Thermal degradation and fire reaction properties of mycelium composites

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Mitchell P. Jones
TU Wien

Tanmay Bhat
Warringtonfire

Chun Hui Wang
UNSW Sydney

Khalid Moinuddin
Victoria University Melbourne

THERMAL DEGRADATION AND FIRE REACTION PROPERTIES OF MYCELIUM COMPOSITES

Mitchell Jones[1], Tanmay Bhat[2], Chun H. Wang[2], Khalid Moinuddin[3] and Sabu John[1]

[1] School of Engineering, RMIT University, Melbourne, Australia
[2] School of Mechanical and Manufacturing Engineering, University of New South Wales, Sydney, Australia
[3] Centre for Environmental Safety and Risk Engineering (CESARE), Victoria University, Melbourne, Australia

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ABSTRACT

Mycelium bio-composites are emerging as a safer and more fire-resistant alternative to commercially available thermoplastics intended for non-structural and semi-structural applications in the building and construction industry. In this paper, the fire reaction and thermal degradation properties of a mycelium bio-composite grown from rice hulls are evaluated and compared with commercially available extruded polystyrene (XPS) foam. The fire reaction properties of these materials are measured under cone calorimeter heating conditions that can generate correlations for a well-developed room fire (e.g. an incident heat flux of 50 kW/m^2). Despite having similar time-to-ignition, the heat release rates (including the peak values), carbon dioxide release, carbon monoxide release and smoke density of the mycelium composite is significantly lower than those of the XPS foam. Thermo-gravimetric analysis (TGA) revealed that the superior fire-retardant characteristics of mycelium composites can be attributed to significant char formation driven by the presence of aromatic compounds (i.e. lignin) in the rice hulls, and phosphorus in the mycelium. The high silica content of rice hulls (15-20 wt%) also contributed to the better fire reaction properties of the mycelium composite. This array of fire retardant mechanisms reduced the amount of heat and toxic fumes released during combustion, thereby making mycelium bio-composites safer for use in construction applications requiring resistance to thermal shock.

1 INTRODUCTION

The past decade has witnessed a steady rise in the use of mycelium-based bio-composites as an environmentally friendly alternative to composites based on synthetic polymers derived from non-renewable resources such as petroleum and natural gas [1]. Mycelium is the vegetative growth of filamentous fungi and comprises of a network of micro-filaments known as hyphae. Hyphae digest and bond to the surfaces of organic material under ambient conditions without additional energy input, thereby acting as natural self-assembling glue [2]. Mycelium provides structural binding properties through the growth of interconnecting fibrous threads that form chitin and beta-glucan based structural oligosaccharides [3]. Mycelium has several main advantages over traditional synthetic polymers including low density, low cost, a less energy-intensive manufacturing process, and perhaps most importantly, biodegradability [1]. Furthermore, the wide variety of substrates on which mycelium grows combined with improvements in processing techniques allows manufacturers to customize the material to meet specific requirements (e.g. impact resistance, thermal and acoustic insulation, etc.) [1, 3-5].

In this paper, the fire reaction and thermal degradation properties of a bio-composite produced from mycelium and rice hulls were evaluated and compared with commercially available extruded polystyrene (XPS) foam, a commonly used insulation material in the construction industry. This bio-composite was developed as a fire-resistant material to replace commercially available thermoplastics for non-structural and semi-structural applications (e.g. insulation foams, furniture, decking, etc.) in the building and construction industry. Building fires accounted for 3,280 civilian fatalities, 15,700 civilian fire injuries and $14.3 billion property damage in 2015 in the United States alone [6]. Recently synthetic polymers have been identified as the root cause of several severe fire incidents worldwide [7-10] due to the significant heat release and toxic fumes generated during the combustion of these materials [7, 8].

The fire reaction properties of the XPS foam and mycelium composite were measured under cone calorimeter heating conditions as per ISO 5660 [11]. Based on FCRC Project Report FCRC-PR 98-02 [12], ISO 5660 test provides correlation for a well-developed room fire (e.g. an incident heat flux of 50 kW/m^2). Thermal and chemical analysis was also performed on rice hulls and pure mycelium to better understand the decomposition and flammability characteristics of these constituents on the resulting composite. The results of this study provide the first quantitative data into the effect of replacing polymers with mycelium on the fire safety of buildings and houses.

2 MATERIALS AND EXPERIMENTAL METHODOLOGY

2.1 Preparation of Mycelium Composites

The fast-growing and commonly available white-rot fungus *Trametes versicolor* (*Basidiomycota*) was selected for this study based on its lignin decomposition ability and rapid growth rate. Fungal inoculum was purchased from Aussi Mushroom Supplies (Melbourne, Australia) as a mycelial mass on digested wheat grain sealed in plastic bags with filter patches. Rice hulls were selected as a substrate material based on their silica content, low cost and polysaccharide (cellulose and lignin) content and purchased from CopRice (Melbourne, Australia).

Rice hulls were soaked (48 hours in Type 1 Milli-Q® ultrapure water) and sterilised (autoclaved at 121°C and 103.4 kPa for 90 minutes) before use. They were subsequently combined with 25 wt% *Trametes versicolor* inoculum using a sterilised blender. A low inoculum mass was chosen to maximise composite rice hull content. The inoculated substrate was then distributed into sterile plastic moulds (duplicate) before being incubated under standard atmospheric conditions (25°C, 50% RH) for 12 days allowing the mycelia to colonise the rice hulls (Fig. 1a) and produce a composite material (Fig. 1b). After the incubation period specimens were dried at 50°C for 48 hours to dehydrate them and denature the fungal material (Fig. 1c).

The fire reaction properties of the mycelium composite were compared against commercially available extruded polystyrene (XPS) foam purchased from Knauf Insulation (Brisbane, Australia).

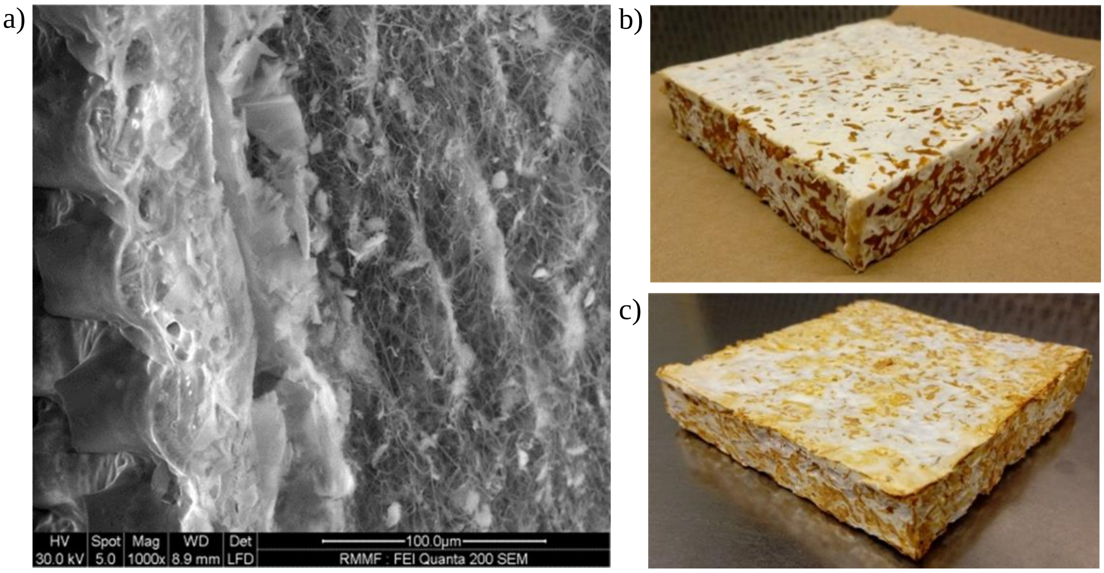


Figure 1: Mycelial growth (a) is used to produce a composite material (b) which is then dehydrated (c).

2.2 Fire Reaction Testing

The fire reaction properties of the mycelium composite and XPS foam were assessed using a three-cell cone calorimeter (Fire Testing Technology, UK) operated in the horizontal testing mode. The samples (100 mm long x 100 mm wide x 20 mm thick) were exposed to a constant incident thermal heat flux of 50 kW/m^2 per ISO 5660 [11]. The heat exposed surface was positioned 25 mm from the cone heater. The fire reaction parameters measured were time to ignition (TTI), heat release rate (HRR), mass loss rate (MLR) and smoke (CO, CO_2 and soot) release.

2.3 Thermogravimetric Analysis (TGA)

TGA was performed on mycelium and rice hulls in air and nitrogen at a heating rate of 20°C/min using a Perkin Elmer Pyris 1 instrument to determine the onset decomposition temperature and residual char content.

2.4 Evolved Gas Analysis (FTIR)

Evolved gas analysis was performed using a Pyris 1 TGA instrument interfaced to the Nicolet 6700 FTIR spectrometer. A sample of approximately 6 mg was placed in an alumina crucible and heated from 25-700°C at a heating rate of 20°C/min under nitrogen.

2.5 X-ray Photon Spectroscopy (XPS)

The surface chemistry of the mycelium composite was assessed using a K-alpha X-ray Photoelectron Spectrometer (XPS) instrument (Thermo Fisher Scientific, USA) with a monochromated Aluminium Kα X-ray source. X-ray spot size was 30-400 µm in 5µm steps. Scans spanned from 1400 to 0 eV binding energy. Peak analysis was performed by means of peak decomposition to fit a Gaussian function.

2.6 Energy Dispersive X-ray Spectroscopy (EDS)

Elemental analysis of rice hull ash burnt at 700°C in an inert nitrogen atmosphere was performed using an FEI Quanta 200 Environmental Scanning Electron Microscope with an Oxford X-Max^N 20 Energy Dispersive X-ray Spectrometer attached. An accelerating voltage of 30 kV was used with a spot size of 5 and subsequent spectra analysis performed using AZtecEnergy EDS software.

3 RESULTS AND DISCUSSION

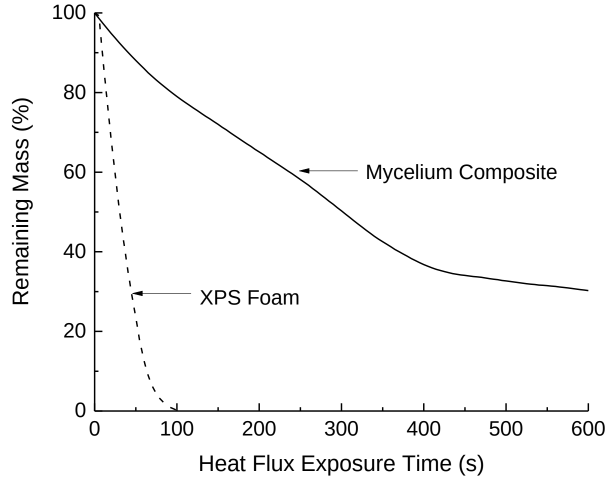
3.1 Composite Fire Reaction Properties

The effect of heat flux exposure time on the fire reaction properties of the composites is shown in Fig. 2 and Table 1. Upon exposure to the radiant heat flux, the mass of all materials decreased with time (Fig 2a), although the mass loss and heat release rates of the mycelium composite were significantly lower indicating superior fire reaction properties (Fig. 2b, 2c).

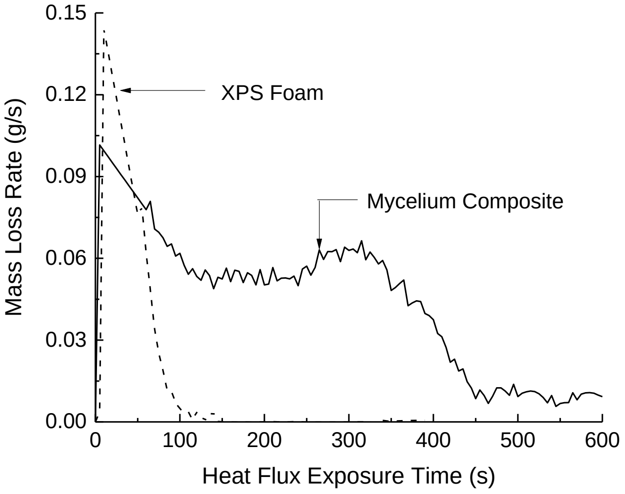
Material Type	**TTI (s)**	**PHRR (kW/m^2)**	**THR (MJ/m^2)**	**MAHRE (kW/m^2)**	**TSR (m^2/m^2)**	**Avg. CO yield (kg/kg)**	**Avg. CO_2 yield (kg/kg)**
XPS Foam	9	536	21	212	1146	0.07	2.32
Mycelium Composite	7	133	45	87	50	0.04	1.42

*****TTI = time to ignition, PHRR = peak heat release rate, THR = total heat release, MAHRE = maximum average rate of heat emission, TSR = total smoke release.

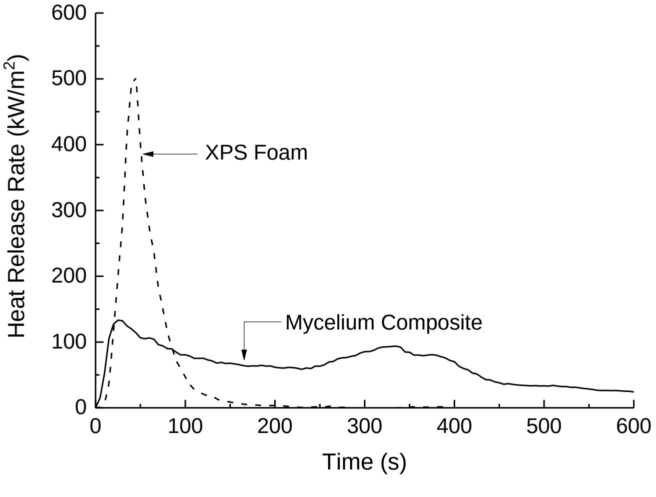
Table 1: Summary of cone calorimetry performance parameters.



(a)



(b)



(c)

Figure 2: Effect of increasing exposure time to the thermal flux of 50 kW/m^2 on (a) mass loss (b) mass loss rate and (c) heat release rate of the XPS foam and mycelium composite.

The lower mass loss and heat release rates of the mycelium composite were attributed to the significant char formation, as witnessed in Fig. 3. The formation of char is known to be beneficial for an increase in flame retardancy [9]. High char yield materials generate less smoke due to the ability of char to impede the release of ultra-small fragments of fibre into the smoke plume [13, 14]. Char also acts as a thermal insulation barrier due to its low thermal conductivity [9].

Figure 3: Char formation on the exposed surface.

In contrast to the mycelium composite, negligible char formation was observed during combustion of the XPS foam. Polystyrene degradation occurs through a radical chain process primarily comprising of random chain scission or C-C bond cleavage [15] in which almost all of the molecular structure becomes fragmented into volatile gases, resulting in a negligible amount of char [9]. Other fire reaction properties (e.g. smoke production, time to ignition, etc.) shown in Table 1 also indicate that mycelium composites pose a lower fire safety hazard than synthetic XPS foams.

3.2 Residual Char and Evolved Gas Analysis

3.2.1 Mycelial mass

Thermogravimetric analysis (TGA) was performed on the individual constituents of the mycelium composite, i.e. mycelial mass and rice hulls, to determine their thermal decomposition characteristics. As seen in Fig. 4, the mycelial mass starts to decompose at approximately 250°C. Decomposition of mycelium occurs by a series of reactions that break down the polymer chains (e.g. amino acids, polysaccharides, chitin, etc.) into low molecular weight volatiles. Stable char starts to form at 500°C (~25wt%) with a negligible drop in mass at higher temperatures.

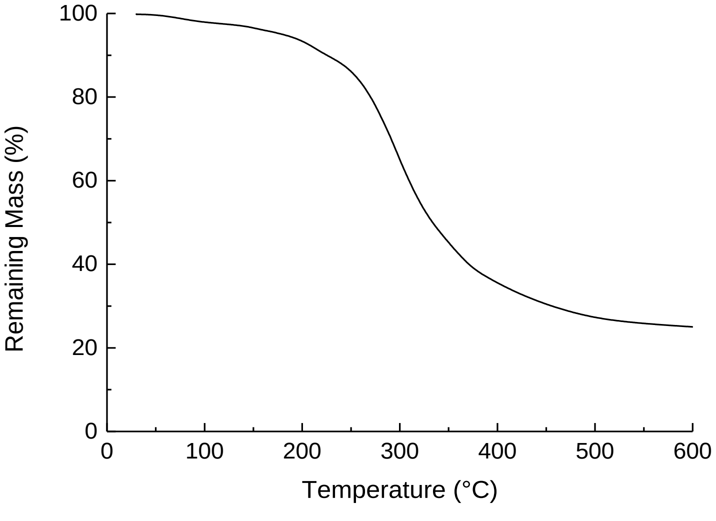


Figure 4: TGA mass loss curve for mycelial mass.

Evolved gas analysis performed using TGA-FTIR also indicated that mycelium released non-toxic and non-combustible volatiles including water vapour and carbon dioxide (CO_2) during combustion (Fig. 5). The release of non-combustible gases from mycelium causes the oxygen content in the pyrolysis zone to be depleted thereby reducing the temperature and slowing the decomposition rate. In contrast, thermoplastic XPS foams release highly flammable and toxic volatile gases during combustion, which significantly increase their associated fire hazard [9].

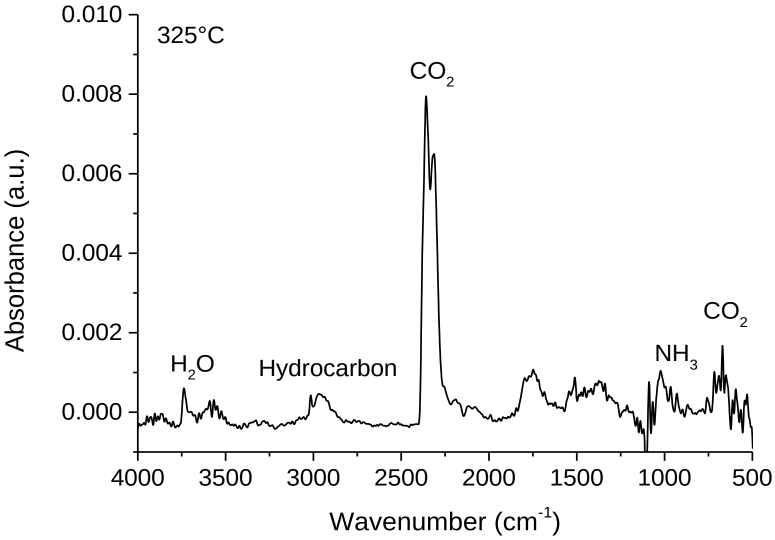


Figure 5: Evolved gas TGA-FTIR analysis for mycelial mass.

Further investigation of the mycelial mass before and after pyrolysis using X-ray Photon Spectrometry (XPS) indicated the presence of phosphorus in the mycelium char (Fig. 6). Phosphorus is widely used as a flame retardant in polymers, and virtually any phosphorus compound can provide some degree of fire resistance [9]. Evidence of phosphorus in the mycelium char indicates that it acts in the condensed phase by promoting char formation through the production of phosphoric and polyphosphoric acids during the combustion process. These acids are non-volatile and can act as dehydration catalysts, catalysing carbonization throughout the polymer substrate and aiding the formation of char [16].

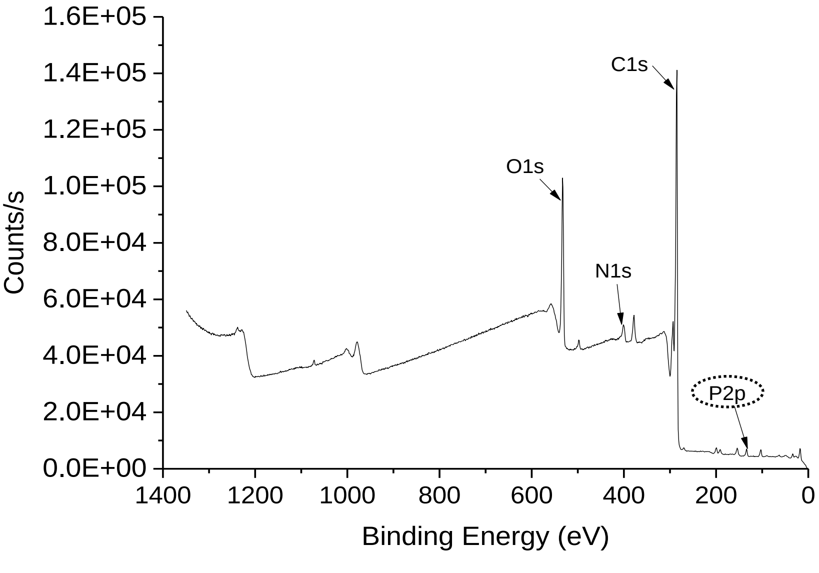


Figure 6: XPS spectrum for mycelial mass.

3.2.2 Rice Hulls

TGA conducted on rice hulls under nitrogen indicated significant char residue of approximately 40 wt%. Rice hulls primarily contain cellulose (~50%), hemicellulose and lignin (25-30%) [17]. Cellulose is a fuel source for combustion [9], but lignin is an aromatic compound containing cyclic rings of very stable bonds which do not easily break apart or react with other substances [18]. These rings decompose into aromatic fragments which are the principal constituents from which char is formed. In addition to their main constituents, rice hulls also contain a significant amount of silica (15-20 wt%) [17]. The silica is distributed in the rice hulls as hydrated grains, which are biosynthesized through the polymerization of silica acid by living organisms [19].

TGA in nitrogen and air coupled with Energy Dispersive X-ray Spectroscopy (EDS) indicated that during combustion, most organic components thermally decomposed to form amorphous carbon and embedded silica (approx. 41%) (Fig. 7). Carbonaceous char on the heat exposed surface of the composite then oxidised leaving inert silica behind as the main constituent of the surface residue (Fig. 7, 8). Progressive accumulation of these silica layers resulted in the formation of a silica-ash layer which acted as a thermal barrier (Fig. 9), preventing oxygen flow to the composite core. The lack of oxygen flow prevented the carbonaceous char from oxidising which further insulated the virgin materials (Fig. 7, 9).

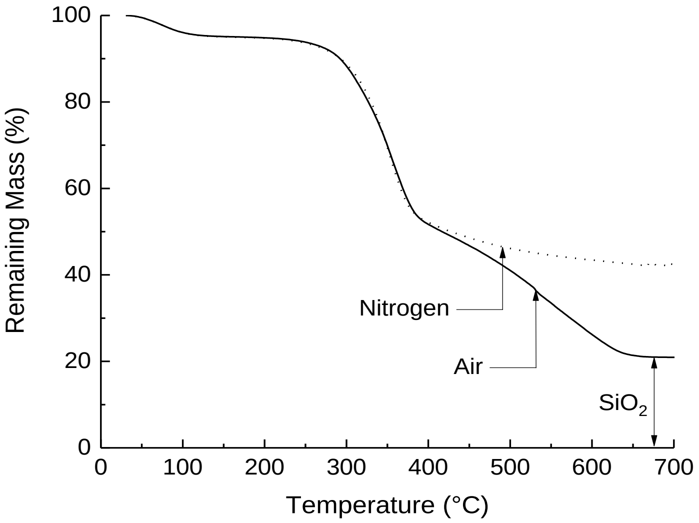


Figure 7: TGA mass loss curve for rice hulls in nitrogen and air.

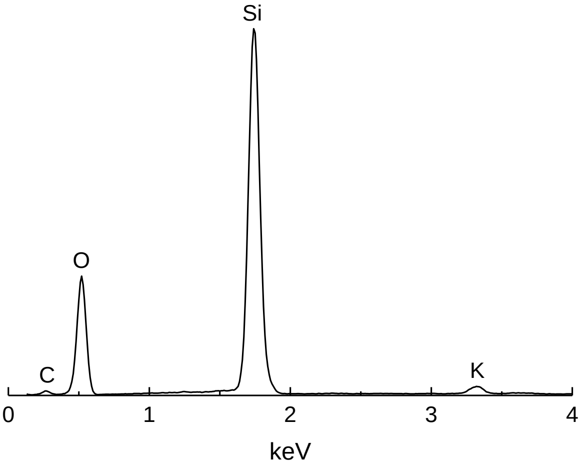


Figure 8: EDS elemental analysis spectrum for rice hull ash.

Figure 9: Decomposed mycelium composite with A: silica-ash layer on the heat exposed surface and B: carbonaceous char through the composite core and on the unexposed surface.

4 CONCLUSIONS

Mycelium composites are a viable fire-resistant material for non-structural and semi-structural applications in place of synthetic foams and similar materials. Despite igniting and burning, these cheap and environmentally friendly organic materials exhibited lower heat release and mass loss rates and reduced carbon monoxide and carbon dioxide production. The favourable fire reaction properties of the mycelium composite were individually attributed to the high char yield of both the mycelium and rice hulls. The composite core was thermally insulated by significant char formation in both the mycelial and rice hull constituents which was catalysed by the presence of mycelial phosphorus. Non-toxic and non-combustible gases evolved from the mycelium also depleted oxygen levels within the pyrolysis zone as did silica layers progressively developed as the material burned which provided thermal insulation, restricted oxygen flow to the unburnt material and may have prevented the release of volatile gases into the combustion zone. The lower flammability of mycelium composites attributed to these factors coupled with their low cost, environmentally friendly manufacturing process and biodegradability makes them suitable replacements for traditional synthetic insulation foams, furniture and decking used in the building and construction industry.

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