

Enhancement of fire resistance and mechanical performance of polypropylene composites containing cellulose fibres and extracellular biopolymers from wastewater sludge

Kim, Nam Kyeun; Bhattacharyya, Debes; van Loosdrecht, Mark; Lin, Yuemei

DOI

[10.1016/j.polymeresting.2023.108185](https://doi.org/10.1016/j.polymeresting.2023.108185)

Publication date

2023

Document Version

Final published version

Published in

Polymer Testing

Citation (APA)

Kim, N. K., Bhattacharyya, D., van Loosdrecht, M., & Lin, Y. (2023). Enhancement of fire resistance and mechanical performance of polypropylene composites containing cellulose fibres and extracellular biopolymers from wastewater sludge. *Polymer Testing*, 127, Article 108185. <https://doi.org/10.1016/j.polymeresting.2023.108185>

Important note

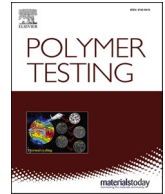
To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.



Enhancement of fire resistance and mechanical performance of polypropylene composites containing cellulose fibres and extracellular biopolymers from wastewater sludge

Nam Kyeun Kim^a, Debes Bhattacharyya^a, Mark van Loosdrecht^b, Yuemei Lin^{b,*}

^a Centre for Advanced Materials Manufacturing and Design, Department of Mechanical and Mechatronics Engineering, University of Auckland, New Zealand

^b Department of Biotechnology, Delft University of Technology, Delft, the Netherlands

ARTICLE INFO

Keywords:

Wastewater-derived biopolymer
Extracellular polymeric substances
Bio-based flame retardant
Thermoplastic polymer
Char formation

ABSTRACT

In the present research, a bio-based flame retardant (FR) was prepared using a biopolymer derived from wastewater sludge to improve the fire performance of polypropylene (PP). Extracellular polymeric substances (EPS), which were extracted from wastewater aerobic granular sludge, were absorbed into cellulose-based fibres, such as flax and toilet papers. Thermogravimetric analysis results indicated that the EPS-cellulose fibres played a significant role in enhancing the char formation of PP composite. Furthermore, the incorporation of the bio-based FR into PP restricted its vertical burning characteristics, and at the same time enhanced the tensile moduli of the composites. The reaction between phosphoric acids from EPS and hydroxyl groups of cellulose fibres improved dehydration and char formation of the composites to enhance the overall fire reaction properties. This study opens up new possibilities for the wastewater-derived biopolymer "EPS" to prepare the bio-inspired FRs for cellulose-based fibres and composites, and enhance sustainability of wastewater sludge treatment.

1. Introduction

Plastics (or polymers) have the ubiquitous presence in our daily lives from electronic devices to insulation panels for building floors or aircraft interiors. In particular, polymers, being integrated into composite products, have expanded their applications [1,2]. Undeniably, one of the major flaws of polymers is their poor fire performance. The relatively shorter ignition times, higher heat release rates and more vigorous melting phenomenon promote further fire propagation, thus resulting in severe fire hazards, such as the Grenfell tower fire disaster [3]. Considering the wide applications of plastics in various industries and increasingly stringent fire standards, there is an urgent need to incorporate flame retardants (FRs) in plastics to enhance their fire performances. Although some of them could be effective from the fire retardancy point of view, not all of them are sustainable and environmentally safe. For instance, halogenated FRs are classified as highly toxic compounds under the Stockholm Convention on Persistent Organic Pollutants; thus, their production and utilisation are banned [4]. On the other hand, this ban on halogenated FRs has prompted the usage of bio-based and sustainable FRs, which are produced from biodegradable chemicals or renewable resources with the intention of improving the

fire performance of plastics in building materials, and at the same time minimising the environmental footprints and harmful effects on human lives [2,5,6].

There have been significant research efforts into developing bio-based FRs as possible alternatives to their synthetic counterparts. Renewable compounds, such as cellulose, starch, casein and keratin, have been investigated as char forming agents and tried for improving the flame retardancy of textiles and polymers [5,7–10]. The char on the material's surface acts as a physical barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and oxygen [11]. In particular, phosphorus-based FRs have higher flame-retardant efficiency than nitrogen-, boron-, silicon- and even halogen-containing FRs because of the effective char formation as a protective layer; hence, the incorporation of phosphorus into the renewable compounds has been intensively explored [12]. Jung and Bhattacharyya have implemented a phosphorylation process of keratinous fibres, such as wool and feather, to enhance char forming ability of the fibres [7,13]. Silicate inorganic coating on the phosphate loaded chicken feather has also shown further improvement of char formation and peak heat release rate (PHRR) reduction of PP with V-0 rating (i.e., self-extinguishment) [13]. Moreover, Sonnier et al. have drafted

* Corresponding author.

E-mail address: Yuemei.Lin@tudelft.nl (Y. Lin).

<https://doi.org/10.1016/j.polymeresting.2023.108185>

Received 16 March 2023; Received in revised form 20 June 2023; Accepted 28 August 2023

Available online 30 August 2023

0142-9418/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

phosphorus molecules onto flax fabrics through electron beam irradiation. The flame-retardant flax fabric has achieved the self-extinguishing behaviour and the composite based on the fabric has decreased PHRR by 41% compared to one of a neat polyester [14].

Recently, extracellular polymeric substances (EPS), recovered from excess aerobic granular sludge at the wastewater treatment plant, has demonstrated its significant effects on reducing flammability of a cellulose-based flax fabric and a polymeric material [9,10]. EPS are defined as “organic polymers of microbial origin which in biofilms systems are frequently responsible for binding cells and other particulate materials together (cohesion). EPS mainly consist of polysaccharides, protein (polypeptides), nucleic acids, lipid (e.g., fatty acids, glycerol and phosphate) and humic substances [15]. In particular, it is noted that the presence of phosphate within EPS as a dehydration agent can be a key compound to form char on the EPS-coated flax fabric. Furthermore, the possible interaction of the phosphate in EPS with cellulose in flax, which can act as a carbonisation agent, can lead further improvement of the char formation to achieve the self-extinguishment. As large-scale production of EPS has been possible (<https://kaumera.com/>), there is a great potential for the practical and economic feasibility of using EPS as a bio-flame retardant. Moreover, recovered toilet papers from wastewater treatment plants have recently been used as a source of cellulose fibres. A large amount of the paper (~5 million tonnes) is collected by a filtration in the sewage treatment plant according to the European Tissue Symposium. As the toilet papers contain high-quality cellulose fibres, the recovery of them from wastewater treatment plants after processing can foster possible reuse of the toilet papers as a source of cellulose. For example, the current trend is that the recovered cellulose fibres from the wastewater treatment plants are used as raw materials for the production of nanocellulose [16].

Based on the previous research finding, it is reasonable to assume that the EPS and cellulose fibre combination (EPS-cellulose) can be used as a sustainable and eco-friendly bio-intumescent FR filler to improve the fire performance of commodity polymers, such as PP. To this end, flax and toilet paper fibres were selected as cellulose sources and a dip-coating method using EPS solution was implemented to prepare two EPS-cellulose FR fibres. The EPS-cellulose FR fibres were first incorporated into PP using melt-blending and then composites were moulded using a hot press. Subsequently, the fire performances of the composites were evaluated by cone calorimetry and vertical burn testing. In addition, the reinforcing effects of EPS-cellulose FR fibres were analysed by measuring tensile strengths and stiffnesses of the composites. To understand the flame retardancy mechanisms, detailed information including types and amounts of phosphorus in EPS, the elemental composition and morphology of the char residue after burning were also investigated. It is envisaged that the results of this study will shed light on the application of biobased material, derived from wastewater sludge, as a flame retardant filler to improve the fire performances of composites.

2. Experimental details

2.1. EPS-cellulose FR system preparation

The extracellular polymeric substances (EPS) were recovered from the aerobic granular sludge collected using Nereda® biotechnology at the municipal wastewater treatment plant (Epe, the Netherlands) [17]. The amounts of phosphorus and orthophosphate in the EPS were measured by the persulfate digestion procedure and the direct colorimetric analysis. Furthermore, the amount of acid-hydrolysable phosphorus was obtained from phosphorus, which was measured by the sulphuric acid hydrolysis procedure, and pre-determined orthophosphates. The hydrolysable phosphorus includes polyphosphorus with some organic phosphorus. In the end, the total organic phosphorus was calculated by deducting acid-hydrolysable phosphorus and orthophosphate from the total phosphorus [18].

An EPS solution with the concentration of 3% (w/v) was prepared by dissolving 3 g EPS into 100 ml 0.1 M NaOH. The pH of the EPS solution was 8.5 [9]. Short flax fibres weighing 1 g (Libero, Belgium, avg. 2.9 mm length) and 1 g of toilet paper (purchased at a local supplier Jumble, the Netherlands) were dipped into the EPS solution for 1 h and air-dried afterwards for 72 h. The content of EPS absorbed in the short flax fibres and the toilet paper was ~4.8 wt%.

2.2. Composites manufacturing

As the materials were agglomerated during the dip-coating process, a granulator (Wanner Technik, Germany) having a 5 mm grid mesh was used to grind them. After drying at 80 °C overnight, the EPS-cellulose FR fibres were blended with PP (HP400L, melt flow rate index: 5.5 g/10min, Lyondell Basell) and maleic anhydride grafted polypropylene (MAPP) (Licocene 6452, Clariant Ltd, as compatibiliser) at an average temperature and screw speed of 190 °C and 70 rpm, respectively, for 5 min using a twin-screw extruder (LTE26, Brabender, Germany). The compounds were pelletised using the granulator to collect the pellets for the compression moulding process, Fig. 1. A hydraulic press (LP-S-20, Labtech, Thailand) was employed to manufacture composite panels. The compression moulding parameters were heating temperature of 200 °C and maximum pressure of 10 MPa. Weight percentage of the EPS-cellulose FR fibres, PP and MAPP was 30 wt%, 67 wt% and 3 wt%, respectively.

2.3. Characterisation methods

2.3.1. Thermogravimetric analysis

Pyrolysis of the EPS-cellulose FR fibres and composites was investigated using a thermogravimetric analyser (PerkinElmer TGA 7, US). Approximately 7 mg of sample was gradually heated at a rate of 10 °C/min until the temperature reached 950 °C. The testing environment was nitrogen with a flow rate of 50 mL/min. Major parameters to explore the thermal decomposition of the materials for this research were mass loss, mass loss rate and amount of final residue.

2.3.2. Fire testing

2.3.2.1. Vertical burn test. Burning characteristics, such as flame time, burnt length and drippings, of the composites in the vertical position were measured using ASTM D3801 protocol and used for a comparative analysis. A sample size was 125 × 13 mm. The testing results determined a classification of the sample, namely V-0, V-1, V-2 or NR (no rating) depending on the burning behaviour.

2.3.2.2. Cone calorimeter. The fire reaction characteristics of the composites under heat radiation were investigated using a cone calorimeter (FTT Ltd., East Grinstead, UK), according to ASTM E1354. A sample was exposed to 50 kW/m² heat flux to measure various properties including time to ignition (TTI), heat release rate (HRR), total smoke release (TSR) and CO yields. A gas analyser (Servomex 1440) using a paramagnetic and infrared systems in the cone calorimeter detected oxygen, CO and CO₂. The sample's exposure area to a conical heater and thickness were 88.4 cm² and 3 mm, respectively. Moreover, all samples were pre-conditioned at 23 °C and relative humidity of 50%.

2.3.3. Tensile testing

Instron 5567 Universal Testing Machine was employed to evaluate tensile moduli and strength values of the composites. According to ASTM D638, a standard dumbbell-shaped samples were tested at crosshead speed of 5 mm/min. A gauge length was 50 mm and a chord modulus between 0.05 and 0.25% strain was selected to measure the tensile moduli of composites.

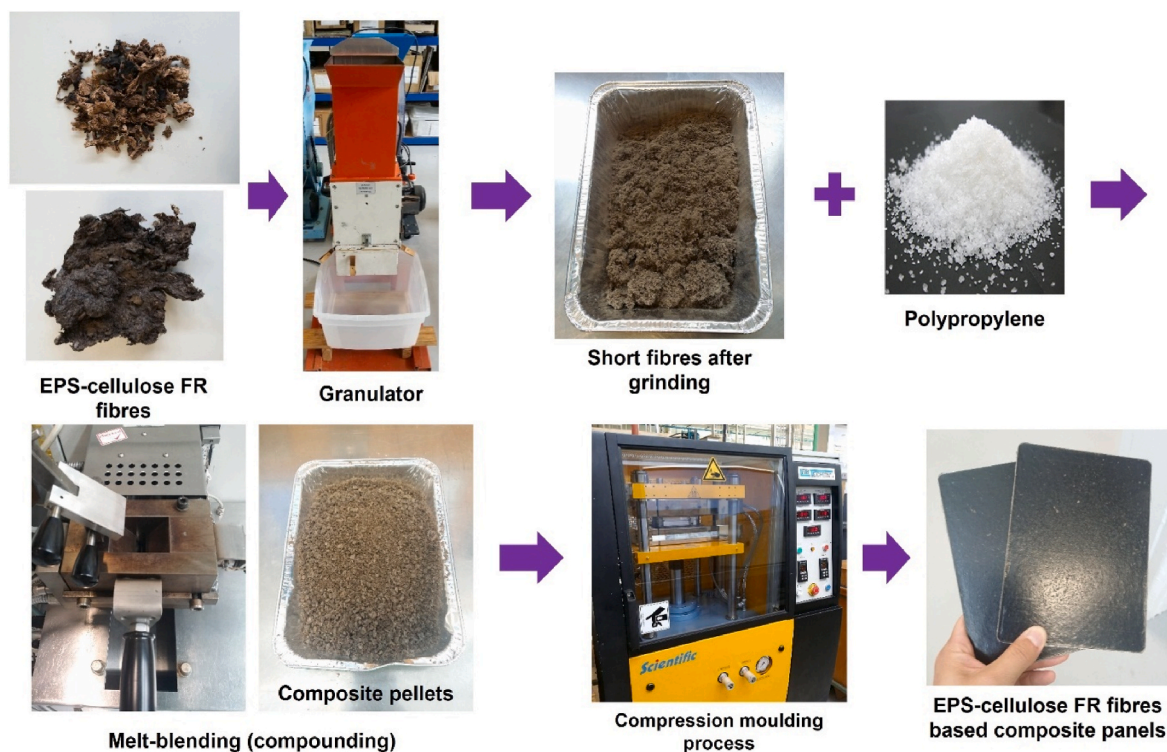


Fig. 1. Manufacturing process of EPS-cellulose FR fibres/PP composites.

2.3.4. Scanning electron microscopy

An environmental scanning electron microscope (ESEM) (FEI Quanta 200F, US) was used to characterise morphologies of char structures and tensile fractured cross-section areas of the composites. In addition, an energy dispersive X-ray spectroscopy, which had been fitted into ESEM, was processed to detect chemical compositions of the samples.

3. Results

3.1. Phosphorus in EPS

The yield of EPS was $27 \pm 3\%$ of granular sludge dry weight, which was similar to the yield reported by Felz et al. (2016) [17]. In the recovered EPS, the total amount of phosphorus (total P) was 2.32 ± 0.22 g/100 g and three major phosphorus compounds were identified: organic phosphorus (0.07 ± 0.53 g/100 g), acid-hydrolysable phosphorus (0.84 ± 0.25 g/100 g) and orthophosphate-P (1.41 ± 0.18 g/100 g).

3.2. Thermal stability of EPS-cellulose FR fibres

The flax fibres show three stages of thermal decomposition, Fig. 2. The first stage at around 100–150 °C corresponds to the moisture evaporation and the second stage indicates the devolatilisation including decomposition of hemicellulose and cellulose at around 250–370 °C and 340–379 °C, respectively [19,20]. No residue or char occurred at the final stage of the thermal decomposition, Fig. 2. On the other hand, the thermogravimetric (TG) curve of EPS-flax FR fibres clearly demonstrates a significant increase of around 29.7% in the residue content. The EPS-toilet paper FR fibres also illustrate a remarkable increase in the final residue of 31.7% compared to that of only toilet paper fibres, Fig. 3. Furthermore, the amounts of residue from both composites at 950 °C are higher than one of EPS (20.4%). These increases are comparable to those using other commercial flame retardants. In particular, ammonium polyphosphate has been reported to

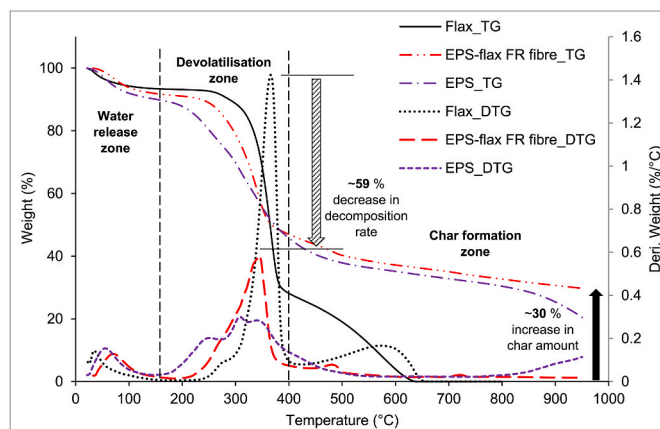


Fig. 2. TG and DTG curves of EPS, flax fibres and EPS-flax FR fibres.

produce an intumescent FR around 29.1 wt% of residue at 700 °C [21]. Since orthophosphate and polyphosphate are the main phosphorus compounds in EPS, it is reasonable to assume that the char formation of both EPS coated flax and toilet paper fibres can be attributed to the interaction of phosphates in EPS with cellulose. It is known that, in a noncatalysed route, cellulose decomposes to levoglucosan by depolymerisation. The levoglucosan then continues decomposing to release combustible volatile fragments [22]. However, when catalysed by acids, the decomposition of cellulose mainly consists of dehydration to water vapour and formation of char [23]. Due to the fact that phosphorus-based FRs form phosphoric acid (polyphosphate turns to polyphosphoric acids) when heated, they are particularly effective to catalyse the dehydration of cellulose [24]. The phosphates in EPS can play the same role in changing the decomposition rates of flax and toilet paper fibres, which can be indicated from derivative thermogravimetric (DTG) curves in Figs. 2 and 3. The maximum decomposition rates of the EPS-flax FR fibres and EPS-toilet paper FR fibres display 59.2% and 71%

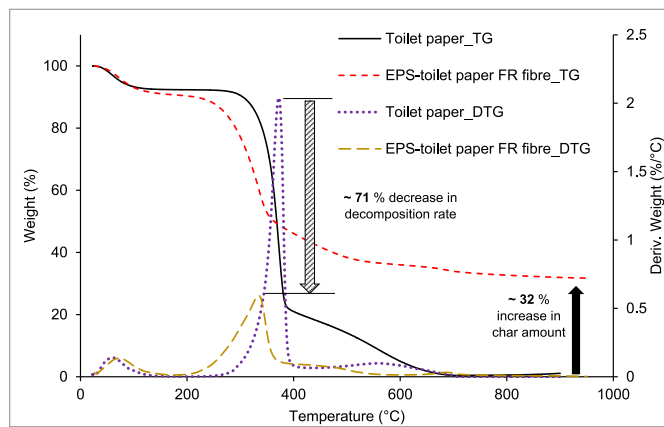


Fig. 3. TG and DTG curves of toilet paper fibres and EPS-toilet paper FR fibres.

decrease, respectively, in comparison to flax and toilet paper fibres themselves. Moreover, Table 1 demonstrates that the weight loss of flax and toilet fibres is higher than those of EPS-flax FR fibre and EPS-toilet paper FR fibre at temperatures at the maximum decomposition rates (T_{max1} and T_{max2}). Hence, both the higher char contents of EPS-cellulose FR fibres at 950 °C and the significant decrease of the decomposition rate clearly indicate that the interaction of EPS with the cellulose fibres contribute to the char forming capability.

The thermal decomposition of the EPS-cellulose FR fibres/PP composites is also identified in Fig. 4. In the composites, the actual EPS content is almost 1.5 wt% based on the total composite's weight but there is still positive effect of the fibres on increase in residue content (~8 wt% from both composites). Moreover, there are two peaks in the DTG curves. The first peak between 200–400 °C corresponds to the decomposition of the EPS-cellulose FR fibres, while the second peak indicates the decomposition of PP with a higher intensity than one from the EPS-cellulose FR fibres. PP is rapidly decomposed due to a hydrocarbon-based structure but the addition of the EPS-flax and EPS-toilet paper FR fibres reduces the decomposition rate of PP. Fig. 4 shows that the maximum decrease in the decomposition rate is around 16% from the EPS-toilet paper FR fibre/PP composite.

3.3. Vertical burn test

The sustained burning behaviour after removing an ignition source was investigated using the vertical burn testing method. The PP without fibres burnt severely with immediate and continuous flaming particles falling from the sample. The dripping particles ignited the cotton underneath the burning sample, Fig. 5(a). In comparison, the EPS-flax and

Table 1

Weight loss of various samples at onset decomposition temperature (T_{onset}) and temperatures at the maximum decomposition rates (T_{max1} and T_{max2}).

| Sample | T_{onset} (°C)/ Weight loss (%) | T_{max1} (°C)/ Weight loss (%) | T_{max2} (°C)/ Weight loss (%) | Total weight loss up to 950 °C (%) |
|--|--------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|
| EPS | 55.6/3.4 | 308.4/32.7 | – | 79.6 |
| Flax | 34.5/1.4 | 366.2/52.1 | 574.2/91.9 | 100 |
| EPS-flax FR fibre | 70.4/3.2 | 344.2/41.1 | 481.1/58.5 | 70.3 |
| Toilet paper | 60.1/3 | 372.1/57.8 | 556.2/91 | 98.9 |
| EPS-toilet paper FR fibre | 72.8/3.9 | 334.2/39.5 | 685.3/65.7 | 68.3 |
| PP | – | 473.3/68.7 | – | 100 |
| EPS-flax FR fibre/PP composite | – | 343.7/13.4 | 483.5/64.5 | 92.5 |
| EPS-toilet paper FR fibre/PP composite | – | 336.3/12.5 | 484/63.6 | 92.1 |

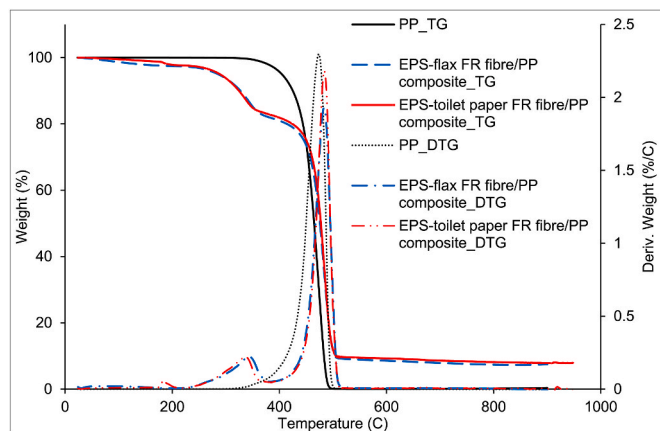


Fig. 4. TG and DTG curves of PP and EPS-cellulose FR fibre/PP composites.

EPS-toilet paper FR fibres/PP composites demonstrated slower flame spread along the sample and less severe burning behaviour. Furthermore, the composites did not start dripping until the flame reached a sample holding clamp, Fig. 5(b) and (c). It can be noted that carbonaceous char around edges of the composites, which was formed by the EPS-cellulose FR fibres, improved the anti-dripping effect and suppressed the burning characteristic of PP.

3.4. Fire reaction

3.4.1. Cone calorimeter results

Both EPS-flax and EPS-toilet paper FR fibres enhance heat and smoke related fire reaction properties of composites (Fig. 6 and Table 2). The EPS-flax FR fibre/PP and the EPS-toilet paper FR fibre/PP composites show 35.4% and 37.8% reduction of PHRR, respectively, compared to one with the neat PP, Fig. 6(a). Additionally, the total heat release (THR), of the EPS-flax FR fibre/PP and EPS-toilet paper FR fibre/PP composites by 23.2% and 20.7%, respectively, Fig. 6(b). Kim et al. have detected the 36.4% decrease in PHRR of a PVA polymer by incorporating 50 wt% EPS [10]. In the current research, the amount of EPS is only 4.8 wt% within the cellulose fibres, which is much lower than the amount incorporated into PVA polymer. Probably, the interaction of EPS-cellulose can effectively diminish the heat release rates of composites under the forced flaming combustion. Furthermore, the effective char formation of EPS-cellulose FR fibres, which was identified by Kim et al. (2019) [9], can contribute to the PHRR and THR reduction of PP.

In addition, Table 2 shows the positive effects of EPS-cellulose FR fibres on reducing total smoke release (TSR), smoke production rates and CO/CO₂ yields of the composites compared to those of PP. In general, char forming-polymers cause an incomplete combustion under fire and release more smoke and CO than polymers, which are completely burnt out without any residue [25,26]. However, both EPS-flax FR fibre/PP and EPS-toilet paper FR fibre/PP composites demonstrate lower TSR in spite of the char formation. The CO yields of the composites are similar to one of a neat PP, but the CO₂ yield is reduced by 25.9%. Furthermore, Fig. 6(c) and (d) illustrate that the CO and CO₂ productions of the composites significantly slow down during the combustion. The EPS-flax FR fibre/PP composite achieves 35% reduction in both CO and CO₂ production rates, while the EPS-toilet paper FR fibre/PP composite shows 35.9% and 41.7% reductions of CO and CO₂ production rates, respectively. In addition, it is interesting to observe that CO production rate curves from EPS and composites have the second peaks (highlighted by dotted lines in Fig. 6(c)). The increase in the CO production rate after flame-out can be attributed to the afterglow, which is a surface oxidation process of carbonaceous char due to glowing of flame residue [27].

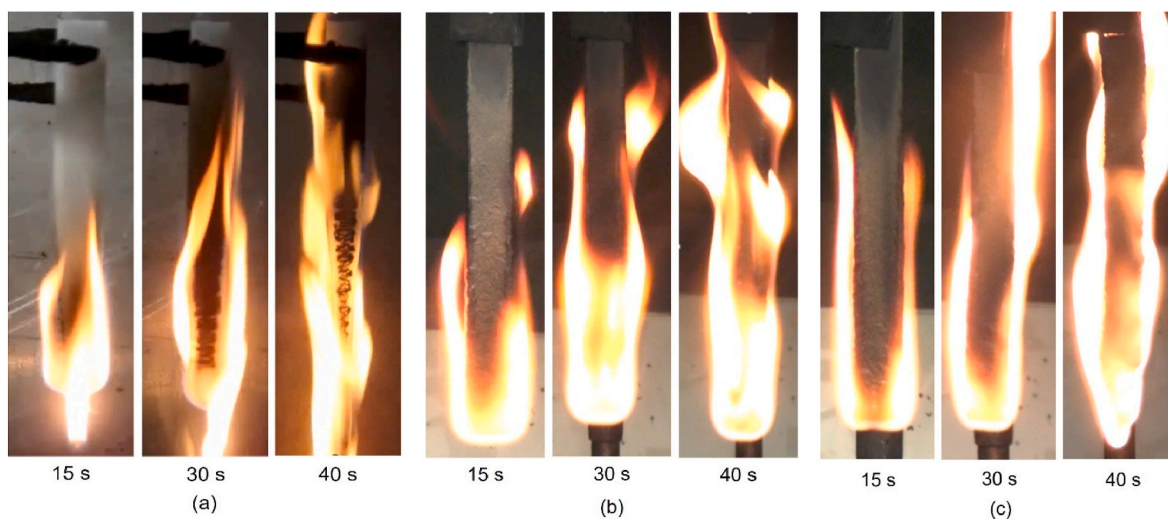


Fig. 5. Images of PP, EPS-flax FR fibre/PP composite and EPS-toilet paper FR fibre/PP composite during the vertical burn test at different time.

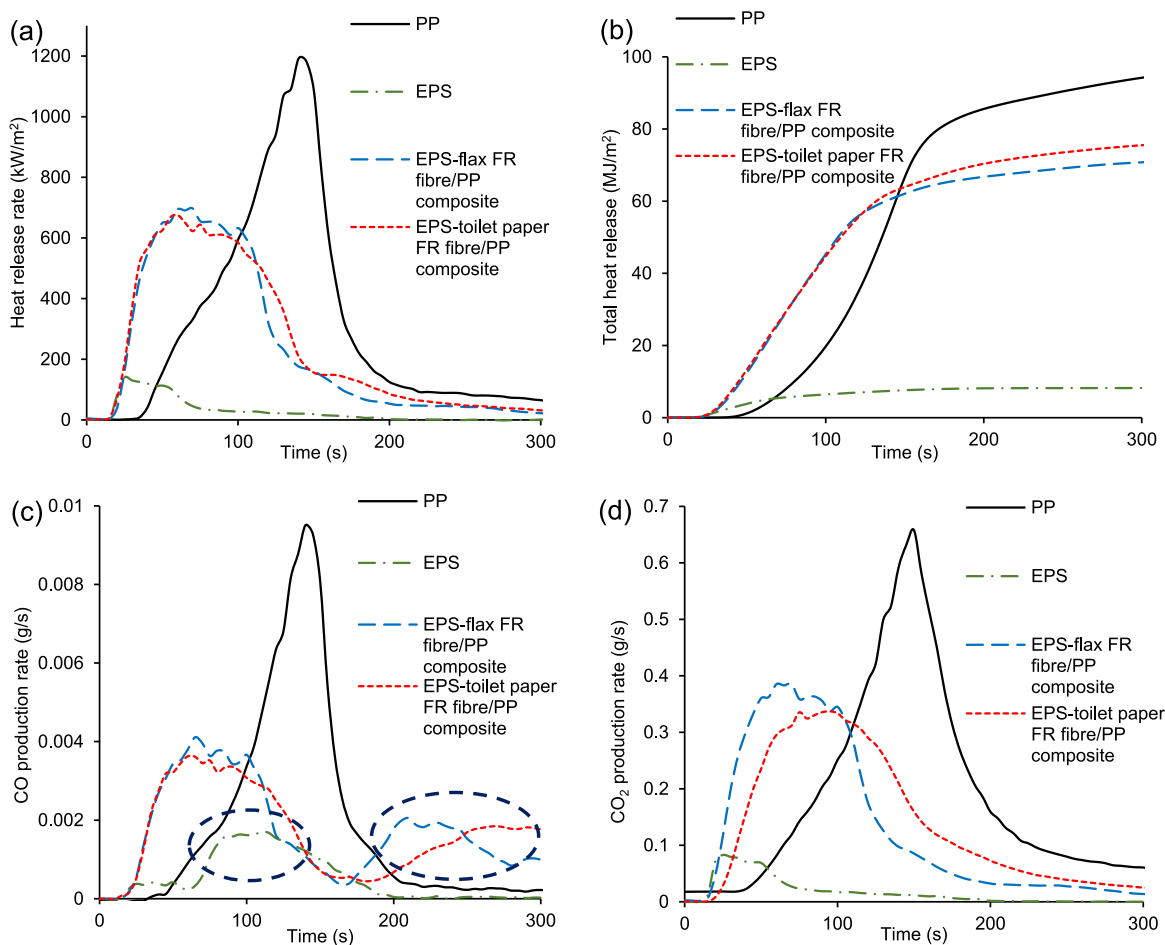


Fig. 6. (a) Heat release rate, (b) total heat release, (c) CO production rate and (d) CO₂ production rate curves of a neat PP, EPS and EPS-cellulose FR fibres/PP composites.

3.4.2. Char formation

Micro-structures of char, which was obtained after the cone calorimeter testing, were investigated to understand the condensed phase flame-retardant mechanisms. Fig. 7(a) and (d) show ESEM images of cross-sections of the EPS-flax FR fibre/PP and EPS-toilet paper FR fibre/PP composites, respectively. It is clear that the flax and toilet paper

fibres, which have around 20 μm in width, are distributed through the PP matrix. During the cone calorimeter testing, the fibres reduced their width due to thermal decomposition but maintained their skeleton structures, Fig. 7(b) and (e). Furthermore, the charring competence of EPS and cellulose fibres induced formation of char residue on the fibres' surfaces and bridged the fibre gaps to construct the interconnected char

Table 2
Cone calorimeter testing results.

| | TTI (s) | PHRR (kW/m ²) | THR (MJ/m ²) | TSR (m ² /m ²) | CO yield (kg/kg) | CO ₂ yield (kg/kg) | CO production rate (g/s) | CO ₂ production rate (g/s) |
|--|------------|---------------------------|--------------------------|---------------------------------------|------------------|-------------------------------|--------------------------|---------------------------------------|
| PP | 29 ± 2 | 1094 ± 137 | 96.9 ± 14 | 1125.6 ± 89.2 | 0.03 ± 0.004 | 3.09 ± 0.26 | 0.008 ± 0.002 | 0.612 ± 0.07 |
| EPS [10] | 3.5 ± 0.7 | 143.3 ± 4.9 | 9.7 ± 2.1 | 33.7 ± 3.8 | 0.035 ± 0.005 | 1.78 ± 0.72 | 0.002 ± 0.0001 | 0.091 ± 0.03 |
| EPS-flax FR fibre/PP composite | 20 ± 0 | 706.3 ± 12.7 | 74.4 ± 4.24 | 972.3 ± 25.9 | 0.031 ± 0.001 | 2.29 ± 0.014 | 0.004 ± 0.00006 | 0.392 ± 0.01 |
| EPS-toilet paper FR fibre/PP composite | 17.5 ± 0.7 | 680.9 ± 7.5 | 76.8 ± 0 | 1015.2 ± 29.8 | 0.031 ± .001 | 2.29 ± 0 | 0.004 ± 0.00005 | 0.357 ± 0.03 |

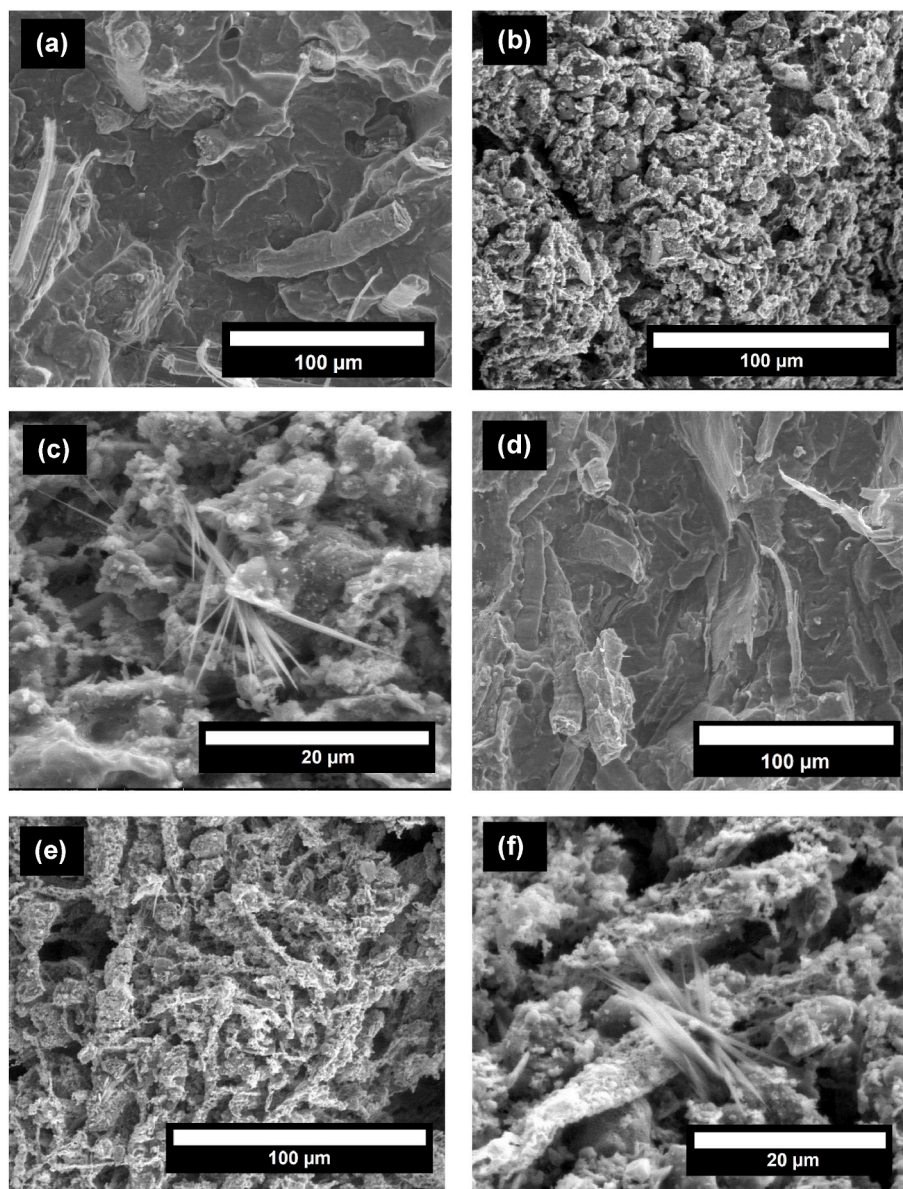


Fig. 7. ESEM images of cross-sections: (a) EPS-flax FR fibre/PP composite and (d) EPS-toilet paper FR fibre/PP composite/char surfaces: (b) and (c) EPS-flax FR fibre/PP composite, (e) and (f) EPS-toilet paper FR fibre/PP composite.

network. Moreover, it is highlighted that there are both amorphous and crystal structures on the char surfaces of the fibres, Fig. 7(c) and (f). The needle-like crystal structures are similar with the hydroxyl apatite (HAP) that was observed in EPS char by Kim et al. [10]. In addition, FTIR spectra of both composites' char, Fig. 8, show peaks at around 1430 cm⁻¹ and 876 cm⁻¹, which can be assigned to carbonate. Furthermore, a

peak at around 710 cm⁻¹ can indicate the presence of phosphorus in char [9]. A possible mechanism is that calcium phosphates in EPS react with OH and/or CO₂, which was released during the decomposition of cellulose fibres, to generate carbonate HAP [28]. As an inorganic substance, HAP is highly stable at elevated temperatures up to 1300 °C and is already a recognised flame retardant [29,30]. An EDX analysis of the

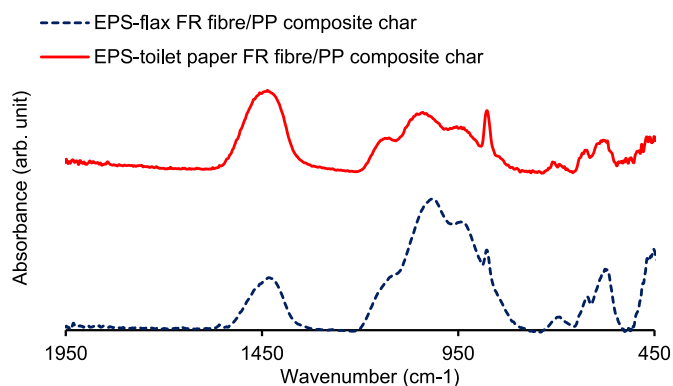


Fig. 8. FTIR spectra of composites' char.

char from both composites demonstrates strong signals of phosphorus, Fig. 9(a) and (b); hence, it can be speculated that the formation of HAP crystals and other types of phosphate/polyphosphates are related to the char formation. Furthermore, it may be noted that the thermal decomposition and char forming process of EPS are similar to those of casein. The (poly)phosphoric acid, which is generated from both materials under heating, reacts with hydroxyl of natural fibres, forming non-stable phosphate ester for dehydration and carbonisation [8].

3.5. Mechanical properties

The incorporation of EPS-cellulose FR fibres significantly improves the tensile moduli of both composites. Fig. 10(a) demonstrates 83.7% improvement of the composites' stiffness compared to that of PP. In general, the addition of natural fibres, especially cellulose-based fibres, enhance the tensile modulus of a composites due to the high stiffness of fibres [31–33]. On the other hand, the composite with EPS-cellulose FR fibres shows a slight reduction of tensile strength. Fig. 10(a) shows only 8.5% decrease in tensile strength of the EPS-flax FR fibre/PP composite compared to one of PP. The reduction can be attributed to a poor interfacial adhesion between EPS coated flax fibres and PP [33,34].

A micrograph of the tensile fractured cross-section, Fig. 11(a), shows good distribution of short fibres through PP. The uniform dispersion of fibres can lead to all the breaking points within the gauge range during tensile testing, Fig. 10(b), and improves the tensile modulus. However, Fig. 11(b) and (c) demonstrate fibres, which were pulled out without fracture under tension loading, and holes (yellow highlights) due to the

weak interfacial bonding. Hence, it may be noted that the incompatibility between the EPS-cellulose FR fibres and PP is one of the major factors behind reducing the composites' strength.

4. Discussion

4.1. Incorporation of EPS-cellulose FR fibres to improve fire performance of PP

The analyses of aforementioned fire testing results have indicated that the char formation is a main flame-retardancy mechanism to the EPS-cellulose FR fibres/PP composites. The incorporation of the EPS-flax and EPS-toilet paper FR fibres into PP increased the char formation capacity, thereby slowing down the decomposition of PP, partially inhibiting composites' flame dripping, and effectively diminishing both the heat release and smoke production rates of PP.

As stated in the result section, phosphates in EPS and cellulose in flax and toilet paper conducted significant role in determining the char formation. Acidic substances (i.e., phosphoric acid) generated from the calcium and iron phosphates within EPS during the combustion process react with hydroxyl or other groups in the cellulose, forming non-stable phosphate ester. Char is then formed on the cellulose fibres against the heat front. This carbon barrier acts as an insulation layer, preventing further decomposition of the materials [9,10,35]. More interestingly, in the char, the morphology of hydroxyapatite (HAP) was detected. HAP can strengthen a role of the char in diminishing flammability. The carbonaceous char layer with HAP can effectively act as a protective barrier, isolating the composite from the direct impact of heat and oxygen, and at the same time, can interfere with the emission of volatile products, suppressing the further combustion of PP [36]. A schematic diagram in Fig. 12 demonstrates the condensed flame-retardant mechanism of the EPS-cellulose FR fibres/PP composites.

In EPS, the total amount of phosphorus (total P) was 1.32 ± 0.22 g/100 g EPS, consisting of 61% orthophosphate-P and 36% polyphosphate-P. As the amount of EPS added in the cellulose-based fibres was around 4.8 wt%, the phosphorus content in the EPS-cellulose FR fibres was only around 0.06 wt%. This is much lower than the phosphorus content (20–30 wt%) in ammonium polyphosphate, which is used as a commercial intumescent FR for thermoplastic polymers [37]. This indicates possible synergistic effects of EPS and cellulose-based fibres on the significant improvement of the composites' fire performance. In addition, there can be other flame-retardant mechanisms of EPS and cellulose to reduce the polymer's flammability. For example, the content of phosphorus in caseins is

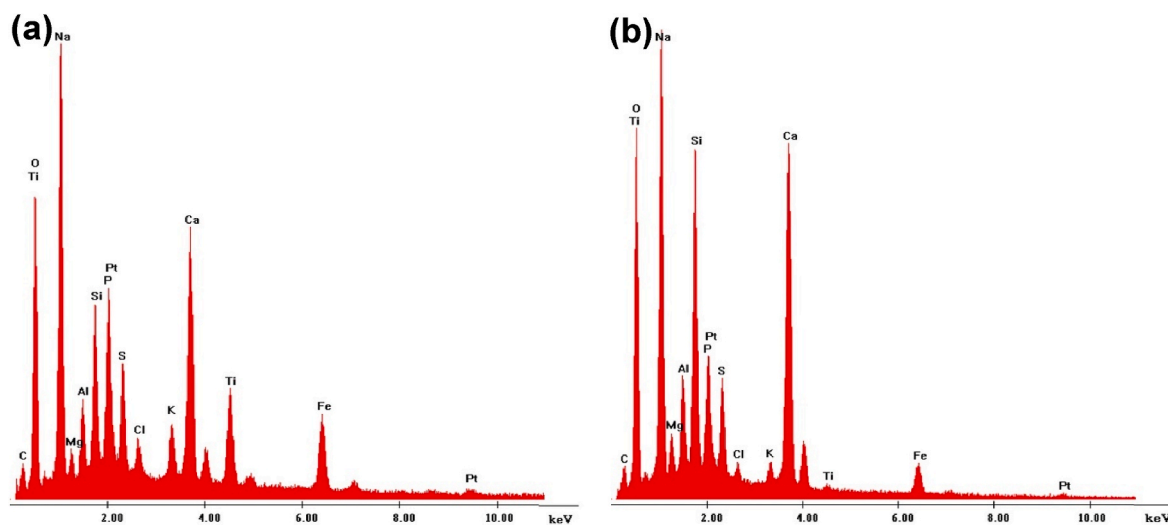


Fig. 9. EDX spectra of char: (a) EPS-flax FR fibre/PP composite and (b) EPS-toilet paper FR fibre/PP composite.

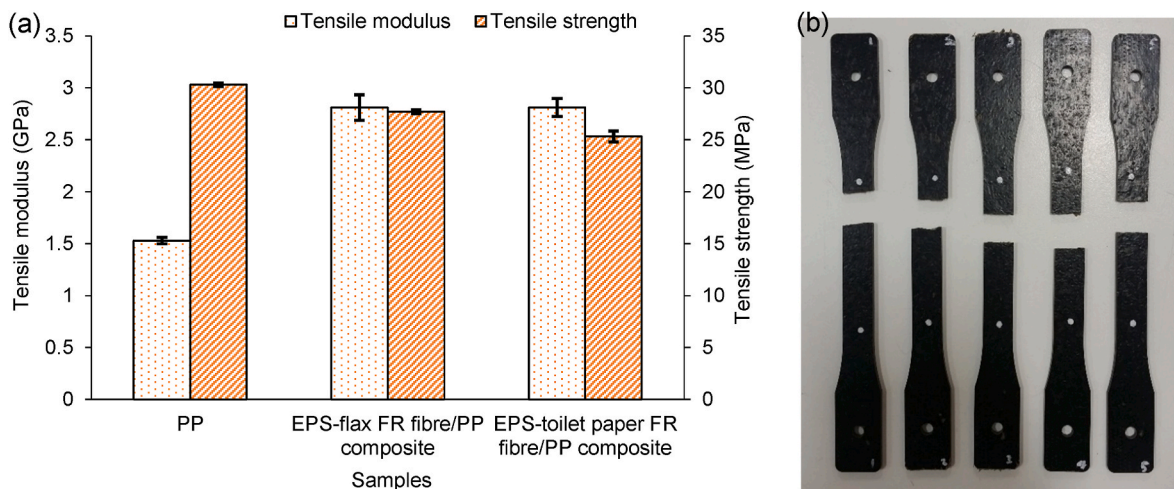


Fig. 10. (a) Tensile properties of PP, EPS-flax FR fibre/PP and EPS-toilet paper FR fibre/PP composites and (b) fractured specimens after tensile testing.

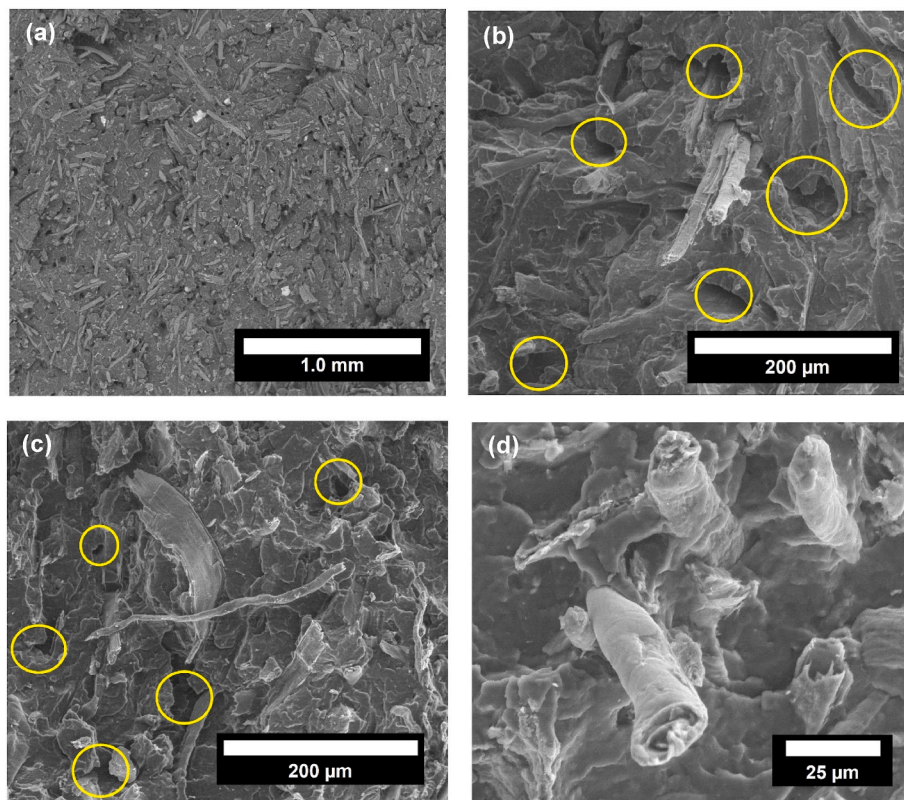


Fig. 11. SEM images of cross-sections of tensile fractured composites: (a) and (b) EPS-flax FR fibre/PP and (c) and (d) EPS-toilet paper FR fibre/PP composites.

also less than 1 wt% but the presence of both phosphorus and ammonia-based molecules has led to the formation of a thermally stable and intumescent char [8]. As EPS is composed of proteins and carbohydrates [38], other synergistic chemical interactions among the components can occur during combustion as well.

The cone calorimeter results also indicate that the CO yields of the composites do not increase in spite of the char formation. It has been reported that the incomplete combustion of hydrocarbon polymers due to charring generally increases smoke release with CO yield [39]. However, the use of EPS-cellulose FR fibres has reduced the total smoke release and kept the CO yields of the composites compared to those of PP. The actual cause of the results has not been identified, but it can be hypothesised that these two FR components can also act in a gas phase

by inhibiting a radical reaction or release water to dilute volatile products [36,39]. Hence, inorganic flame retardants, such as alumina trihydrate and magnesium hydroxide, can be incorporated with EPS to diminish smoke and toxic gases due to release of water and reaction with decomposed hydrocarbon species [40]. Further research is required to establish a complete understanding of influences of EPS and cellulose-based fibres on both condensed and gas phase flame-retardant mechanisms of composites.

4.2. Reinforcing effects of EPS-cellulose FR fibres on composites' mechanical properties

The reinforcing effects of EPS-cellulose FR fibres on composites'

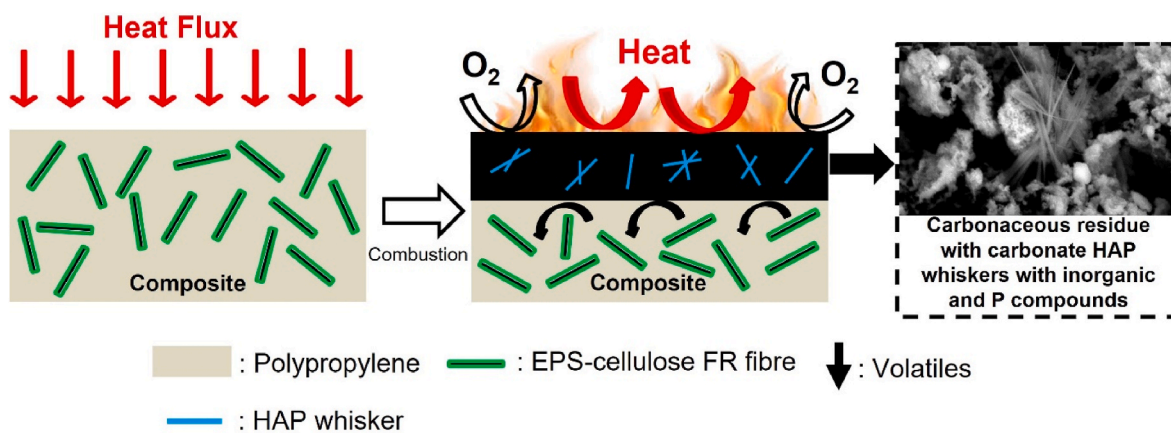


Fig. 12. Schematic diagram of fire reaction mechanism of EPS-cellulose fibres/PP composites.

tensile properties have been investigated for the first time in the current research. We have identified in the result section that the EPS coating on flax and toilet fibres enhanced the composites' tensile moduli. It can be highlighted that EPS might not affect structures and properties of the natural fibres; therefore, relatively higher stiffness of fibres (e.g., elastic modulus flax: 27.6 GPa [33]) than that of PP (i.e., 1.5 GPa) still conducts an important role in determining the composites' stiffness. For the tensile strength, it has been found out that the weak interfacial adhesion between EPS-cellulose fibres and PP within the composites cause lower strength values compared to one of PP. It is noted that the MAPP coupling agent may be used to enhance the compatibility between hydrophilic natural fibres and hydrophobic PP [41]. However, as EPS is amphiphilic by nature [42], it can already make the surfaces of flax and toilet paper hydrophobic when the EPS-flax and EPS-toilet paper fibre samples were air dried during preparation. Hence, the addition of MAPP might not be a favourable approach to improve the interfacial adhesion and composite's strength. Additionally, due to the different structure between flax and toilet paper fibres, the strength of EPS-toilet paper fibre/PP composite was reduced further 8.6%.

In general, there are two main methods to introduce FRs in plastics: covalent attachment and physical blending process. FRs can be dispersed in a polymer matrix or chemically bound to a polymer during manufacturing. The dispersion of inorganic FRs in polymers tends to reduce their mechanical strength. The integration of $Mg(OH)_2$ in plastics with the load of 40–60 wt% has a negative impact on the processability and mechanical properties of plastics [43]. As discussed earlier there is a slight reduction of EPS-cellulose FRs on the strength of PP. It is interesting to study further the correlation between the loading of EPS-cellulose on the processability, mechanical strength and fire performance of PP.

4.3. Environmental aspect

In the current research, the potential of the waste material from a sewage treatment plant as a renewable resource for the bio-based flame retardant additives was investigated. With the promising improvement of the fire performance of PP after incorporation of the EPS-flax and EPS-toilet paper FR fibres, it will be highly required to conduct the life cycle analysis to eliminate the toxic chemicals and pay more attention to the "safe and sustainable by design" of these flame retardants right at the beginning of the developments. Furthermore, it is important to ensure the sustainable management of the EPS-cellulose FR fibre/PP composites at the end of their lives to prevent any harmful effects on the environment.

5. Conclusions

The role of the bio-based flame retardants based on wastewater-derived biopolymer "EPS" and cellulose fibres in determining the flame resistant and mechanical properties of composites was investigated for the first time by the comprehensive set of experiments. EPS was successfully extracted from wastewater sludge and the EPS solution was coated onto the natural fibres, such as flax and toilet paper fibres. The TGA data clearly indicated that the EPS-cellulose FR fibres significantly increased final residue (max. 32%) and reduced the thermal decomposition rates (max. 71%) compared to those of the fibres without EPS. Furthermore, increase in thermal stability of composites was observed in the DTG curves. The EPS-cellulose FR fibres were also able to slow down burning of composites without flaming particles due to their char forming capability. The EPS-cellulose FR fibres/PP composites achieved lower PHRR and gas (e.g., CO and CO₂) production rates than those of neat PP. The micro-structure image and elemental analyses of char after the combustion tests indicated that the combination of EPS and cellulose fibres possibly enhanced char formation of composites with HAP inorganic matters. It can be suggested that phosphoric acid from EPS reacted with cellulose fibres under heat flux to construct char and disrupt a combustion cycle of the composite under the condensed phase. Moreover, the increases in the composites' moduli specified the reinforcing effects of both EPS-flax and EPS-toilet paper FR fibres, whereas further research is required to improve the interfacial adhesion between fibres and polymer. The research designated the potential of EPS coated natural fibres as the bio-based FRs and reinforcements to enhance the overall composites' performances and sustainability of the waste-based biopolymers.

Author statement

Nam Kyeun Kim: Conceptualization, Methodology, Formal analysis, Investigation, Writing- Original draft preparation **Debes Bhattacharyya:** Investigation, Writing- Reviewing and Editing, Supervision. **Mark van Loosdrecht:** Investigation, Writing- Reviewing and Editing, Supervision. **Yuemei Lin:** Conceptualization, Methodology, Formal analysis, Investigation, Writing- Original draft preparation.

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.

Acknowledgement

The authors would like to acknowledge the financial support of Ministry of Business, Innovation & Employment (UOAX 1415).

References

- [1] X.-H. Shi, X.-L. Li, Y.-M. Li, Z. Li, D.-Y. Wang, Flame-retardant strategy and mechanism of fiber reinforced polymeric composite: a review, *Compos. B Eng.* (2022), 109663.
- [2] N.K. Kim, S. Dutta, D. Bhattacharyya, A review of flammability of natural fibre reinforced polymeric composites, *Compos. Sci. Technol.* 162 (2018) 64–78.
- [3] S.T. McKenna, N. Jones, G. Peck, K. Dickens, W. Pawelec, S. Oradei, S. Harris, A. A. Stec, T.R. Hull, Fire behaviour of modern façade materials—Understanding the Grenfell Tower fire, *J. Hazard Mater.* 368 (2019) 115–123.
- [4] M. Maqsood, G. Seide, Biodegradable flame retardants for biodegradable polymer, *Biomolecules* 10 (7) (2020) 1038.
- [5] L. Costes, F. Laoutid, S. Brohez, P. Dubois, Bio-based flame retardants: when nature meets fire protection, *Mater. Sci. Eng. R Rep.* 117 (2017) 1–25.
- [6] R.A. Mensah, V. Shanmugam, S. Narayanan, J.S. Renner, K. Babu, R.E. Neisiany, M. Försth, G. Sas, O. Das, A review of sustainable and environment-friendly flame retardants used in plastics, *Polym. Test.* (2022), 107511.
- [7] D. Jung, D. Bhattacharyya, Keratinous fiber based intumescent flame retardant with controllable functional compound loading, *ACS Sustain. Chem. Eng.* 6 (10) (2018) 13177–13184.
- [8] J. Alongi, F. Cuttica, A.D. Blasio, F. Carosio, G. Malucelli, Intumescent features of nucleic acids and proteins, *Thermochim. Acta* 591 (2014) 31–39.
- [9] N.K. Kim, N. Mao, R. Lin, D. Bhattacharyya, M.C.M. van Loosdrecht, Y. Lin, Flame retardant property of flax fabrics coated by extracellular polymeric substances recovered from both activated sludge and aerobic granular sludge, *Water Res.* 170 (2020), 115344.
- [10] N.K. Kim, R. Lin, D. Bhattacharyya, M.C. van Loosdrecht, Y. Lin, Insight on how biopolymers recovered from aerobic granular wastewater sludge can reduce the flammability of synthetic polymers, *Sci. Total Environ.* 805 (2022), 150434.
- [11] S.-Y. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, *Prog. Polym. Sci.* 27 (8) (2002) 1661–1712.
- [12] K.D. Lokhande, M.A. Bhakare, M.P. Bondarde, P.S. Dhumal, S. Some, Bio-derived efficient flame-retardants for cotton fabric, *Cellulose* (2022) 1–11.
- [13] D. Jung, D. Bhattacharyya, Combined effect of silicate coating and phosphate loading on the performance improvement of a keratinous fiber-based flame retardant, *Chem. Eng. J.* 424 (2021), 130484.
- [14] R. Sonnier, B. Otazaghine, A. Viretto, G. Apolinario, P. Ienny, Improving the flame retardancy of flax fabrics by radiation grafting of phosphorus compounds, *Eur. Polym. J.* 68 (2015) 313–325.
- [15] J. Wingender, T.R. Neu, H.-C. Flemming, *What Are Bacterial Extracellular Polymeric Substances?* Springer, 1999.
- [16] S.P. Espíndola, M. Pronk, J. Zlopassa, S.J. Picken, M.C. van Loosdrecht, Nanocellulose recovery from domestic wastewater, *J. Clean. Prod.* 280 (2021), 124507.
- [17] S. Felz, S. Al-Zuhairy, O.A. Aarstad, M.C.M. van Loosdrecht, Y.M. Lin, Extraction of structural extracellular polymeric substances from aerobic granular sludge, *J. Vis. Exp.* 115 (2016).
- [18] E.W. Rice, L. Bridgewater, A.P.H. Association, *Standard Methods for the Examination of Water and Wastewater*, vol. 10, American public health association, Washington, DC, 2012.
- [19] G. Dorez, L. Ferry, R. Sonnier, A. Taguet, J.-M. Lopez-Cuesta, Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers, *J. Anal. Appl. Pyrol.* 107 (2014) 323–331.
- [20] R.K. Mishra, K. Mohanty, Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis, *Bioresour. Technol.* 251 (2018) 63–74.
- [21] N. Kim, D. Bhattacharyya, Development of fire resistant wool polymer composites: mechanical performance and fire simulation with design perspectives, *Mater. Des.* 106 (2016) 391–403.
- [22] R. Rowell, *The Chemistry of Solid Wood*, The chemistry of solid wood, Washington, DC, 1984.
- [23] D. Bakoš, M. Košík, K. Antoš, M. Karolyova, I. Vyskočil, The role of nitrogen in nitrogen–phosphorus synergism, *Fire Mater.* 6 (1) (1982) 10–12.
- [24] A. Horrocks, An introduction to the burning behaviour of cellulosic fibres, *J. Soc. Dye. Colour.* 99 (7-8) (1983) 191–197.
- [25] D. Purser, Toxicity of fire retardants in relation to life safety and environmental hazards, in: A.R. Horrocks, D. Price (Eds.), *Fire Retardant Materials*, CRC press, New York, 2001.
- [26] N.K. Kim, R.J.T. Lin, D. Bhattacharyya, Effects of wool fibres, ammonium polyphosphate and polymer viscosity on the flammability and mechanical performance of PP/wool composites, *Polym. Degrad. Stabil.* 119 (2015) 167–177.
- [27] B. Schartel, T.R. Hull, Development of fire-retarded materials—interpretation of cone calorimeter data, *Fire Mater.* 31 (5) (2007) 327–354.
- [28] J.C. Elliott, *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*, Elsevier, 2013, p. 213.
- [29] S.J. Omelon, M.D. Grynpsas, Relationships between polyphosphate chemistry, biochemistry and apatite biomineralization, *Chem. Rev.* 108 (11) (2008) 4694–4715.
- [30] B.Q. Lu, Y.J. Zhu, F. Chen, Highly flexible and nonflammable inorganic hydroxyapatite paper, *Chem.–Eur. J.* 20 (5) (2014) 1242–1246.
- [31] A. El-sabbagh, L. Steuernagel, G. Ziegmann, Low combustible polypropylene/flax/magnesium hydroxide composites: mechanical, flame retardation characterization and recycling effect, *J. Reinforc. Plast. Compos.* 32 (14) (2013) 1030–1043.
- [32] L. Yan, N. Chow, K. Jayaraman, Flax fibre and its composites—A review, *JEC Compos. Part B: Engineering* 56 (2014) 296–317.
- [33] H. Ku, H. Wang, N. Pattarachaiyakoop, M. Trada, A review on the tensile properties of natural fiber reinforced polymer composites, *Compos. B Eng.* 42 (4) (2011) 856–873.
- [34] N. Kim, R. Lin, D. Bhattacharyya, Extruded short wool fibre composites: mechanical and fire retardant properties, *Compos. B Eng.* 67 (2014) 472–480.
- [35] O. Das, N.K. Kim, M.S. Hedenqvist, D. Bhattacharyya, The flammability of biocomposites, in: *Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*, Elsevier, 2019, pp. 335–365.
- [36] X. Wang, E.N. Kalali, J.-T. Wan, D.-Y. Wang, Carbon-family materials for flame retardant polymeric materials, *Prog. Polym. Sci.* 69 (2017) 22–46.
- [37] A. Hanna, M. Nour, E. Souaya, A. Abdelmoaty, Studies on the flammability of polypropylene/ammonium polyphosphate and montmorillonite by using the cone calorimeter test, *Open Chem.* 16 (1) (2018) 108–115.
- [38] S. Felz, T.R. Neu, M.C. van Loosdrecht, Y. Lin, Aerobic granular sludge contains Hyaluronic acid-like and sulfated glycosaminoglycans-like polymers, *Water Res.* 169 (2020), 115291.
- [39] T. Hull, R. Law, Å. Bergman, Environmental drivers for replacement of halogenated flame retardants, in: C. Papaspyrides, P. Kiliaris (Eds.), *Polymer Green Flame Retardants*, Elsevier, 2014, pp. 119–179.
- [40] S.H. Chiu, W.K. Wang, The dynamic flammability and toxicity of magnesium hydroxide filled intumescent fire retardant polypropylene, *J. Appl. Polym. Sci.* 67 (6) (1998) 989–995.
- [41] M. Kabir, H. Wang, K. Lau, F. Cardona, Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview, *Compos. B Eng.* 43 (7) (2012) 2883–2892.
- [42] Y. Lin, K. Nierop, E. Girbal-Neuhauser, M. Adriaanse, M. Van Loosdrecht, Sustainable polysaccharide-based biomaterial recovered from waste aerobic granular sludge as a surface coating material, *Sustain. Mater. Technol.* 4 (2015) 24–29.
- [43] J. Liang, J. Feng, C.P. Tsui, C.Y. Tang, D. Liu, S. Zhang, W. Huang, Mechanical properties and flame-retardant of PP/MRP/Mg (OH) 2/Al (OH) 3 composites, *Compos. B Eng.* 71 (2015) 74–81.