Supporting Information for

Efficient Heat Shielding of Steel with Multilayer Nanocomposite Thin Film

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In thermal radiation, the sum of transmissivity (τ), reflectivity (ρ), and absorptivity (α), is always equal to 1. Kirchhoff's law notes that the absorptivity and emissivity (ε) are equivalent at equilibrium. By measuring the reflectance using Fourier transform infrared spectroscopy (FTIR), with an attenuated total reflectance (ATR) accessory, there is no transmission, therefore:

$$\rho(\lambda) + \varepsilon(\lambda) = 1 \tag{1}$$

where both ρ and ε are functions of wavelength, and ρ is measured by FTIR (Thermo Scientific, Nicolet 380). The spectral emissive power per unit area (emissive flux) for a blackbody ($B(\lambda, T)$) is a function of the wavelength (λ) and the blackbody temperature (T). The relationship is given by Planck's law:

$$B(\lambda,T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \tag{2}$$

where k_B is the Boltzmann constant, h is the Planck constant, and c is the speed of light in vacuum. The spectrally averaged emissivity (ε) of a surface at a given temperature T can be determined from equation 3 below by integrating the measured emissivity as a function of wavelength (λ) and weighting it with the spectral emissive flux for a black body at that temperature (T):

$$\varepsilon = \frac{\int B(\lambda,T) \times \varepsilon(\lambda) d\lambda}{\int B(\lambda,T)} \tag{3}$$

Measurements were done at room temperature, and a weighting blackbody temperature of 700 °C was used as an approximation of the temperature of the surface exposed to the flame. The emissivity values reported in **Figure 8** are the weighted and spectrally-averaged emissivity over a range of wavelengths (2.5 to 25 μm).

Figure S1 shows the heat shielding behavior of 5% PEI-THAM/VMT films of varying thickness. The change in macro-bubbling is not as apparent as with 0.1% PEI-THAM/VMT, likely because these films are thicker, with more PEI content to assist in generating the bubble.

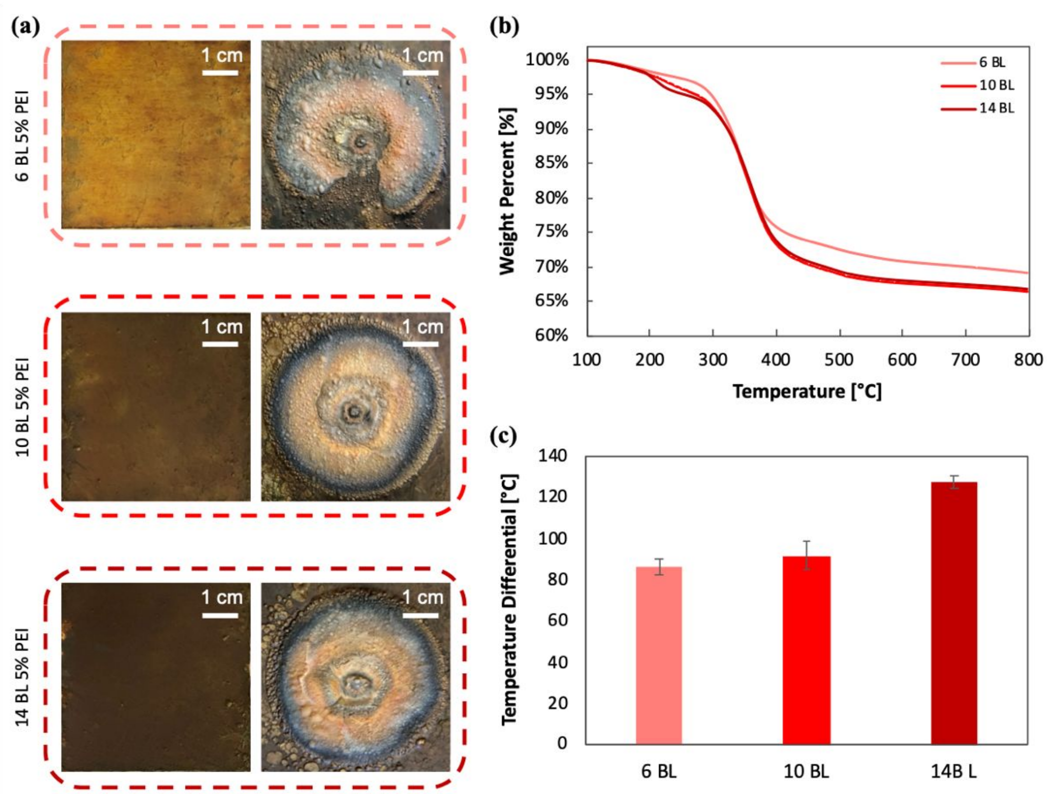

Figure S1. Heat shielding of 5% PEI-THAM/VMT films. (a) Digital images of films pre-burn (left) and post-burn (right). (b) Thermogravimetric analysis and (c) temperature differential between uncoated and coated steel.

Table S1. Average thickness of films (in µm) prepared with varying PEI concentration.

Bilayers	0.1%	0.5%	1.0%	5.0%
6 BL	2.6	4.6	5.9	14.4
10 BL	5.7	8.1	10.6	27.0
14 BL	6.8	11.9	16.2	36.3

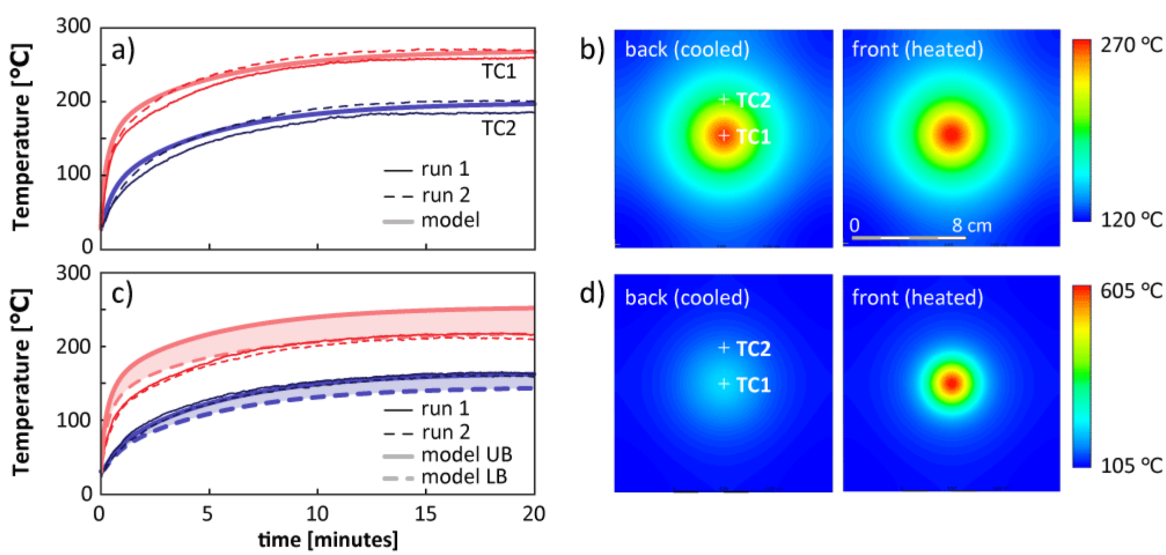

Figure S2. Measured and simulated temperature on the back (uncoated) side of the steel plate, as shown in **Figure 2** for a) baseline steel plate with no polymer-clay multilayer film, and c) 0.1% PEI-THAM/VMT 6 BL film, as an example. Red lines are the temperature measured in the center of the hot spot, blue lines are offset to the edge of the hot zone by 2.54 cm. In c), multiple simulations are run to best align with the temperatures measured at TC1 and TC2, in the center and on the edge of the hotspot, respectively, resulting in the upper and lower bounds of net thermal resistance shown in **Figure 7**. b) and d) illustrate the resulting temperature distribution on the front and back side of the simulated plate at a time of 20 min for the baseline and the 0.1% PEI-THAM/VMT 6 BL film, respectively.

Table S2. Resulting minimum and maximum net thermal resistance of the intumesced coating, as extracted from the transient thermal model.

% PEI	# BL	$R_{net,min}$ [$m^2 \cdot C \cdot W^{-1}$]	$R_{net,max}$ [$m^2 \cdot C \cdot W^{-1}$]
0.1	6	1.00E-03	4.17E-03
0.1	10	9.09E-04	5.00E-03

0.1	14	2.86E-03	6.67E-03
0.5	14	2.86E-03	6.67E-03
1	14	2.86E-03	7.69E-03
5	6	3.85E-03	1.00E-02
5	10	3.33E-03	1.18E-02
5	14	6.67E-03	2.00E-02