility. Although more involved, the CBUF protocol gave reproducible results with good reproducibility. Representative Heat Release Rate (HRR) profiles and Smoke Production Rate (SPR)

profiles, selected from the triplicate test data of each composite are shown in Figs. 4 and 5, respectively.

The heat flux of 35 kW m⁻² was chosen to be greater than the thermal attack that a piece of furniture was designed to withstand, to ensure that all test pieces ignited, without being so large that it failed to differentiate the fire performance of different samples. In one case, BrFR-fabric/PET filling, ignition of the fabric, followed by collapse of the PET wadding, led to intermittent flaming. This makes quantitative comparison of fire performance with the other fabric-filling combinations more difficult.

Fig. 4 shows the representative heat release rate during burning for the nine fabric-filling combinations, while Table 4 summarises the average values of the main burning behaviour parameters for each test. Representative graphs were chosen through analysis of cone calorimetry data parameters in Tables S1–S3 (in Supplementary Information). The test run that resulted in the most median values was chosen for the representative graphs. It should be noted that initial sample density was not included as this parameter is derived from the initial sample mass. In instances where two runs had an equal number of median values, the test run that had the greatest number of median values for the parameters of Average HRR₁₈₀, Total Smoke, and CO Yield was chosen as the representative graph.

Fig. 4(a) shows the burning behaviour of the three fillings under the NoFR fabric. This shows very similar times to ignition for the two polyurethane foam fillings (NoFR-PU and CMHR-PU) of around 16 s, but a much longer time to ignition for the PET filling (105 s). The delayed ignition and burning of NoFR fabric/PET filling combination is due to both components of the composite being entirely composed of polyester, which melts and pools when exposed to the cone heater. This delays the volatilization and ignition of the composite. In each case, the peak heat release rates (pHRR) are similar, with the lower density NoFR-PU foam showing a higher peak at 430 kW m⁻² than either the CMHR-PU foam (364 kW m⁻²) or PET wadding (380 kW m⁻²).

Fig. 4(b) shows the burning behaviour of the three fillings under the BrFR fabric. The time to ignition is similar for the two polyurethane foams, at 14 s and 8 s for NoFR-PU and CMHR-PU respectively, and longer (26 s) for the PET. The time to ignition for the BrFR fabric in combination with PET fillings is significantly shorter than for the NoFR fabric. It was observed that the BrFR fabric retained its shape for longer than the NoFR fabric during the test. This may be due to the back-coating on the BrFR fabric adding rigidity, slowing collapse of the fabric, thus preventing it from shrinking away from the heat source. In each case, the pHRR is similar, and significantly lower than for the NoFR fabric. Surprisingly, the NoFR-PU foam shows consistently lower HRR than the CMHR-PU foam, while the PET ignites then extinguishes, reigniting at around 300 s, presumably due to the post ignition melting and collapse of the PET wadding.

Table 3

Results of the fabric-filling combination when tested to regulatory furniture flammability test procedures.

Fabric-filling composite	Smouldering Ignition Source (BS 5852, EN 1021-1)	Match Flame Equivalent Ignition Source 15 s exposure (EN 1021-2)	Match Flame Equivalent Ignition Source 20 s exposure (BS 5852)
NoFR-Fab/NoFR-PU	Pass	Fail	Fail
NoFR-Fab/CMHR-PU	Pass	Pass	Pass*
NoFR-Fab/PET	Pass	Pass	Pass*
BrFR-Fab/NoFR-PU	Pass	Pass	Pass
BrFR-Fab/CMHR-PU	Pass	Pass	Pass*
BrFR-Fab/PET	Pass	Pass	Pass*
EGFR-Fab/NoFR-PU	Pass	Pass	Pass
EGFR-Fab, CMHR-PU	Pass	Pass	Pass*
EGFR-Fab, PET	Pass	Pass	Pass*

* 20 s exposure to match flame equivalent ignition source is in line with BS 5852. However, if BS 5852 had been followed for the 20 s flame exposure test, the fabric would have been tested directly over NoFR-PU filling, not the filling specified in the table.

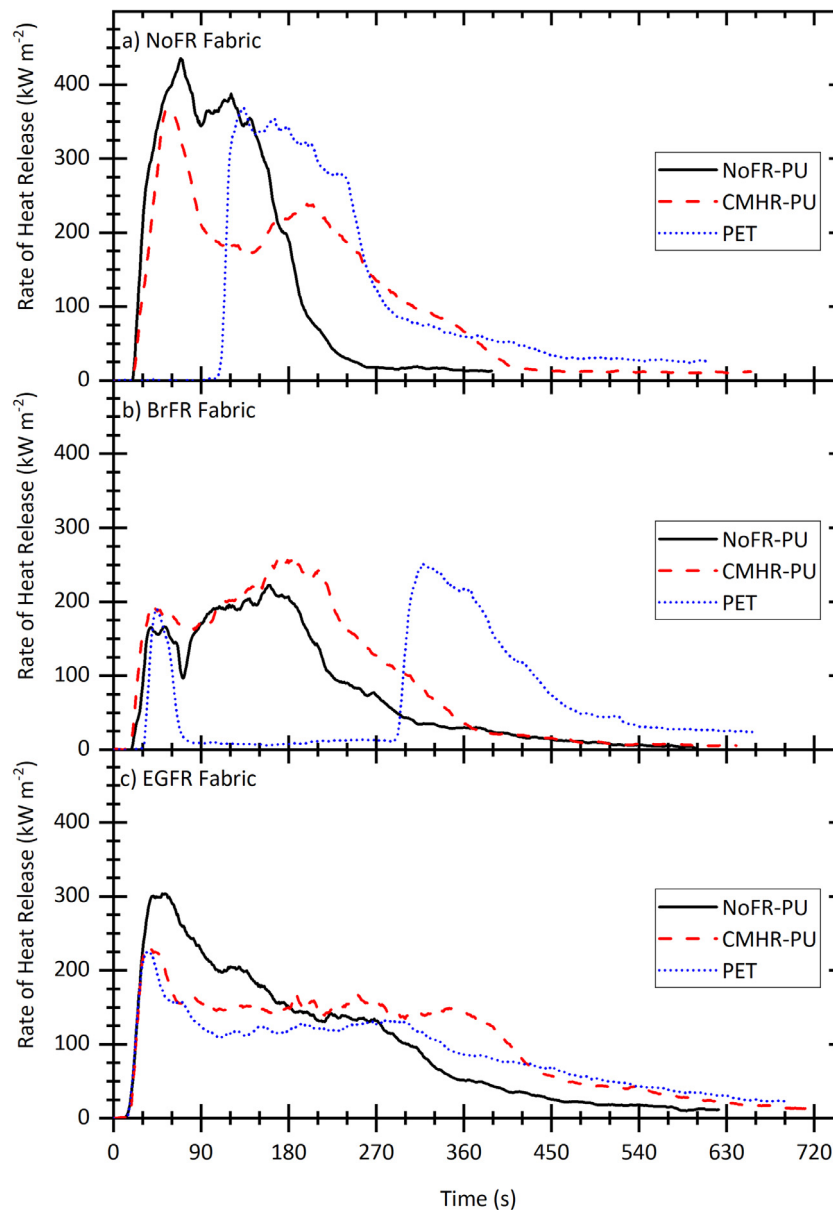


Fig. 4. Representative Rate of Heat Release profiles of the three fabrics: (a) NoFR Fabric, (b) BrFR Fabric, (c) EGFR Fabric over the three different fillings: NoFR-PU foam, CMHR-PU foam and PET wadding.

Fig. 4(c) shows the HRR of the three fillings when covered by the EGFR fabric. In this case, all fabric-filling combinations show very similar times to ignition and fire growth rates. However, while the PET and CMHR-PU foam reach a peak of around 230 kW m^{-2} , the NoFR-PU foam reaches a peak of 300 kW m^{-2} . The total heat releases in each case are fairly similar.

For both the NoFR and EGFR fabric covered samples (Fig. 4(a) and (c)), the HRR increases rapidly following ignition, reducing the pHRR within 60 s. For the BrFR covered samples (Fig. 4(b)), the pHRR occurs later, reaching a lower maximum value. This is likely to be due to the generation and consequent exhaustion of HBr from the BrFR during the initial 90 s of exposure to the cone heater. As a result, the pHRR is delayed until release of HBr is complete, and the fillings are burning alone. Comparing the total heat release (THR) of the three fabric coverings (THR is the area under the curves in Fig. 4 and presented as averages in Table 4), the BrFR fabric covered samples show consistently lower THR compared to the NoFR and EGFR covered samples, while the mass loss was simi-

lar, at around 90 % for all the samples. This demonstrates that BrFR reduces the HRR compared to NoFR and EGFR, without increasing the char/residue yield, indicating gas phase flame quenching. This is likely to be due to the Br· radical from the BrFR interfering with the radical flame reaction, reducing the availability of OH· radicals, and so inhibiting the main heat release step [43] (Eq. (1)). However, by inhibiting the reaction shown above, it increases the yield of the asphyxiant CO (and coincidentally the other main asphyxiant HCN). The yields are shown in Table 4.



Based on the extensive test programme of 225 large-scale and 1270 Cone Calorimeter tests in the CBUF project, Sundström [39] argued that furniture composites which exhibited an average $\text{HRR}_{180} \leq 65 \text{ kW m}^{-2}$ when exposed to a 35 kW m^{-2} radiant heat source in the cone calorimeter were obtained from fabric-filling combinations from upholstered seating that when burnt as

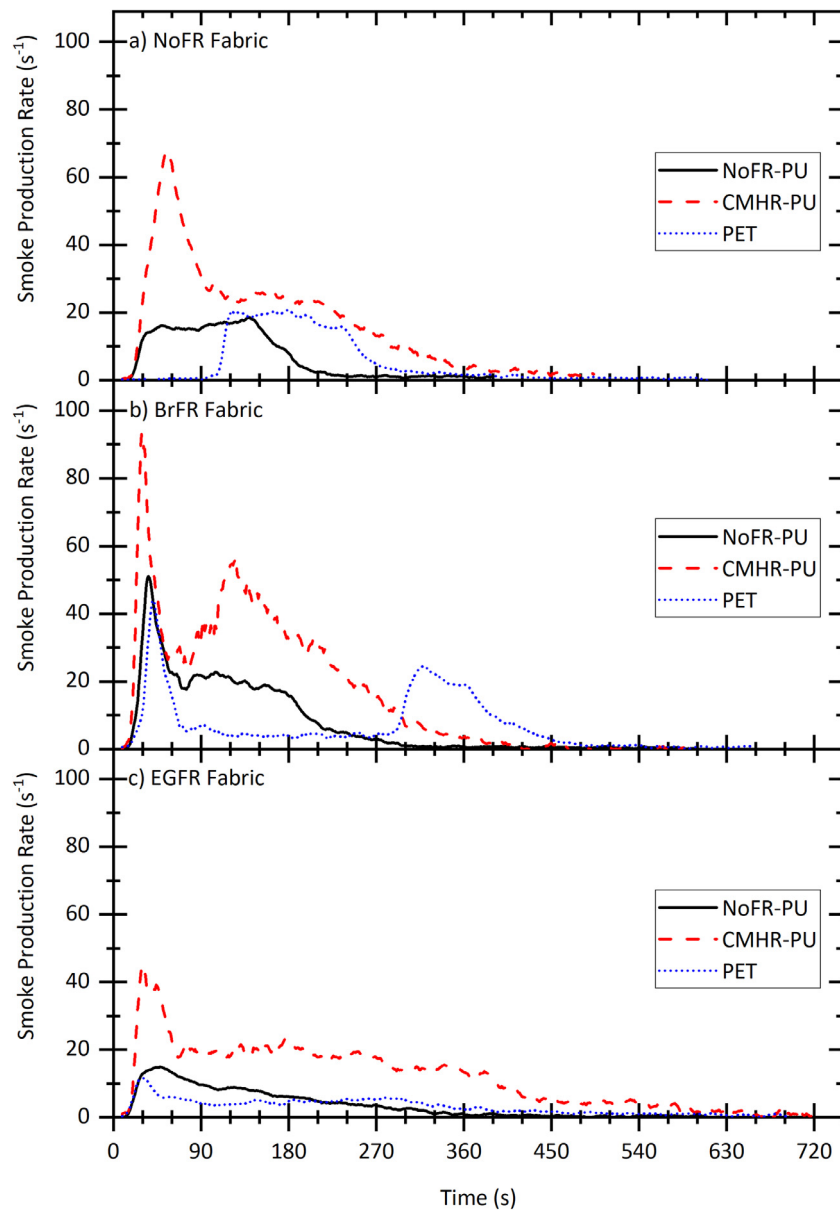


Fig. 5. Representative Smoke Production Rate profiles of the three fabrics: (a) NoFR Fabric, (b) BrFR Fabric, (c) EGFR Fabric over the three different fillings: NoFR-PU foam, CMHR-PU foam and PET wadding.

Table 4

Averaged cone calorimetry data ($n = 3$) where HRR is Heat Release Rate, and Average HRR₁₈₀ is the average heat release rate for the initial 180 s after ignition.

Fabric	NoFR	NoFR	NoFR	BrFR	BrFR	BrFR	EGFR	EGFR	EGFR
Filling	NoFR-PU	CMHR-PU	PET	NoFR-PU	CMHR-PU	PET	NoFR-PU	CMHR-PU	PET
Initial Sample Density (kg m^{-3})	53 ± 0.4	66 ± 0.6	60 ± 0.4	63 ± 0.6	74 ± 1.0	70 ± 1.2	58 ± 0.4	70 ± 1.0	65 ± 1.6
Initial Sample Mass (g)	26.7 ± 0.2	32.8 ± 0.3	30.0 ± 0.2	31.6 ± 0.3	37.2 ± 0.5	35.2 ± 0.6	28.9 ± 0.2	34.8 ± 0.5	32.7 ± 0.8
Residual Sample Mass (g)	1.9 ± 0.5	3.7 ± 0.8	2.8 ± 0.6	1.9 ± 0.3	3.9 ± 0.3	2.7 ± 0.3	2.3 ± 0.9	5.3 ± 0.4	3.3 ± 0.6
Mass Loss (%)	93 ± 1.8	89 ± 2.4	91 ± 2.0	94 ± 0.9	90 ± 0.8	92 ± 1.1	92 ± 3.1	85 ± 1.0	90 ± 1.1
Time to Ignition (s)	16 ± 1.1	16 ± 2.2	113 ± 19.6	14 ± 1.2	9 ± 3.5	27 ± 5.9	10 ± 0.8	11 ± 2.9	10 ± 2.6
Total Heat Release (MJ m^{-2})	60 ± 0.6	64 ± 1.8	59 ± 2.6	46 ± 2.1	58 ± 1.2	44 ± 4.4	69 ± 2.2	68 ± 2.7	62 ± 3.1
Average Effective Heat of Combustion (MJ kg^{-1})	24.2 ± 0.6	21.9 ± 0.9	21.6 ± 0.5	15.5 ± 0.5	17.5 ± 0.3	13.4 ± 1.0	22.5 ± 0.1	22.9 ± 0.7	21.1 ± 0.9
Initial Peak HRR (kW m^{-2})	463 ± 52	363 ± 11	378 ± 24	173 ± 10	208 ± 33	158 ± 22	305 ± 8	229 ± 9	238 ± 19
Time to Initial Peak HRR (s)	72 ± 8	58 ± 2	150 ± 17	47 ± 11	44 ± 8	46 ± 8	47 ± 4	38 ± 4	34 ± 3
Overall Peak HRR (kW m^{-2})	463 ± 52	363 ± 11	378 ± 24	234 ± 20	259 ± 53	253 ± 50	305 ± 8	229 ± 9	238 ± 19
Time to Maximum HRR (s)	72 ± 8	58 ± 2	150 ± 17	122 ± 26	159 ± 54	311 ± 56	47 ± 4	38 ± 4	34 ± 3
Average HRR ₁₈₀	301 ± 6	197 ± 15	253 ± 15	170 ± 17	179 ± 25	32 ± 8	198 ± 14	170 ± 13	133 ± 4
FIGRA "Line" ($\text{kW m}^{-2} \text{s}^{-1}$)	7.6 ± 0.3	6.6 ± 0.2	2.5 ± 0.4	5.2 ± 0.4	5.9 ± 0.7	3.8 ± 0.8	8.0 ± 0.5	7.0 ± 0.8	7.8 ± 0.5
FIGRA ($\text{kW m}^{-2} \text{s}^{-1}$)	6.5 ± 1.2	6.2 ± 0.3	2.4 ± 0.4	2.0 ± 0.5	1.7 ± 0.6	0.8 ± 0.2	6.3 ± 0.6	6.2 ± 0.7	7.1 ± 0.7
Total Smoke (m^2/m^2)	2620 ± 41	8328 ± 427	2952 ± 156	4415 ± 52	11,295 ± 884	4556 ± 301	2247 ± 271	8356 ± 270	2292 ± 364
CO Yield (mg/g)	41 ± 6	62 ± 11	68 ± 5	125 ± 20	229 ± 37	118 ± 25	60 ± 10	82 ± 24	37 ± 9
HCN Yield (mg/g)	1.3 ± 0.1	3.2 ± 0.03	0.11 ± 0.03	5.8 ± 0.4	7.8 ± 0.3	0.14 ± 0.04	1.1 ± 0.1	2.6 ± 0.3	0.14 ± 0.04

full-scale furniture items could be considered safe in most situations. However, this finding only applied to upholstered seating, and the testing did not take smoke toxicity into consideration. The average heat release rate for the 180 s after ignition (Avg HRR₁₈₀) is shown in Table 4. Only the BrFR fabric covering the PET filling exhibited such a low Avg HRR₁₈₀, due to the self-extinguishing of the flame after the initial 60 s. This is thought to be due to a combination of the added rigidity from the fabric backcoating, gas phase FR inhibiting heat release and fire growth and the large difference between melting and combustion temperatures of PET wadding. The rigidity of the backcoating stops the fabric from collapsing when the PET wadding melts, allowing the fabric to ignite, but shielding the molten PET from radiant heat. The BrFR slows the fire growth rate causing self-extinguishment of the fabric. Reignition occurs when the molten PET reaches its ignition temperature (typically 270 s to 300 s after the start of the test).

The fire growth rate (FIGRA) is defined as the ratio of HRR to elapsed test time. Here FIGRA is given for the pHRR at the corresponding time. However, a “FIGRA line”, derived from the HRR profile, is the gradient of the straight line from the origin to the earliest, highest point on the HRR profile. The FIGRA line is often greater than the overall FIGRA, most notably for the BrFR fabric covered samples.

3.2. Fire hazards: smoke and toxic gases

Smoke is a hazard in itself, obscuring means of escape. It is also a good indicator of incomplete combustion. The evolution of smoke is dependent on the composition and burning behaviour of both the fabric and the filling. Similarly, CO and HCN, as the main asphyxiant gases, initially prevent escape by causing incapacitation, before causing death by starving the body of oxygen. CO and HCN are both products of incomplete combustion. Although not assessed in the current work, smoke opacity and smoke toxicity usually increase significantly with under-ventilation [44,45].

Fig. 5 and Table 4 show the total smoke for each fabric-filling combination. The CMHR foam consistently shows the greatest smoke evolution, as both a higher peak and a greater total. The NoFR foam and the PET show broadly similar smoke evolution. The BrFR fabric consistently shows higher peak and total smoke, the NoFR fabric shows lower peak and total smoke, while the EGFR shows the lowest smoke. The highest smoke comes from the BrFR fabric and CMHR foam combination.

Fig. 6 and Table 4 show the carbon monoxide (CO) production rate, CO yield and hydrogen cyanide (HCN) yield. The most notable feature in Fig. 6 is the three to six fold increase in the CO production rate for all samples covered with the BrFR fabric, compared to the NoFR or EGFR fabrics. This is clearly a consequence of the flame retardant mechanism of BrFR, quenching the flame reactions prior to the formation of carbon dioxide, leading to much higher yields of CO, as discussed at the end of the ignition and heat release section. There is a broadly similar trend in the CO production rate and the smoke production rate, although the consistently greater smoke evolution of the CMHR foam is not mirrored in the CO production rate data, despite both smoke and CO being products of incomplete combustion. The samples filled with CMHR foam have amongst the highest CO yields, although the CO yield is slightly higher for PET with a NoFR cover than for CMHR foam with a NoFR cover. For the HCN yield, clearly, nitrogen is abundant in the polyurethane foam and therefore significant yields of HCN would be expected and were observed from the NoFR and the CMHR foams. These consistently exceeded the HCN yields for the PET filled samples. In the absence of halogens in the fabric, there is a factor of 2.5 increase in the HCN yields for the CMHR

foam, compared to the NoFR foam. This difference is too large to be explained by the different masses of the different foams and suggests gas phase inhibition by the TCiPP. In the presence of the BrFR fabric, the HCN yield rises further, increasing by a factor of 4 to 5 for the NoFR foam and by a factor of around 3 for the CMHR foam. As in the case of the smoke, the highest CO and HCN yields are found from BrFR fabric and CMHR foam combinations. Again, this suggests that halogen-based CFRs are increasing the yield of the main asphyxiants, CO and HCN.

The smoke production shown in Fig. 5 does not mirror heat release rate (Fig. 4), although peak shapes are similar. The smoke production rate is much greater for samples containing CMHR foam, showing a larger initial peak for BrFR for all combinations.

Fig. 6 shows that the CO production rate is strongly affected by fabric, but less by filling. The CO production from CMHR-PU is almost twice that of NoFR-PU foam or PET filling with noFR-fabric. The initial peak is very large and similar for all three fillings when covered with BrFR fabric. Both the peak and steady burning concentrations of CO are very low and similar for the NoFR-foam and CMHR foam when covered with EGFR fabric, with PET filled EGFR around three times lower.

3.3. Prediction of toxic effects

The toxicity of a fire effluent can be expressed as a Fractional Effective Dose (FED), based on its chemical composition. When FED = 1 %, 50 % of a healthy, adult exposed population would be predicted to suffer incapacitation or death. ISO 13571 [46] stipulates the use of Eq. (2) for estimation of incapacitation by the asphyxiant gases carbon monoxide (CO) and hydrogen cyanide (HCN):

$$FED = \left\{ \sum_{t_1}^{t_2} \frac{[C, O]}{350, 00} \Delta t + \sum_{t_1}^{t_2} \frac{[HCN]^{2.36}}{1.2 \times 10^6} \Delta t \right\} \times V_{CO_2} \quad (2)$$

Gas concentrations in [] are expressed in $\mu\text{L L}^{-1}$ or ppm; time (t) is in minutes. Eq. (3) from ISO 13344 [47] provides an estimation of lethality for a 30-minute exposure, using the ratio of each toxicant concentration to its lethal concentration (LC₅₀). An acidosis factor, Z_a, is included to account for CO₂ toxicity via acidosis. Carbon dioxide (CO₂) increases respiration rate and so a multiplication factor for CO₂-driven hyperventilation, V_{CO₂}, is included in both calculations. AGI are acid gas irritants and OI are organic irritants, for which data were unavailable in the current work.

$$FED = \left\{ \frac{[CO]}{LC_{50, CO}} + \frac{[HCN]}{LC_{50, HCN}} + \frac{[AGI]}{LC_{50, AGI}} + \frac{[OI]}{LC_{50, OI}} \dots \right\} \times V_{CO_2} + Z_a + \frac{21 - [O_2]}{21 - 5.4} \quad (3)$$

$$V_{CO_2} = 1 + \frac{\exp(0.14[CO_2]) - 1}{2} \quad (4)$$

The acidosis factor Z_a = [CO₂] × 0.05. O₂ and CO₂ concentrations are expressed in vol.%. The concentration of the other toxicants is in $\mu\text{L L}^{-1}$ or ppm.

Eq. (2) has been used to assess the potential for the smoke from each fabric-filling combination to cause incapacitation, as shown in Fig. 7. These estimates have been based on a specific scenario, of a headboard burning and the smoke filling a house. The prediction is based on the fabric and filling of a single bed headboard (69 cm × 90 cm × 5 cm) burning completely, but not involving the wooden frame. Uniform dispersal of the effluent into 140.3 m³ was assumed, representing a single storey, 2 bed, 3 person occupancy dwelling, as described in Technical Housing Standards – Nationally Described Space Standard [48]. In this scenario, only the BrFR fabric in combination with CMHR PU has a fractional effective dose

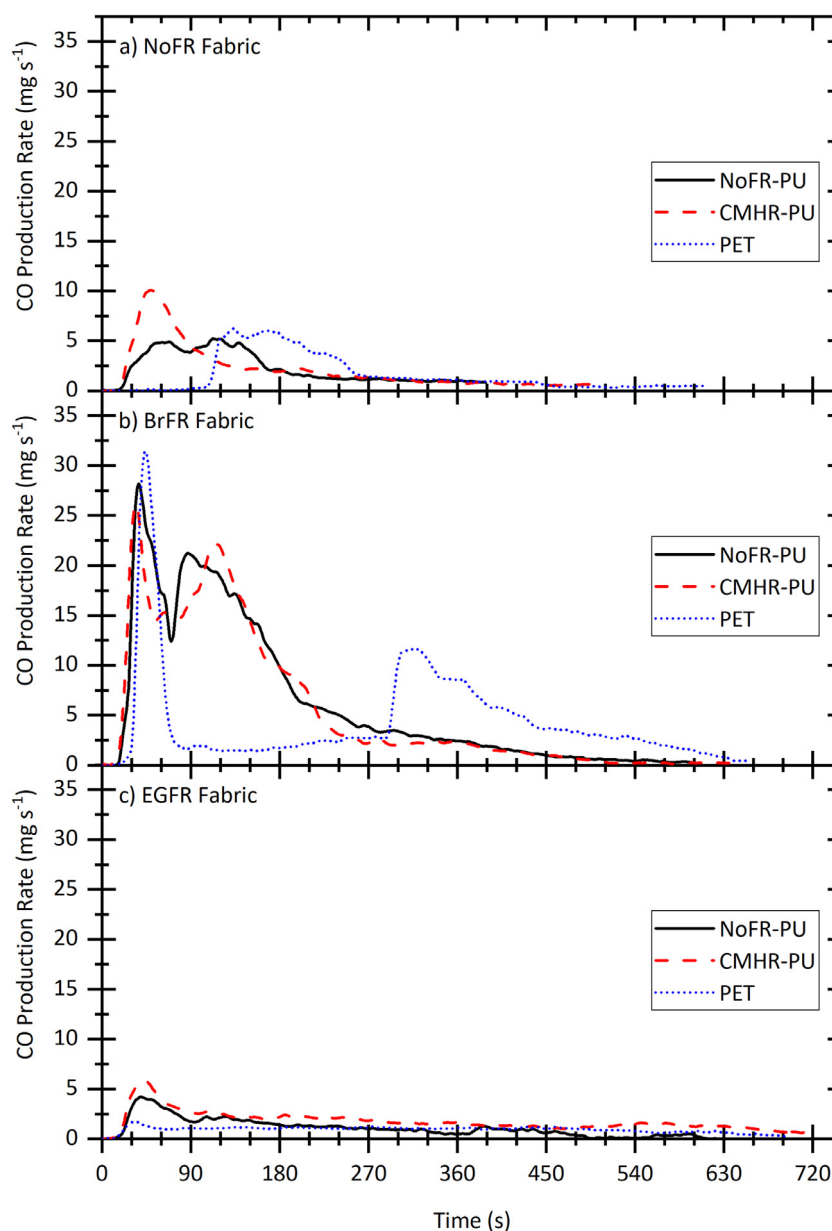


Fig. 6. Representative CO Production Rate profiles of the three fabrics: (a) NoFR Fabric, (b) BrFR Fabric, (c) EGFR Fabric over the three different fillings: NoFR-PU foam, CMHR-PU foam and PET wadding.

(FED) greater than 1. Unfortunately, this fabric filling combination is the most common in upholstered furniture items (headboards, sofas, etc.) which are compliant with the current FFFSRs, showing how small the extent of a fire needs to be before it makes the surrounding atmosphere so toxic that escape is no longer possible. The incapacitative effect of HCN is not proportional to dose, but rises very rapidly as the HCN concentration exceeds 100 ppm. In the predictions described here, most HCN concentrations are below that critical threshold. Incapacitation by asphyxiants leads to loss of consciousness, but respiration continues. Thus, unless rescued, the victim is likely to continue to inhale toxic gases until they are killed by them.

Fig. 8 shows the estimated FED for lethality for 30 min exposure to the effluent using Eq. (3). In the case of lethality, the effects of CO and HCN are dose dependent, thus a smaller amount of HCN has a greater impact on lethality than incapacitation. However, this situation would be reversed if a 70 m³ volume for effluent dilution, or a double bed-sized headboard had been used in the prediction.

Typical irritant gases in upholstery fires are volatilised acids such as HCl, HBr, H₂PO₄, and H₂SO₄ [49]. The source of these gases in upholstery fires may originate from the combustion of CFRs (e.g. TCiPP generating HCl and H₃PO₄). These gases were also measured but have been omitted from this report. This is due to a large and inconsistent variation in the concentration of these gases. In particular, bubbler solutions collected from burning composites that contained no halogens contained relatively high concentrations of halogen acids. This is thought to be due to the hygroscopic nature and relatively low dew point temperatures of these gases, which allowed them to condense onto soot particles and flue of the cone calorimeter. As the flue warmed up during subsequent tests, these soot particles released their absorbed gases, resulting in the inconsistencies described above. There is also a possibility that some HCN was adsorbed and subsequently released onto soot particles prior to being sampled from the exhaust duct. However, the HCN yields in Table 4 show small variation from run to run and show the

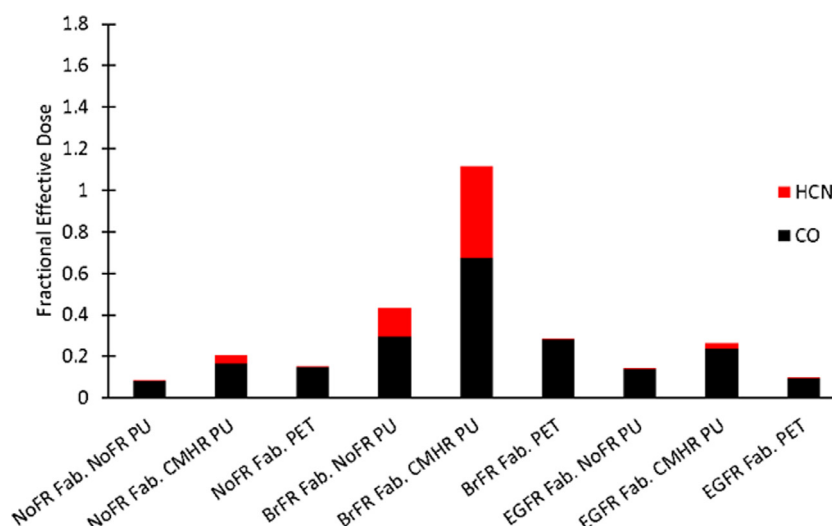


Fig. 7. Fractional Effective Dose for incapacitation at 300 s, assuming a single headboard (69 cm × 90 cm × 5 cm) in a total volume of 140.3 m³.

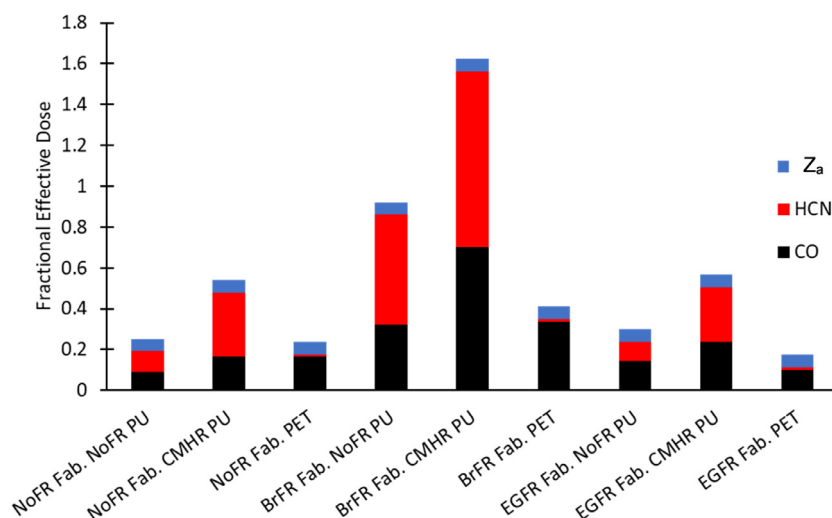


Fig. 8. Fractional Effective Dose for lethality, assuming full combustion of a single headboard (fillings and fabric dimensions 69 cm × 90 cm × 5 cm) in a volume of 140.3 m³ and 30 min exposure. Z_a is the acidosis factor.

highest yields with the combinations of PU foam and BFR fabric, as expected.

4. Conclusions

This study has investigated the controlled burning behaviour of nine fabric-filling combinations under a constant heat flux of 35 kW m⁻². A cone calorimeter, capable of independently quantifying a range of fire parameters, was used to obtain a scientific assessment of the influence of composite composition and flame retardant performance on the fire hazard. In order to test composites effectively and reproducibly, the CBUF protocol, developed in the 1990s, was successfully resurrected and found to be well-suited to the task. In addition to quantifying the burning behaviour, the smoke toxicity from the main asphyxiant gases, under well-ventilated conditions was also assessed.

The work shows that for the upholstered furniture fabric-filling composites used here, their fire performance is better than indicated by the regulatory compliance testing applied to the individual components. This demonstrates that with appropriate selection of components, chemical FR loading can be reduced while maintaining fire safety. It also shows that certain gas phase flame retardants approximately double the yields of the two main as-

phyxiants, while using expandable graphite in upholstery fabrics achieves compliance with the Furniture and Furnishing Fire Safety Regulations (1988) without increasing smoke toxicity.

For all the composites, the total heat release varied from 46 MJ m⁻² to 68 MJ m⁻² while the time-to-ignition (tti) ranged from 8 s to 105 s and pHRR from 230 kW m⁻² to 430 kW m⁻². The composite filled with PET showed the longest tti while the expandable graphite fabric on the fire retardant (FR) foam showed the lowest pHRR. The composite with the brominated FR fabric and the FR polyurethane foam had the shortest tti, the greatest smoke, the second highest carbon monoxide yield and the highest hydrogen cyanide yield. The composite with the non-FR fabric treatment and the polyester filling had the longest tti. For all the fabrics, the transition from non-FR to FR foam resulted in significant increases in the smoke, CO and HCN yields, except that the CO yield from the brominated fabric and FR foam was slightly lower than that of the non-FR foam. The results show very clearly that focusing regulatory requirements on ignitability rather than heat release and smoke toxicity fails to discriminate between the safest and the least safe fabric-filling combinations.

These results help to explain why 50 % of UK fire related casualties are due to smoke and toxic gas inhalation. Switching from problematic gas-phase FRs to either condensed phase FRs like

expandable graphite or less ignitable materials like PET could help reduce the number of fire deaths while continuing to deliver the enhanced fire safety that the current FFSRs are claimed to provide. However, the fractional effective doses reported in Figs. 6 and 7 are only indicative of a well-ventilated fire, due to the open nature of the cone calorimeter fire model. In a dwelling fire, as the fire grows, but the ventilation (from a doorway or window) remains fixed, the carbon monoxide and hydrogen cyanide yields increase [50], resulting in higher incapacitation and lethality fractional effective doses.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: This work was undertaken when Dr Jacob Lane was employed at University of Central Lancashire. He is now employed by Silentnight Beds Ltd. We do not believe there is any conflict of interest. We are declaring this information to ensure full transparency.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jmst.2024.02.034](https://doi.org/10.1016/j.jmst.2024.02.034).

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