Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Journal of Materials Chemistry A RSCPublishing

SUPPLEMENTAL INFORMATION

Iron-containing, High Aspect Ratio Clay as Nanoarmor that Imparts Substantial Thermal/Flame Protection to Polyurethane with a Single Electrostatically-deposited Bilayer

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Butane torch testing is a qualitative screening tool used to assess nanocoatings before coated samples are sent for cone calorimetry testing. Fig. S1 shows images of foam coated with both nanobrick wall thin films before (top row) and after torch testing (2nd row: top-down, 3rd row: torch side, 4th row: bottom, 5th row: cross-section). Standard, uncoated polyurethane foams melt away from the flame and instantly ignite. As depicted, all coated foams prevented melt dripping. The torch flame burrowed holes in all samples except 4 BL MMT-coated foams. Both 4 BL samples retained their original shape and protect a portion of the coated foam from the flame (white, undamaged polyurethane). These images of samples after torch testing indicate that fire performance increases with nanocoating weight addition for both MMT and VMT nanobrick wall thin films. Cone calorimetry testing quantitatively assesses heat release and flammability, through oxygen-consumption calorimetry, by exposing samples to heating rates that mimic fire conditions. Table S1 includes cone calorimetry results for control polyurethane and polyurethane coated with 1, 2, and 4 BL of MMT- and VMT-based nanobrick wall (vermiculite HTS-SE) thin films. Unlike MMT-based nanobrick wall systems, fire performance of polyurethane coated with 4 BL VMT-based nanocoatings are very similar to 2 BL VMT-HTS-SE systems. These results suggest the addition of polymer/clay layers does not always provide enhanced heat shielding.

Fig. S2 shows weight loss as a function of temperature in air atmosphere for control foam and foam coated with nanobrick wall thin films (Fig. S2a). Fig. S2b shows coating weight (% add-on) before thermogravimetric analysis and the remaining % residue at 400 ℃, 500 ℃, and 600 ℃. The final mass of the coated materials at each temperature is greater than the weight addition of the nanobrick wall nanocoatings on the polyurethane foam, suggesting the thin film does alter the degradation cycle of polyurethane, preserving some of the foam.

Fig. S3 shows top-down and cross-sectional SEM micrographs of both 1 BL nanobrick wall systems and 4 BL MMT-coated samples after cone calorimetry testing, along with corresponding energy-dispersive X-ray spectroscopy (EDX). SEM images highlight how the single bilayer MMT-coated foam shrank during burning. After cone calorimetry testing, all coated samples displayed elemental peaks of carbon, nitrogen, oxygen, magnesium, aluminium, and silicon (non-coated polyurethane foam spectrums display peaks of carbon, nitrogen, and oxygen). VMT-coated samples additionally showed elemental peaks of iron and potassium. Phosphorous was not detected. Some MMT-coated samples had traces of calcium, iron, and tin, but all contained sodium. EDX spectra was obtained using an accelerating voltage of 7 kV. These samples were evaluated without the conductive platinum/palladium sputter coating due to the overlap of spectral identification peaks of P and Pt.

Fig. S4 and Table S1 show heat release rate curves (and corresponding fire performance data) for control foam and foam coated with 1 and 2 BL nanobrick wall thin films comprised of two types of vermiculite (vermiculite HTS-SE and vermiculite 963++). Vermiculite 963++ slurry does not contain chemical additives. All four HRR curves are representative of thermally thick charring materials, which display an initial high HR and then the HRR plateaus before terminating. Both 2BL VMT-based systems have lower overall flammability and smoke release than 1 BL VMT-based systems. Final chars of VMT-coated polyurethane retain their original shape and are black and fluffy. Nanobrick wall thin films with VMT-963++ as bricks have a slightly higher initial peak heat release rate for both 1 and 2 BL systems, but there is negligible change in THR. Although the silicone binder is reported to reduce smoke release at higher temperatures, it is more reasonable to assume that the performance difference in TSR for VMT-HTS-SE and VMT-963++ is related to nanocoating weight addition.

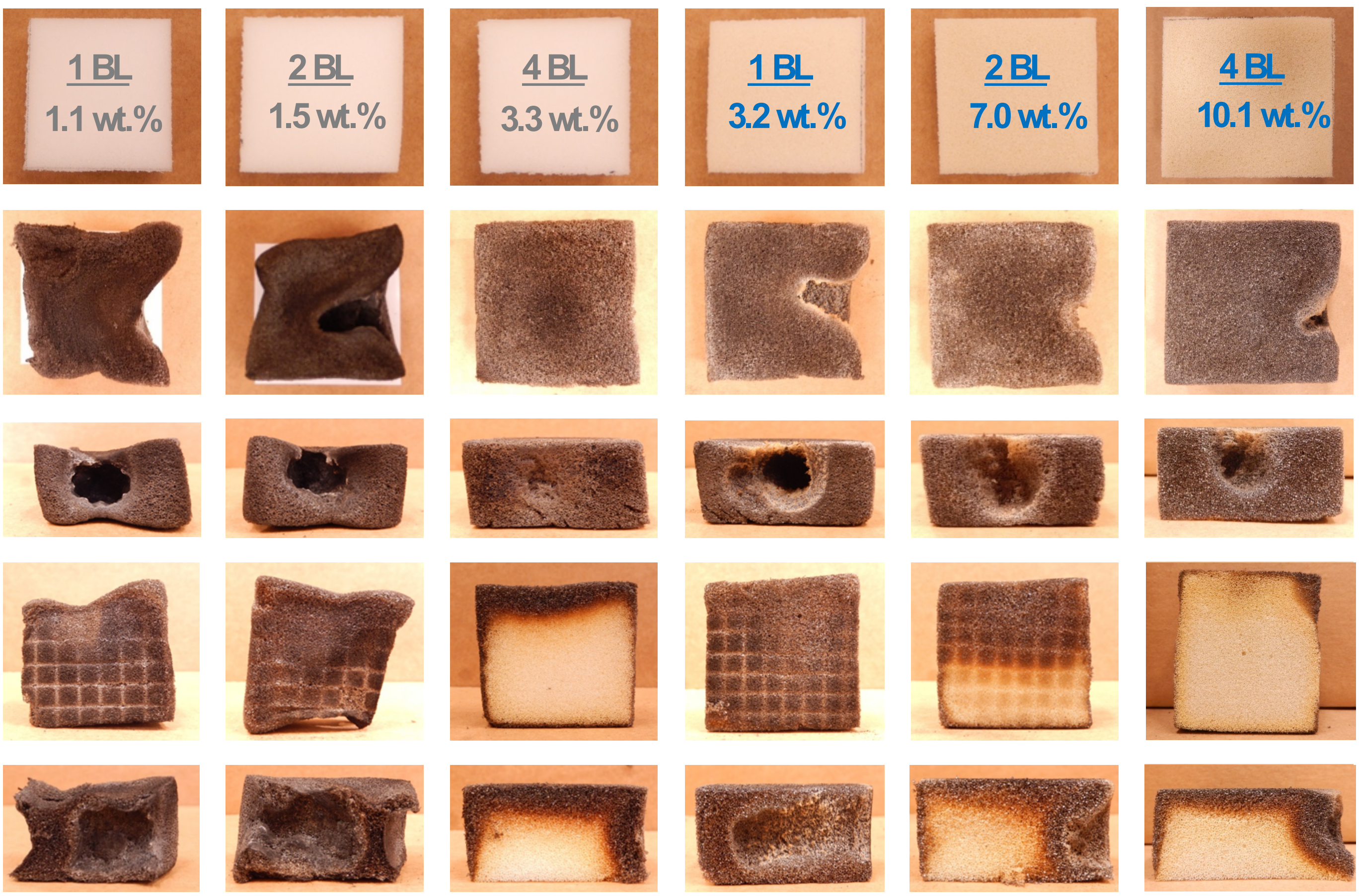

Fig. S1 Images of nanobrick wall coated polyurethane before (top row) and after 10 s of direct exposure to a flame from a butane torch.

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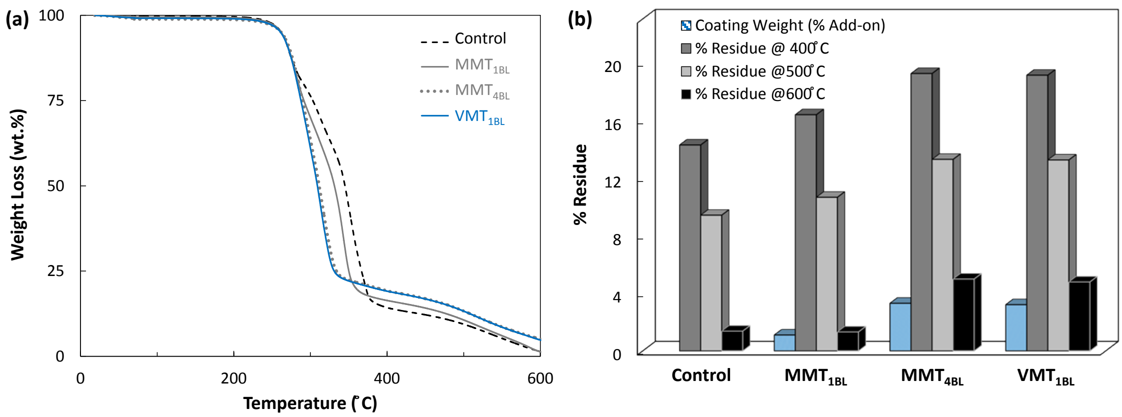

Fig. S2 a) Weight loss as a function of temperature in air atmosphere for control foam and foam coated with nanobrick wall thin films. b) Percent residue of control and coated polyurethane foam samples at 400℃, 500℃, and 600℃.

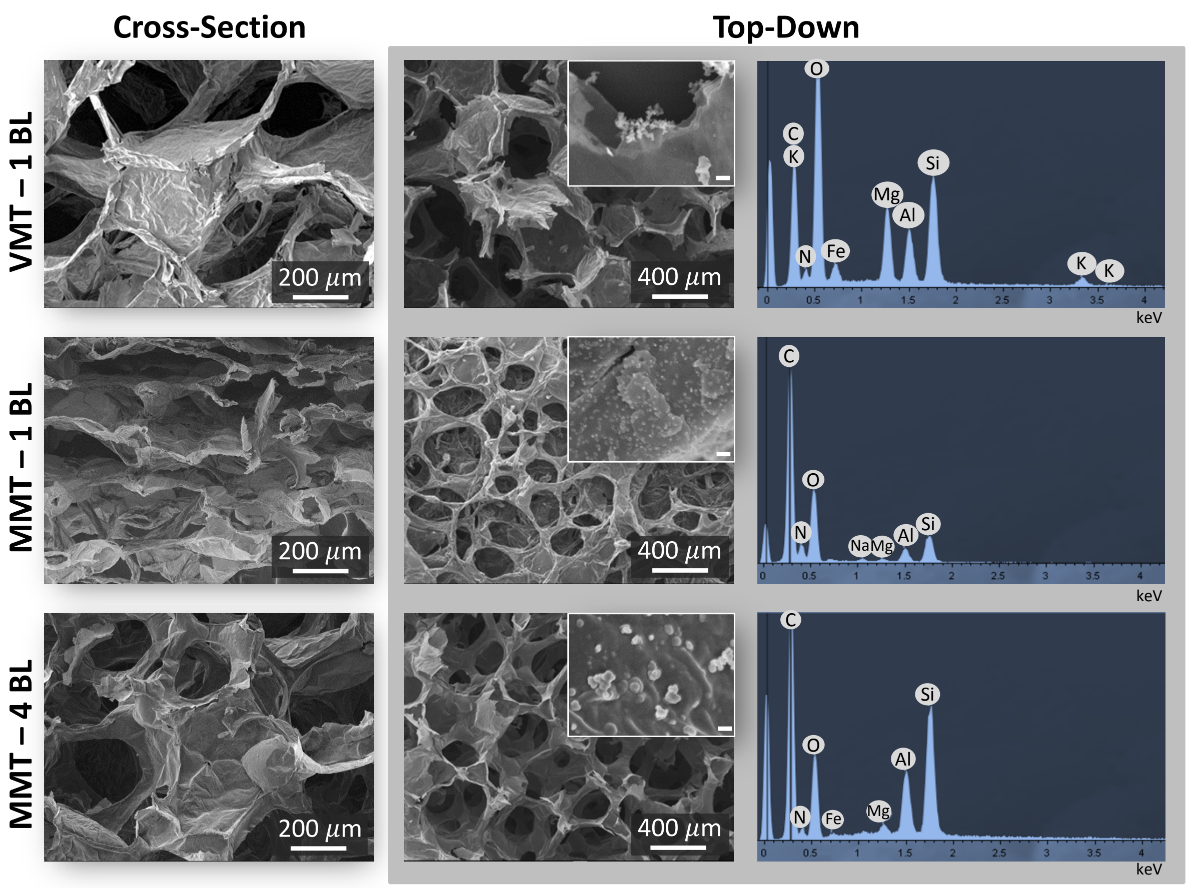

Fig. S3 SEM images of foam coated with a single VMT layer, a single MMT layer, and a 4 BL MMT-based coating. The scale bar in the inset is 200 nm. EDX spectra of nanobrick wall coated foam after cone calorimetry testing.

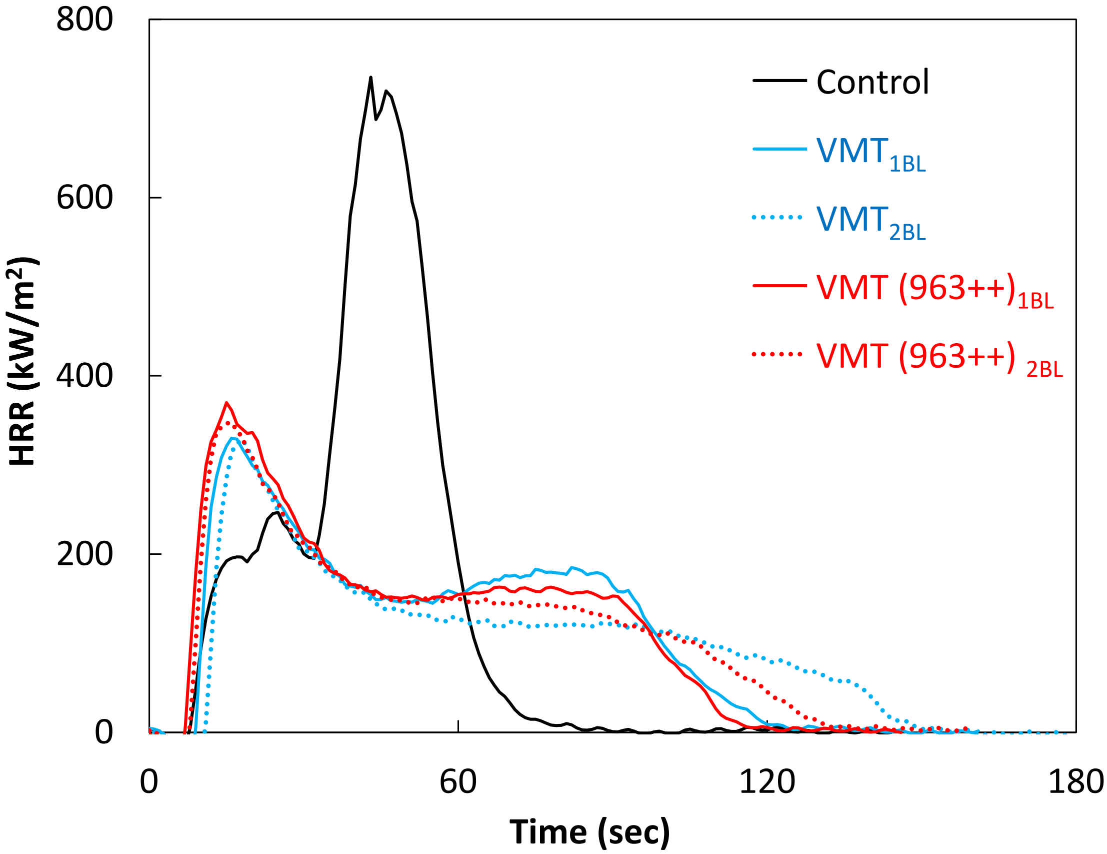

Fig. S4 Heat release rate as a function of time for control foam and foam coated with nanobrick wall thin films as a function of the number of layers deposited. 1 and 2 BL nanobrick wall thin film were comprised of two types of vermiculite (blue: vermiculite HTS-SE and red: vermiculite 963++).

Table S1. Cone calorimeter results for polyurethane foam samples.

Sample [units]	Wt. Gain [%]	pkHRR[a)] [kW m^{-2}]	THR[b)] [MJ m^{-2}]	Wt. Lost [%]	TSR[c)] [m^2 m^{-2}]	MARHE[d)] [kW m^{-2}]
Control		735 ± 11	19.5 ± 0.2	100	146 ± 4	318 ± 5
$(PEI/VMT)_1$	3.2 ± 0.2	339 ± 12	17.9 ± 0.6	87 ± 7	101 ± 12	195 ± 11
$(PEI/VMT963{+}{+})_1$	4.1 ± 0.1	378 ± 18	18.0 ± 0.2	92 ± 8	88 ± 4	220 ± 13
$(CH/VMT)_2$	7.0 ± 0.4	322 ± 7	17.1 ± 0.5	89 ± 1	61 ± 1	178 ± 4
$(CH/VMT963{+}{+})_2$	5.5 ± 0.3	344 ± 4	17.6 ± 0.4	91 ± 0	73 ± 3	198 ± 4
$(CH/VMT)_4$	10.1 ± 0.4	325 ± 22	16.7 ± 0.6	85 ± 2	57 ± 2	177 ± 13

[a)]pkHRR = peak heat release rate; [b)]THR = total heat release; [c)]TSR = total smoke release; [d)]MARHE = maximum average rate of heat emission

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