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# Gas evolution in self-extinguishing and insulative nanopolysaccharide-based hybrid foams



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# ABSTRACT

Lightweight, energy-efficient materials in building construction typically include polymeric and composite foams. However, these materials pose significant fire hazards due to their high combustibility and toxic gas emissions, including carbon monoxide and hydrogen cyanide. This study delves into the latter aspects by comparing hybrid systems based on nanofiber-reinforced silica-based Pickering foams with a synthetic reference (polyurethane foams). The extent and dynamics of fire retardancy and toxic gas evolution were assessed, and the results revealed the benefits of combining the thermal insulation of silica with the structural strength of biobased nanofibers, the latter of which included anionic and phosphorylated cellulose as well as chitin nanofibers. We demonstrate that the nanofiber-reinforced silica-based Pickering foams are thermal insulative and provide both fire safety and energy efficiency. The results set the basis for the practical design of hybrid foams to advance environmental sustainability goals by reducing energy consumption in built environments.

#### 1. Introduction

Lightweight materials, including insulative components, account for a large volume fraction in modern buildings. Contrarily to traditional concrete, which has a high thermal capacity and conductivity (and therefore poor indoor temperature regulation), polymeric and composite foams offer superior thermal insulation, even compared with timber, thus reducing energy consumption of residential structures. However, polymeric materials are highly combustible, and pose fire toxicity. While lightweight insulating materials help meeting carbon emission targets, the associated fire hazard still is a major consideration that demands attention (Stec & Hull, 2011).

Various reports showed that inhalation of hazardous fire gases and

smoke causes most fire deaths and injuries (Stec & Hull, 2011). The bulk of fire fatalities are caused by toxic gases, with carbon monoxide (CO) poisoning accounting for the majority of these deaths. In most cases, the combustible source of these gases are polymers. Polyurethane (PU) foams, for example, dominate the market of building enveloping materials (Szycher, 1999). Indeed, they are strong and highly efficient thermal insulators (Barksby et al., 2014; McKenna & Hull, 2016; Usta, 2012; Zatorski et al., 2008). However, PU foams are highly flammable, and the gases generated from their combustion are extremely toxic. Depending on the combustion temperature, a PU foam exposed to fire can produce a variety of thermal byproducts and harmful gases such as carbon monoxide (CO) and hydrogen cyanide (HCN), the main airborne toxicants (Hull et al., 2002). They also produce hydrogen halides, and nitrogen

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oxides (NO<sub>2</sub>). CO and HCN, both known as chemical asphyxiants, can be fatal by binding to hemoglobin in the case of CO and hindering cellular respiration in the case of HCN, e.g., by binding to cytochrome *c* oxidase (Ikegaya et al., 2001; Kaplan et al., 1984; Piantadosi, 2002; Schnipper et al., 1995). Therefore, many efforts have introduced fire-retardant elements as well as new classes of materials that are thermal insulators, fire retardant and non-toxic. The latter represents a safer, more sustainable and often less energy intensive strategy, since the high flammability of polymeric foams demand high loads of metal-based synthetic compounds to inhibit combustion.

Concurrently, silica porous materials have been proposed as super insulators (conduction coefficient as low as 0.12 W m<sup>-1</sup> K<sup>-1</sup>) and as fireretardants (Belmoujahid et al., 2015; Papa et al., 2016; Ruckdeschel et al., 2017; Yu et al., 2018); however, pure silica aerogels are brittle and prone to fracture or collapse (Parmenter & Milstein, 1998). On the other hand, there is a biobased porous materials that are strong, lightweight, and high performance thermal insulator; however, they are typically highly flammable (Guo et al., 2019, 2018; Pirzada et al., 2020) unless chemical modifications take place (Carosio et al., 2021; Jiang et al., 2021; Zhu et al., 2023). In this work, we put forward silica foams reinforced with biobased nanofibers in order to combine strength, lightweight, insulation, and fire-retardancy in the same material. The nanofibers can superstructure with particles to form extremely high cohesive systems. Nevertheless cellulose nanomaterials (Kedzior et al., 2021; Lam et al., 2014), are known to induce Pickering stabilization, most effectively when combined with (partially) co-components (e.g., surfactants, chitin) (Bai et al., 2022). Adding nanofibers to a particle network is expected to improve foaming index, and to increase foam stability (Abidnejad et al., 2021; Ahsan et al., 2020; Lam et al., 2014). The organic-inorganic blending is a recurring strategy to generate insulating and fire resistance material; however, there is a need to systematically understand the effect of formulation and structure on insulating and principally combustion properties. Therefore, we used a range of Pickering foams prepared with hydrophobic silica nanoparticles as foaming agent and biobased nanofiber binders to demonstrate fire retardancy and insulating properties developed in organicinorganic materials. Alongside with unmodified cellulose nanofibers, we used chitin nanofibers, which contain nitrogen functional groups, which provide thermal oxidative features (Pan et al., 2015; Riehle et al., 2019), and phosphorylated cellulose nanofibers (phosphorous modification has been recognized to yield fire resistance) (Ghanadpour et al., 2015). In addition to what was stated above, we also hypothesize that due to the structural difference between these nanofibers, distinctive thermal stabilities should also be observed (Lengowski et al., 2016). By combining silica particles with a variety of biobased nanofibers we combined microstructural and chemical features in foams that were comprehensively evaluated for their insulation and combustion properties.

#### 2. Experimental

#### 2.1. Materials

Evonik Industries supplied hydrophobic fumed SiO<sub>2</sub> (silica) nanoparticles (Aerosil-R812S) with a specific surface area ranging from 195 to 245 m<sup>2</sup>/g, particle size of 7–16 nm, SiO2 content >99.8 % and tamped density Approx. 60 g/l (CAS number 68909–20-6). Hexamethyldisilazane (HDMS) was used to hydrophobize silica particles. Altia Company provided absolute ethanol (Etax AA, CAS number 64–17-5) and deionized water was utilized in all experiments. Fibrillated cellulose nanofibers (CNF) were produced through microfluidization (6 passes) of never-dried, fully bleached sulfite hardwood (birch) fibers. The fibers were cleaned with 0.01 M HCl before defibrillation, and they were then rinsed in deionized water until reaching pH = 5 (Mattos et al., 2020). The cellulose nanofiber (CNF) has an average thickness of 5 nm and an average length of 2500 nm (**Fig. S1 b and c**). The Calculated surface charge of fiber from conductometric titration was 0.18 mmol/g, while the average hydrodynamic size distribution of fibers was 436.4 nm, and the mean zeta potential was -50.1 mv (**Fig. S1 d-f**).

Chitin nanofibers were made from shrimp shell's chitin flakes. To begin, residual proteins were extracted with KOH (5 wt%, 6 h, 100 °C). Following a pH neutralization wash, the fibers were immersed in HCl (5 %, 48 h, 25 °C) to remove minerals. The chitin was then deproteinized again with KOH (5 wt%, 48 h, 25 °C), followed by bleaching with sodium chlorite to remove the protein residues (Greca et al., 2021) (2 h at 80 °C). Finally, the fibers were defibrillated with a Masuko grinder to produce chitin nanofibers (Pasquier et al., 2021, 2022). The nanofibers has an average diameter of 2.5 nm and an average length of about 436.5 nm (Fig. S2 b and c). The Calculated surface charge of fiber from conductometric titration was 0.13 mmol/g, while the average hydrodynamic size distribution of fibers was 330 nm, and the mean zeta potential was 47.93 mv (Fig. S2 d-f).

Phosphorylated cellulose nanofibers (PCNF) were produced at The VTT Technical Research Institute of Finland. The precursor fiber suspension (25 % solids) was transferred to a reactor equipped with a temperature controller before being evenly sprayed with a commercial cellulase cocktail (Khakalo et al., 2021) in 0.1 M sodium acetate buffer. The enzymatic treatment was conducted at 70 °C, pH 5, and 30 rpm mixing speed. Once the enzymes were inactivated for 5 h, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and urea were introduced at given molar ratios while the reactor's temperature was raised to 90 °C for 30 min while the mixing rate remained the same. Microfibrillated cellulose impregnated with (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and urea was then dried in an oven at 105 °C until reaching constant mass, it was then cured for 1 h at 150 °C (Khakalo et al., 2021). The nanofibers has an average diameter of 2.5 nm and an average length of about 900 nm (Fig. S3 b and c). The calculated surface charge of fibers from conductometric titration was 0.79 mmol/g, while the average hydrodynamic size distribution of fibers was 214.4 nm, and the mean zeta potential was -27.29 mv (Fig. S3 d-f).

Conventional polyurethane (PU) foam (FF-PIR) samples, used as reference, were purchased locally. The PU foam, initially, had a fire-retardant coating, which was removed before evaluations (Fig. 1).

## 2.2. Methods

# 2.2.1. Particle-stabilized foams (Pickering foams)

Fumed silica nanoparticles (4 wt% of the total mass of the foam precursor) were mixed with a water:ethanol (70 %:30 %) suspension. In all cases, the fiber-to-particle ratio was calculated based on the solid content of fiber suspension, kept constant at 25:75. Ethanol was used to adjust the surface tension of the aqueous medium and to control the wettability of superhydrophobic silica nanoparticles (Abidnejad et al., 2021). The nanofiber suspension was added, and the system placed in a foam dispenser (Amazy-Sahnespender) pressurized by nitrous oxide gas cartridge. The prepared foams, were then cast in 3D-printed molds (10  $\times$  10  $\times$  1 cm<sup>3</sup>), stored at -20 °C overnight (non-directional freezing), and then subjected to freeze drying (Labconco Freezone 2.5 Freeze Dryer), Fig. 1a. Neat nanofiber cryogels (with no silica nanoparticles) were prepared by freeze-thawing and used for comparison. The silicacontaining Pickering foams, referred to as thermal foam (TF), were labelled according to the nanofibrous binder used: TF-CNF, TF-Chitin and TF-PCNF.

#### 2.2.2. Morphology, elemental analysis, and mechanical properties

The microstructure of the foams was examined by field emission scanning electron microscopy (Zeiss Sigma VP, Germany), using 3 kV acceleration voltage. Specimens were coated with a 6 nm gold/palladium layer using a Leica EM ACE600 high vacuum sputter coater prior to image capturing. Moreover, to have an understanding regarding the elemental analysis of Pickering and PU foams (before and after burning), energy dispersive X-ray spectra (EDX, Bruker) were taken from 8 randomly selected places across the samples.



Fig. 1. Structural properties of the silica-nanofiber Pickering foams. a) Photographs of the Pickering foams (here demonstrated with TF-CNF sample) and PU foam as comparisons. b-e Scanning electron microscopy of the cross-section of b) PU, c&f) TF-CNF, d&g) TF-PCNF, and e&h) TF-Chitin foams. i) Nitrogen adsorption isotherms j) and pore size distributions of Pickering foams. k) Mechanical properties of Pickering foams under axial compression test.

A Micromeritics Tristar II fitted with an automated surface area and pore size analyzer was used to perform  $N_2$  adsorption-desorption tests at 77 K. The samples were pretreated for 2 h under  $N_2$  flow in a degas system (Micromeritics II, Flow Prep 060) at 120 °C prior to the measurements. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore volume and pore size distributions were determined using the Barrett-Joyner-Halenda (BJH) method and the DFT(Borghei et al., 2017).

The mechanical strength of the cubical specimens  $(2 \times 2 \times 1 \text{ cm}^3)$  was determined under axial compression following a TA.XTplusC texture analysis (Stable Micro Systems, UK). The experiments were conducted at a compression rate of 0.10 mm/s.

#### 2.2.3. Thermal and fire characterization

Thermogravimetric analysis (TGA, Netzsch STA 449 F3 Jupiter) and gas evolution (mass spectrometer, Netzsch QMS 403 Aëolos Quadro) analyses were carried out by using ca. 25 mg of samples placed inside an alumina crucible. The heating program was initially set 40–800 °C and ran at a constant heating rate of 10 °C/min. Herein, each specimen was tested using three atmospheres, nitrogen, helium and air. The furnace was continuously purged with the given atmosphere (70 ml/min). The onset thermal degradation temperature of any event was considered when 3 % mass is lost. We used the first derivative of the thermogravimetric curve to highlight peaks related to thermal events.

For gas evolution analysis, the mass-to-charge ratio (m/z) of selected gases was obtained from according to the National Institute of Standards and Technology (NIST, U.S. Department of Commerce) and added to the initial setting for gas evolution analysis. As an example, see **Fig. S4**, the hydrogen cyanide (HCN) spectrum was obtained from NIST. As can be seen, the spectrum shows six relative intensity lines from 12 to 28 m/z, however, the most significant intensity is at 27, which strongly correlates with the presence of HCN. **Table 2** shows m/z, designated to gases, which exhibit some overlapping, for instance,  $C_2H_4$  and CO both are at 28 m/z.

To understand the mass loss over specific time (MLST) and fire interaction of specimens (SI video), the samples were placed 4 cm away from a butane flame (> 1500 °C) while the mass loss was acquired as a function of time (see setup and 3 specimens in Video S1).

The forced combustion of the foams was studied following the ISO 5660 using cone calorimetry (Concept Equipment Ltd., UK) with an irradiative heat flux of 35 kW m<sup>-2</sup>. The standard sample size was  $10 \times 10 \times 1 \text{ cm}^3$ . Samples were placed on an aluminum foil, with folded corners and placed on a ceramic backing pad. Heat release rate (HRR) and mass loss rate per unit area (MLRPUA) were then analyzed using MATLAB. The thermal conductivity was studied utilizing the transient source plane method on a C-Therm thermal conductivity analyzer

#### (Gholami Haghighi Fard & Hostikka, 2024; Yazdani et al., 2021).

#### 3. Results and discussion

#### 3.1. Foam formation, microstructure, and mechanical properties

Here we used amorphous hydrophobic silica to as a foaming agent, thus enabling particle-stabilized multiphase air-liquid system. Cellulose nanofibers were added to strength the air-liquid interface by physical entanglement with the silica particles, which prevented the foam to collapse, reduced drainage, coalescence, and ripening. Ethanol, at 70:30 H<sub>2</sub>O:EtOH ratio, lowered the surface tension of the continuous medium to 35.0 mN m<sup>-1</sup> (Binks, 2002). Manipulation of surface tension has been a common method to adsorb particles at interfaces (Dufour et al., 2013; Gonzenbach et al., 2007; Ketola et al., 2020). This enabled the preparation of a stable co-suspension of silica and cellulose nanofibers, which generated a foam with a volume gain of 150 % after pressurization with gas (Abidnejad et al., 2021). We used commercial PU foams as a reference throughout the manuscript (Fig. 1 a,b).

The macro and microstructure affect heat transfer by convection in insulating materials via gas transport, which becomes negligible if the pore size is too small – usually below 1 mm (Apostolopoulou-Kalkavoura et al., 2021). Scanning electron microscope (SEM) images of prepared Pickering foams and PU are shown in Fig. 1b-h. The morphology of silica-nanofiber thermal foams (TF for short) differ drastically from PU foams, and of cryogels obtained solely from freeze drying nanofiber suspensions (**Fig. S5**). The latter observation is a result of the presence of gas pockets stabilized by the hydrophobic silica particles within the TF foam precursors, which disrupts ice crystal growth and leads to dense nanofiber network entanglement.

Fig. 1c and f and e and h show TF-CNF and TF-Chitin foam microstructures. The combination of nanofibers with silica nanoparticles resulted in a partially open cell foam, where nanofibers and particles became interconnected during consolidation, principally, at the cells' edges and at the surfaces of the cells. A different structure was seen for TF-PCNF (Fig. 1d&g). Unlike the TF-CNF and TF-Chitin foams, the pore structure was not evident as a consequence of nanofiber-particle phase separation. The limited compatibility between PCNF and silica nanoparticles led to a dense layered structure, where the cohesion effect otherwise expected for PCNF was rather limited. In contrast to the cryogels and Pickering foams, a clean cut cross-section of PU (Fig. 1b) showed a honeycomb structure with closed cells (Andersons et al., 2021; Szycher, 1999). The cell morphology (close versus open) is a factor that affects both heat transport and compressibility. A closed-cell foam shows a reduced convective heat transmission and thermal conductivity. By contrast, an open-cell foam facilitate the circulation of air and increases thermal convection. The thermal insulation of closed-cell foams is in principle better than those of open-cell foams but other factors such as pore wall composition play a role (Soloveva et al., 2022).

The microstructure also plays a role in gas and heat transfer within the porous materials. Gas and heat transfer by conduction is drastically decreased if the average pore size of the material is smaller than the average free path of air molecules (< 50 nm), also known as the Knudsen effect (Apostolopoulou-Kalkavoura et al., 2021). Therefore we investigated the mesopore structure of the foams using N2 adsorptiondesorption tests (Fig. 1i-j and Table S1). Fig. 1i and j show the pore size distribution and the pore incremental volume of the Pickering foams, respectively. The Pickering foams displayed a much higher surface area (near 200  $m^2/g$ ) when compared to neat nanofiber cryogels (ca. 20  $\text{m}^2/\text{g}$  Fig. S6), with a range of mesoscale pores with diameters ranging from 1.7 nm to 300 nm. These pores are much smaller in size than the foam macropores, which were generated mainly by gas pockets, and to a less extent due to ice crystals growth. The latter are not measurable in the BET analysis. The hydrophobic silica particles used to stabilize the Pickering foam had a specific surface area (SSA) of  $225 \text{ m}^2/$ g (Paternina et al., 2023). Thus, the addition of biobased nanofibers did not impact drastically the foam's SSA but brought structural integrity (Fig. 1k). The pore morphology was consistent among all samples, regardless the binding nanofibers, as observed from the shape of the isotherm. A detailed discussion on pore morphology of TF-foams and cryogels is found in the Supporting information Discussion 1.

The impact on the multi-scale structures on the mechanical properties of the Pickering foams was evaluated by axial compression (Fig. 1k). Overall, the structured TF foams presented compressive strength higher than their respective cryogels, up to 4-fold higher (Fig. 1k and Fig. S7). The values within the elastic regime, at 20 % strain, ranged from 5 to 15 kPa, which enabled safe handling, without material failure. Note that insulating foams are not load-bearing materials, and mechanical cohesion is expected mostly to enable preparation, assembling, and handling.

#### 3.2. Thermal characterization

The TF foams displayed thermal conductivity ranging from 32.5 to 34 mW m<sup>-1</sup> K<sup>-1</sup>, slightly lower than that for the reference PU foam (36 mW m<sup>-1</sup> K<sup>-1</sup>). PU usually exhibits low thermal conductivity due to its closed cell, being tethered to the blowing agent used. Thermal conductivity in PU varies from 28 to 46 mWm $^{-1}$  K $^{-1}$  depending on the morphology (Apostolopoulou-Kalkavoura et al., 2021; Munier et al., 2019; Soloveva et al., 2022; Zhang et al., 2017). The nanopolysaccharide binder played a minor role in the thermal conductivity of TF foams (Fig. S8). Within this range of thermal conductivity, it is reasonable to infer that entrapped air was the most important factor affecting the insulation performance since while the apparent density of PU was 0.0401 g/cm<sup>3</sup>, the hybrid foams presented 0.0376, 0.0505, and 0.0446 g/cm<sup>3</sup> for TF-CNF, TF-Chitin, and TF-PCNF, respectively. Nevertheless, our results on thermal conductivity, supported by density values, are attributed primarily to macroscopic air pockets (foam pores), where Knudsen effect is negated. Foams based on silica nanoparticles have been reported to introduce an isotropic structure with an average pore size of ca. 50 nm (and isotropic thermal conductivity). Moreover, the relatively small pore size, as well as the interfacial thermal resistance of the fibrils in the aerogel/foam walls, lowered the thermal conductivity.

TGA was employed to understand the thermal behavior and degradation of the samples. Fig. 2 (Fig. S9 for cryogels) includes the derivative thermogravimetry (DTG- profile) and mass change (TG – red profile). The Pickering foams showed similar mass loss, up to 20 %. The derivative of mass loss (DTG) indicated only one degradation peak at around 300 °C. In contrast, PU showed 60 % mass loss at 800 °C and exhibited two degradation peaks at 250 °C and 350 °C (Fig. 2d). The cryogels reached a maximum decomposition at 800 °C; however, the degradation process for neat PCNF, as expected, was slower compared to CNF and Chitin (Fig. S9). In general, the PU foam started its thermal decomposition at earlier temperatures when compared to TF foams (Fig. 2 and Table 1), showing the potential of nanopolysaccharide-silica foams for uses at high temperatures.

PU showed a different thermal profile compared to that of TF foams. It began decomposing at a lower temperature, slightly above 200 °C, and exhibited a near-total volatilization by the end of the test. This behavior is typical of many synthetic polymers and reflects PU's inherent properties and low thermal stability. On the other hand, the Pickering foams showed only one degradation temperature, at around 300 °C. Similar results were also observed with silica-based aerogels (a single mass loss was observed between 250 and 500 °C due to the decomposition of organic -CH<sub>3</sub> groups). A 86-91 % residual mass at 800 °C for various aerogels was reported (C. Li et al., 2017; Z. Li et al., 2016). This supports the results of Pickering foams evaluated in this study, indicating significant thermal stability. PU has been reported to have two stagethermal degradation and a residual mass of 30 %, as also observed in Fig. 2d (Jiao et al., 2013). The thermal resistance of the TF foams is related to the high content of inorganic material that is bound cohesively by small amounts of biobased nanopolysaccharides - the only degrading



Fig. 2. (a) Mass loss and (b) derivative of mass loss at increasing temperatures of TF-CNF, TF-PCNF, TF-Chitin and reference PU foam.

 Table 1

 Onset values, Derivative thermogravimetry peaks, mass corresponds to each peak and residual mass of each specimen.

Specimen	Onset T.	DTG peaks T.	DTG peaks T. Mass at peaks		
	C°	C°	%	%	
TF-CNF	227	321	95	87	
		463	89		
		508	88		
TF-PCNF	190	277	91	76	
		492	79		
TF-Chitin	227	315	92	78	
		478	83		
PU	105	137	99	41	
		216	95		
		338	77		
		537	52		

component in the system.

#### 3.3. Gas evolution

The gases emitted during thermal decomposition of the Pickering foams were analyzed in situ following the mass-to-charge ratio (M/Z) by mass spectroscopy (Table 2). In the table, green (\*) and red cells (•) respectively indicate the absence or presence of the gaseous compounds. The orange cells in Table 2 indicate gases overlapping with other compounds, which cannot be determined with accuracy. These are marked as uncertain. Elemental analysis by EDX was performed to determine the elemental changes before and after combustion. As shown in Table 2, when reaching 800 °C under air atmosphere, polyurethane released HCN, HCL and CO, usually associated with asphyxiant gases. In contrast, no asphyxiant gas evolution was observed with silicananopolysaccharide TF foams. Interestingly, TF-CNF and TF-PCNF, exhibited CO under pure nitrogen atmosphere and as expected, CO<sub>2</sub> was detected in all specimens. It is also worth mentioning that the presence of NH3 in TF-PCNF can be related to the use of (NH4)2HPO4 and urea during the phosphorylation process; however, there have not been any strong traces of harmful asphyxiant gasses such as HCN since there are not significantly high content of nitrogen compounds in TF-foams compared to PU which was further studied by EDX. Nevertheless, uncertainties in the measurements could have been a result of the decomposition of surface functionalities of hydrophobic silica, which are prepared from hexamethyldisilazane (as known as bis(trimethylsilyl)amine). Based on efforts reported by McKenna and Hull (2016), PU showed initially volatile compounds such as amines, isocyanate and a yellow gas when reaching 300 °C. At 600 °C, PU started to show a char resulting from decomposition of polyols. At 800 °C, polycyclic aromatic hydrocarbons (PHAs) started to appear in the gas phase. The reaction between PHAs and volatile compounds resulted in nitrogen-containing

fragments which decompose at 800 °C into CH<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, CO and HCN. The aforementioned reactions were accelerated when by increasing oxygen in the system (McKenna & Hull, 2016). This also supports our finding that toxic gas evolution was higher under air atmosphere. Furthermore, the overall hazard of PU foams assessed by the "yield of HCN" and the HCN production rate has a direct relationship with the production of free nitrogen compounds after decomposition (McKenna & Hull, 2016). Considering the EDX results (**Table S2**), the increase in the Nitrogen wt% of PU after combustion c corresponds to results in **Table 2**. Finally, we note that the addition of fire retardants to PU accelerates the production of HCN and CO at high temperatures (McKenna & Hull, 2016).

#### 3.4. Mass loss and fire hazard

For applications in building enveloping materials, fire retardancy is as important as thermal insulation. Hence, the fire hazard of our foams was assessed by quantifying mass loss over time while exposed to fire and through a cone calorimetry (also to study ignition properties) (Fig. 3a). As shown in Fig. 3b, the total mass loss after 60 s was 20–25 % for the TF foams (compared to ca. 40 % for the PU reference). The neat nanopolysaccharide materials displayed near complete mass loss upon exposure to fire (shade colors in Fig. 3b). The TF foams quickly burns the contact area when exposed to flame, revealing a highly recalcitrant layer of silica that extinguished the flame and protected the surrounding areas (Fig. 3c). The TF-PCNF showed slightly better flame retardancy compared to TF-CNF and confirmed that the major contribution to the retardancy is associated with silica. All Pickering foams stopped losing mass after ca. 40 s, while mass loss remained constant for the PU (Fig. 3a). In general, all Pickering foams showed competitive characteristics compared to PU.

The heat release rate (HRR) and mass loss rate per unit area (MLRPUA) as a function of time of all foams are shown in Fig. 3d-e (and Fig. S10 for control cryogels). Generally, low HRR indicates significant fire resistance (Pinto et al., 2021). The nanopolysaccharide-silica Pickering foams resulted in HRR of ca. 50 kW/m<sup>2</sup>, much lower than that of PU, ca. 200 kW/m<sup>2</sup> (Fig. 3d). Interestingly all the foams (and cryogels) showed a single heat release event, while PU combustion underwent two events, before 10 s and between 10 and 20 s. This is potentially from an initial charring on the outer are of the PU foam followed by a fire propagation to the core. The TF foams reached a peak HRR between 0 and 10 s; by contrast, PU's peak HRR happened at 15 s after exposure to fire. This can be explained by the fact that PU has a slightly higher resistance to burning compared to the TF foams. Regardless, our nanopolysaccharide-silica hybrid foams were better flame retardants as they exhibited lower HRR. The Nanofiber binder did not play a major role in both HRR and MLRPUA results. Even though both Pickering foams and PU showed low values, the Pickering foams deterioration stopped earlier than PU, Fig. 3e.

# Table 2

Gas evolution analysis under various purging atmospheres (air, He, and N2).

	Air				Color Guid	
Gas	TF-CNF	TF-PCNF	<b>TF-Chitin</b>	PU	No Trace	
HCN	*	*	*	•	Undefined	
NO	*	*			Present	
NO <sub>2</sub>		*		*		
CO <sub>2</sub>	•	•	•	•		
NH3	*	*	*	•		
СО	*		*	•		
HCl	*	*	*	•		
Gas	Не					
	TF-CNF	TF-PCNF	<b>TF-Chitin</b>	PU		
HCN			*	•		
NO			*			
NO <sub>2</sub>			*	*		
CO <sub>2</sub>	•	•	*	•		
NH3			*	*		
СО		*	*	•		
HCl	*	*	*			
Gas	N <sub>2</sub>					
	TF-CNF	TF-PCNF	<b>TF-Chitin</b>	PU		
HCN				*		
NO						
NO <sub>2</sub>	*	*	*	*		
$CO_2$	•	•		•		
NH3	*	•	*	*		
СО	•	•	*	•		
HCl	*	*	*			
HCI			*			



Fig. 3. (a) Average mass loss (b) mass loss of Pickering foams and PU as a function of time (C) actual picture of TF-CNF after burning (d) Heat release rate (HRR) as a function of time (e) Mass loss rate per unit area (MLRPUA) as a function of time.

Finally, scanning electron microscopy was used to evaluate the impact of fire exposure on the morphology of Pickering and PU foams. Except for surface changes, the former foams underwent no significant morphology change after burning in the cone calorimeter (Fig. 4d

compared to Fig. 4c). The PU foam, however, suffered significant structural changes after burning, Fig. 4a and b: it collapsed, and the closed cell structure was no longer visible. Related studies on PU foams with and without fire retardant showed significant changes after



Fig. 4. Scanning electron micrographs of PU and TF-CNF foam before (a and c) and after (b and d) burning. Insets in each panel display photographs of the surface of the foams at the same stages.

burning. The fire retardant prevented combustion to a certain extent but did not prevent damage (Szczotok et al., 2021). In closing, the fire retardancy of our hybrid foams is associated to the fast burning of the biobased nanofibers and rapid exposure of fire resistant silica layer at the surface (Yan et al., 2021). For instance, wood aerogel carrying silica reduced the heat release rate by 67 % compared to natural wood (Yan et al., 2022). Also, a CNF aerogel had a HRR of 38.36 W/g, which was reduced by 52 % upon addition of 5 % of silica. Further addition of silica (25 %) resulted in an additional 53 % HRR reduction, reaching 10.29 W/g. Overall, silica makes the material incombustible due to the formation of the Si-O-Si networks expanding and fusing a flame-resistant interfacial layer, which keeps flammable gas products and heat out of the combustion zone (Yan et al., 2021).

#### 4. Conclusion

This study demonstrates the potential of nanofiber-reinforced silicabased Pickering foams as a safer and more sustainable alternative to conventional polymeric foams for building insulation. The hybrid foams exhibit comparable thermal insulation properties to PU foams while significantly improving fire resistance and reducing the emission of toxic gases. Addition of the nanopolysaccharide binder remarkably improved the properties, although there was not a clear effect of the binder type on the macroscopic properties of the foams. Key findings include:

## 4.1. Thermal insulation

The nanofiber-reinforced silica-based foams showed thermal conductivities in the range of 32.5 to 34 mW m - 1 K - 1, slightly lower than that of PU foams, indicating excellent thermal insulation properties.

#### 4.2. Fire retardancy

The hybrid foams demonstrated superior thermal stability, with a single degradation peak around 300  $^{\circ}$ C and a high residual mass at 800  $^{\circ}$ C, indicating significant thermal stability compared to PU foams.

#### 4.3. Gas evolution

Unlike PU foams, the hybrid foams did not emit toxic gases such as HCN and CO under high-temperature conditions (air atmosphere), highlighting their safety in fire scenarios.

# 4.4. Mechanical properties

The hybrid foams exhibited enhanced mechanical strength, enabling safe handling and application in building insulation without compromising structural integrity.

These results set the foundation for the practical design and implementation of nanofiber-reinforced silica-based foams in energy-efficient and fire-safe building materials, advancing environmental sustainability goals by reducing energy consumption and enhancing fire safety in built environments. By addressing the critical issues of fire hazards and toxic gas emissions, this research paves the way for developing innovative insulation materials that combine safety, sustainability, and performance.

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# CRediT authorship contribution statement

**Roozbeh Abidnejad:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Daria Robertson:** Formal analysis, Data curation. **Alexey Khakalo:** Formal analysis, Data curation. **Morteza Gholami** 

Haghighi Fard: Formal analysis, Data curation. Ari Seppälä: Writing – review & editing, Methodology, Formal analysis, Data curation. Eva Pasquier: Investigation. Blaise L. Tardy: Writing – review & editing, Conceptualization. Bruno D. Mattos: Writing – review & editing, Supervision, Project administration, Data curation, Conceptualization. Orlando J. Rojas: Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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