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Insight on how biopolymers recovered from aerobic granular wastewater sludge can reduce the flammability of synthetic polymers

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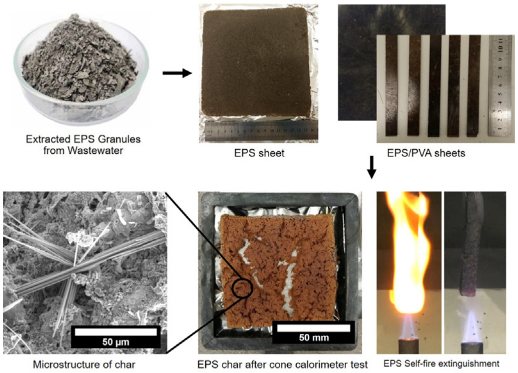
HIGHLIGHTS

- Extracellular polymeric substances (EPS) from water sludge were self-extinguishing.
- Presence of EPS reduced heat and CO release rates of a polymeric composite.
- Phosphate was a major chemical element determining flame-retardant mechanism of EPS.

GRAPHICAL ABSTRACT



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ABSTRACT

Eco-friendly flame retardants are greatly required to meet the expectations of low-toxicity, environmental compatibility and sustainability. Extracellular polymeric substances (EPS), the biopolymers recovered from excess granular wastewater sludge, have been successfully incorporated into poly(vinyl alcohol) (PVA) by a solution casting method. Self-extinguishment of EPS was observed in a vertical burn test. Positive effects of EPS on the reduction of heat release rate and CO emission of EPS/PVA composites were also demonstrated. The presence of various types of phosphates was detected in the EPS and a possible flame-retardant mechanism has been proposed. The investigation of using granular sludge EPS to reduce the flammability of synthetic polymers may open the possibility of converting wastewater sludge into bio phosphorus-based flame retardants.

1. Introduction

Flame-retardant treatments to polymeric materials are essential to reduce fire risk and meet safety regulations for their industrial applications (e.g., in construction and aerospace sectors). The incorporation of flame retardants has been identified as an effective and simple way among different methods to minimise combustibility of materials.

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Notably, a wide range of flame retardant products, including halogens, phosphorus, mineral based additives and nanofillers, have been developed and applied to plastics and textiles for decreasing heat and smoke production, restricting fire growth and spread, and overall enhancing the materials' fire resistance to ignition and combustion (Wannomai et al., 2021; Kim et al., 2018).

The halogenated flame retardants have been recognised as a cost-effective additive to scavenge reactive free radicals by evolving halogens that can inhibit combustion in vapour phase, but their release of toxic gases causes harmful effects on humans and environment; thus, their applications have been strictly regulated. Phosphorous based flame retardants as non-halogenated additives can provide an alternative solution to produce less toxic fumes and form an insulating carbonaceous char layer on a material surface in condensed phase. These compounds basically act in the condensed phase by altering the pyrolytic path of the polymeric material and reducing the amount of gaseous combustibles, thereby suppressing generation and propagation of flame (Lu and Hamerton, 2002).

The non-halogenated flame retardants have been intensively investigated and developed for the plastics industry, but the end-of-life disposal of products containing synthetic flame retardants is still a critical environmental issue due to their limited biodegradability. Therefore, the developments of sustainable and biodegradable flame retardants are in high demand to resolve the environmental issues (Costes et al., 2017). Recently, extracellular polymeric substances (EPS) extracted from wastewater sludge have been characterised to measure physical properties and chemical components (Lin et al., 2013, 2018; Pronk et al., 2015). These polymers are currently commercially developed as a valorisation of wastewater sludge and the trade name Kaumera. The positive effects of EPS coating on self-extinguishing property of flax fabric have recently been reported (Kim et al., 2020). It was shown that the phosphate in EPS could contribute to effective char formation of flax for achieving good flame-retardant performance. It is worth pointing out that, during the coating of EPS on flax surface, water-based EPS solution was used due to the high-water solubility of EPS. Although EPS is amphiphilic in nature (Cao, 2017), it is hardly soluble in most organic solvents. It is also difficult to form a thick and stable EPS coating layer on most plastics. Therefore, for the application of EPS to reduce the flammability of plastics, more appropriate methods, other than the surface coating, have to be established.

Polyvinyl alcohol (PVA) has been broadly used in various applications for textile and paper sizing, adhesives and filament production due to its excellent chemical resistance and physical properties (Mohareb et al., 2011). Significant volumes are also produced for the building industry, where PVA is widely employed as a binding and thickening agent for latex paint and seals (Marten, 2002). In addition, it has also been used as a modifier and fibre reinforcement in cement-based composite materials (Thong et al., 2016). However, its high flammability has been a limiting factor for its application (Wang et al., 2007). Thus, a strategy to reduce the flammability of PVA has attracted considerable interest in recent years. As both PVA and EPS are of hydrophilic nature, it is possible to mix EPS with PVA in water-based solution. It is hypothesised that blending EPS may reduce the flammability of PVA. Hence, the aim of the current research is to evaluate the flammability of EPS/PVA composite and investigate the role of EPS in improving the flame-retardant property of PVA. Possible flame-retardant mechanisms for the EPS/PVA composite have also been suggested, based on the chemical elements and microscopic analyses.

2. Experimental details

2.1. EPS extraction from aerobic granular sludge

Aerobic granular sludge was collected from the municipal wastewater treatment plant (WWTP) using Nereda® technology in the Netherlands. The wastewater treatment process in the WWTP achieved complete carbon, nitrogen and phosphorus removal. Specifically, the phosphorus removal was carried out via the Enhanced Biological Phosphorus Removal (EBPR) process.

The EPS was recovered from the granules according to the technique developed by Felz et al. (2019). In short, granular sludge (20 g dry weight) was extracted in 1 L 0.5% Na_2CO_3 at 80 °C for 40 min. After centrifuging at 5366 ×g for 20 min, the pellet was discarded. The supernatant pH was adjusted to 2 by adding 1 M HCl. The precipitate was collected by centrifugation (5366 ×g, 30 min), washed three times with Mili-Q di-deionised water and dissolved in 0.1 M NaOH. This EPS solution was dialysed with a dialysis membrane (3.5 K MWCO, SnakeSkin) for 24 h against Mili-Q water and lyophilised.

2.2. Composites manufacturing

EPS based PVA composite was prepared by a solution casting method. An aqueous PVA (Sigma-Aldrich, Germany) solution (50 wt%) and lyophilised EPS (50 wt%) were blended at 80 °C for 30 min. The composite mixture was then dried at 30 °C, pelletised and further dried at 90 °C to remove the remaining moisture content. A compression moulding process was also carried out to manufacture EPS/PVA composite films. The pressing temperature and pressure were 250 °C and 23 MPa maximum, respectively. A PVA film and the lyophilised EPS as reference samples were also fabricated using the same compression moulding process.

2.3. Characterisations

2.3.1. Thermogravimetric analysis

The thermal decomposition of the EPS, PVA and EPS/PVA composite was investigated using a thermogravimetric analyser TGA-50 (Q5000, TA Instruments, US). The samples (ca. 7 mg) were heated under a nitrogen flow (25 mL/min) in the thermo balance at a linear heating rate of 10 °C/min up to 800 °C.

2.3.2. Scanning electron microscopy

An environmental scanning electron microscope (ESEM – FEI Quanta 200F, Houston, US) was used to observe the surface morphologies of char residue after the cone calorimeter test on the constituent materials and the composites. Furthermore, chemical compositions of the char were identified by an energy dispersive X-ray spectroscopy (EDX) during the ESEM observation. The samples were coated with platinum using the Quorum Q150RS sputter coater (Quorum Technologies Ltd., East Sussex, UK).

2.3.3. X-ray powder diffraction analysis

The XRD patterns of the sample after vertical burning test were recorded in a Bragg-Brentano geometry of a Bruker D5005 diffractometer, equipped with Huber incident-beam monochromator and Braun PSD detector. Data collection was carried out at room temperature using monochromatic Cu $K\alpha 1$ radiation ($\lambda = 0.154056$ nm) in the 2θ region between 5° and 90°, step size of 0.038°. Samples of about 20 mg were deposited on a Si <510> wafer and rotated during measurement. Data evaluation was performed with the Bruker program EVA.

2.3.4. Cone calorimeter experiments

Fire reaction properties of EPS, PVA and EPS-PVA composites were evaluated by a cone calorimeter (FTT Ltd., East Grinstead, UK). Overall testing procedure were followed according to ASTM E1354. An exposed area of the sample to a cone heater was 88.4 cm^2 and the external heat flux was 50 kW/m^2. In this research, among the fire reaction properties heat release and smoke density parameters with CO and CO_2 production rates have mainly been presented for discussion.

2.3.5. Vertical burn test

Vertical burn tests based on ASTM D3801 were conducted to measure flammability of the samples after two 10 s flame applications. As the response to a small-flame ignition source, burning characteristics, such as sustained flaming time, glow time and dripping, were recorded.

3. Results

3.1. Thermal stability and flammability

The thermal decomposition curves of EPS, PVA and EPS/PVA composite, Fig. 1(a), show the clear difference in residue formation. As temperature increases to 800 °C, PVA is almost fully decomposed, while approximately 44 wt% of EPS remains as residue. The addition of EPS in PVA significantly increases the final amount of residue of the composite, resulting in the formation of around 31.7 wt% residue. It can be clearly noted that the char forming ability of EPS under heating plays an important role in forming the carbonaceous residue of the composite without any flame-retardant additives.

The combustion behaviour of the three samples was further investigated by cone calorimetry, which gathers data, such as heat release rate (HRR), smoke production and other parameters correlated with the fire behaviour of the samples (Table 1). HRR is defined as the quantity of heat released per second per unit area of a material when the material is subjected to a fire. It is not only an important parameter to characterise fire behaviour but also serves as a determining factor in defining a phenomenon, such as fire hazard. Peak HRR (PHRR) refers to the highest amount of heat emitted during combustion and the area under the HRR curve represents the total heat release (THR). The generation of smoke, hazardous gases and other types of fire hazards increases in parallel with the HRR. HRR curves of the three tested materials are shown in Fig. 1(b). The curve of EPS displays the typical burning behaviour of residue-forming materials (Schartel and Hull, 2007). The EPS is quickly ignited (time to ignition (TTI) less than 5 s) with a comparatively small PHRR than those of PVA and the composite. The plateau of the HRR curve implies the formation of a carbonaceous protective layer to suppress fire propagation. In comparison to EPS, the ignition of PVA takes a longer time (average TTI of 35 s) but reaches a much higher PHRR with a prolonged burning period. Interestingly, the addition of EPS into PVA speeds up the ignition with significantly reduced HRR (by 36.4%) and slightly shortened burning time (by 10%) in comparison with those of neat PVA.

EPS itself shows a PHRR of about 143.3 kW/m^2 and the incorporation of EPS in PVA results in a 36.4% reduction of PHRR, when compared to that of neat PVA (Table 1). The decrease in heat release can be attributed to the formation of residue, which can act as a thermal barrier as well as a physical barrier to interrupt the heat and oxygen transfer between the combustion zone and the PVA/EPS composites (Khalili et al., 2020). It has been reported that calcium phosphate in the EPS can react with CO$_2$ emitted from combustion of a textile material to produce carbonated hydroxyapatite (HAP), which improves the flame retardant performance of the fabric containing EPS (Kim et al., 2020).

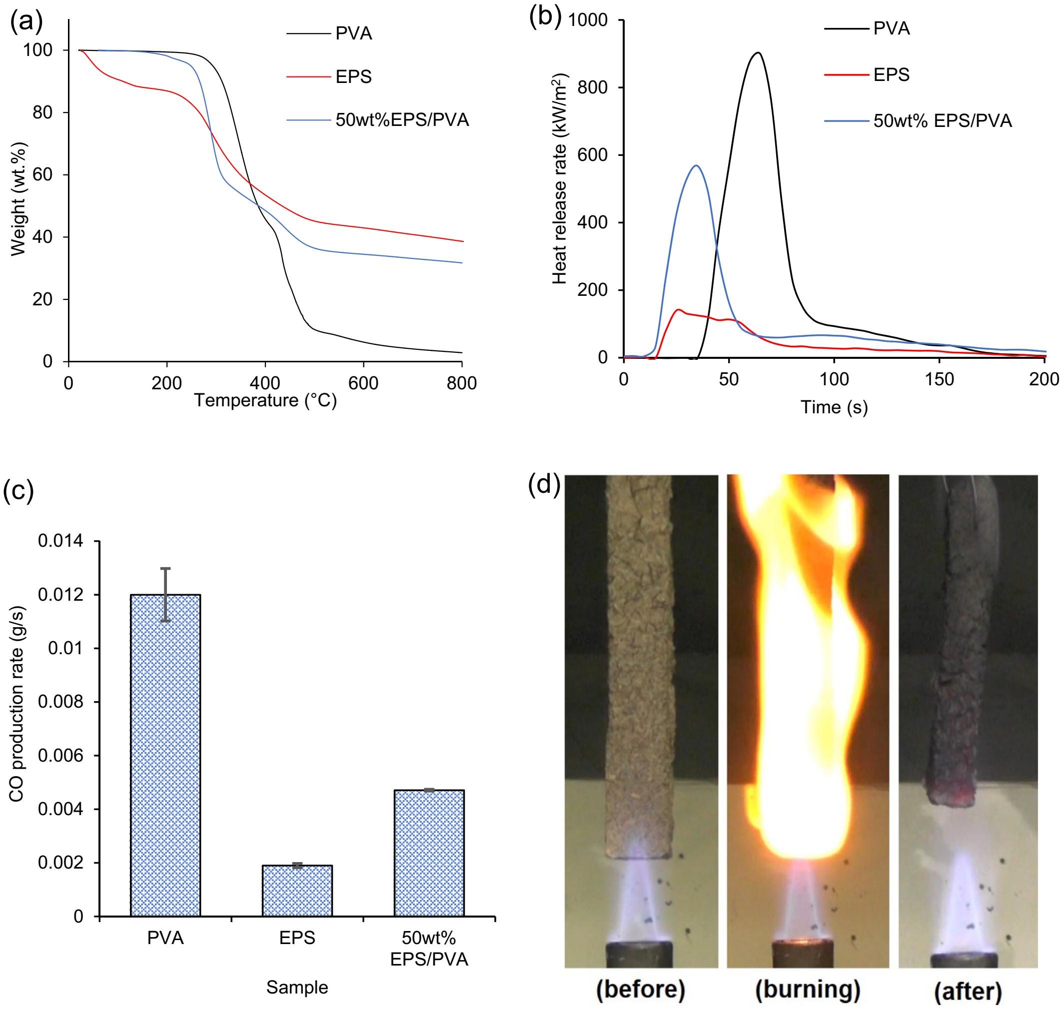

Fig. 1. (a) Thermogravimetric curves of PVA, EPS and 50 wt% EPS/PVA composite, (b) heat release rate curves of PVA, EPS and EPS/PVA composite, (c) CO production rates of PVA, EPS and EPS/PVA composite (d) UL-94 vertical burn test: EPS sample before, during and after burning.

Table 1
Cone calorimetry data of PVA, EPS and EPS/PVA composite.

Sample	Peak heat release rate (PHRR) (kW/m^2)	Total heat release (THR) (MJ/m^2)	Total smoke production (TSP) (m^2)	Total smoke release (TSR) (m^2/m^2)	Specific extinction area (SEA) (m^2/kg)	CO production rate (g/s)	CO$_2$ production rate (g/s)
EPS	143.3 ± 4.9	9.7 ± 2.1	0.3 ± 0.0	33.7 ± 3.8	56.3 ± 9.04	0.0019± 0.0001	0.0911± 0.0253
PVA	903 ± 66	31.6 ± 0.8	6.2 ± 0.4	703.1 ± 48.5	470.3 ± 21.8	0.012 ± 0.002	0.606 ± 0.032
50 wt% EPS/PVA	574.6 ± 9.5	20.8 ± 0.4	2.1 ± 0.1	238.1 ± 17.6	242.6 ± 17.7	0.0047 ± 0.0004	0.3765 ± 0.005

Additionally, during continuous heating, the phosphate in the EPS can migrate to the surface of the sample to form a protective char layer with release of H_3PO_4 that limits the mass transfer of oxygen and volatile products, which further contributes to the reduction of composites' flammability.

Smoke emission during a fire scenario plays an important role in life safety due to its toxicity and reduced visibility. From the cone calorimetry test, several important smoke properties, such as total smoke production (TSP), total smoke release (TSR) and specific extinction area (SEA), were collected. Since the char formation with inorganic materials of EPS has led to low smoke production, which is only 1/20 of that of PVA, blending of EPS greatly (by 66%) reduced the smoke production of PVA. Within the smoke produced, CO is the most toxicologically significant fire gas as exposure to CO causes asphyxia. It is, therefore, worth noting that the gas analysis clearly indicated a 60% reduced CO production rate with the addition of EPS into PVA.

Specific extinction area (SEA) is a parameter corresponding to the light absorption by the surface of smoke particles generated during burning of 1 kg of a substance. It is used to evaluate the visibility during a fire scenario. In terms of SEA, the EPS/PVA composite again shows 50% reduction in comparison to neat PVA, Table 1. This can be due to the incorporation of EPS, which helps the formation of a thermally stable insulating char layer, leading to a lower burning rate and lesser generation of combustion products, such as volatiles and smoke.

Self-extinguishing behaviour of EPS is displayed by a vertical burn test, Fig. 1(d). After second flame application, the EPS sample showed the flame-out without any flame or residue dripping. However, for both PVA and EPS/PVA composite, the vertical burning test has shown continuous burning with drips after removal of the fire source, whereas the neat PVA burnt more rapidly and intensely with many flaming drips. In summary, the addition of EPS to PVA significantly changed its thermal property and reduced the flammability.

3.2. Char analysis

After the cone calorimeter testing, the char formed by EPS and EPS/PVA was collected to investigate its microstructure and the presence of inorganic materials. It is interesting to see the needle-like whiskers appearing in the chars of both EPS and EPS/PVA composite, Fig. 2(a) and (c), with a difference in the length and diameter of the needle. These whiskers in EPS are about 40 μm in length and 2 μm in diameter, Fig. 2(a), while in EPS/PVA, they are about 10 μm in length and <1 μm in diameter, Fig. 2(c). The intensity of phosphorus and oxygen of those whiskers in the char is relatively high in EDX spectra, Fig. 2(b) and (d), indicating the presence of phosphate in both EPS and EPS/PVA. The needle-like whisker in char can be related to the formation of HAP crystals and/or other types of phosphate. Chen et al. have investigated the pressing effects on crystal structures of HAP since properties of the HAP crystal highly depend on the morphologies, crystallite size, composition and 3D structure (Chen et al., 2011). They have found that the increase in pressure transformed whisker-like structure of HAP into plate-like crystals, hexagonal prism-like crystals and crystal flakes. Hence, the needle-like structures within the char of EPS and EPS/PVA composites might be formed by a high internal pressure build-up due to the release of volatiles during pyrolysis of the materials. The EPS and EPS/PVA composite might have the different pressure during the combustion process, thereby leading to the different needle sizes. The formation of char and inorganic phosphate crystals (e.g., HAP) in EPS can act as a protective layer to restrict mass and heat transfer between flame and underlying materials, thereby reducing heat and smoke production of the polymeric material.

XRD analysis was also performed to identify phosphate crystals in both EPS and EPS/PVA char, Fig. 3(a) and (b). Besides hydroxyapatite, which was reported in previous study by Kim et al., 2020, other types of phosphate, such as different types of iron phosphate and sodium phosphate, were detected as well. The detection of these phosphate variants within the char further strengthens the claim of flame-retardant mechanism of the surface-migrating phosphate forming the protective char layer that limits the mass transfer of oxygen and volatile products.

4. Discussion

The EPS/PVA composite had a better fire performance with lower peak heat release rate, and reduced smoke generation, especially CO generation, compared to those of PVA without any additives. These improved properties are mainly attributed to the char forming ability of EPS that limits mass and heat transfer between flame and underlying material during the combustion process of the composites.

4.1. Converting phosphorus in the wastewater into flame retardants

In the municipal wastewater treatment plants, phosphorus removal is carried out via Enhanced Biological Phosphorus Removal (EBPR) process and the phosphorus content in EPS is approximately 3.1 wt%, which corresponds to around 9.5 wt% of the EPS to be phosphate (PO_4^{3-}). Generally, the phosphorus in EBPR sludge is considered to be mainly stored inside the cells of microorganisms in the form of polyphosphate (Seviour et al., 2003). However, a large amount of phosphorus has also been reported to get accumulated in the EPS (Li et al., 2010). According to Zhang et al. (2013), ^{31}P NMR spectroscopic analysis showed that total 6.6–10.5% of the extracted EPS comprises three main species of phosphorus, such as orthophosphate, pyrophosphate and polyphosphate. The phosphorus with diverse species in the EPS matrix could be the main source that imparts the flame-retardant property to EPS. Importantly, the phosphorus originating from municipal wastewater, via biological conversion, can be used as a resource to produce phosphorus-based flame retardants, which may reduce the consumption of limited natural phosphorus resource for the synthesis of phosphorus-based flame retardants.

Additionally, phosphorus recovery as EPS may be economically favourable for the wastewater treatment plant if municipal wastewater is no longer be perceived as a waste stream but 'water resource factories' to recover water, energy, fertiliser and other products (Kehrein et al., 2020). Phosphorus in the municipal wastewater can be recovered as struvite fertiliser. While phosphorus fertilisers are relatively cheap (Puyol et al., 2017), EPS are a potentially high value product (van der Roest et al., 2015). According to the possible process designs and models made by Kehrein et al. (2020), it is reasonable to argue that the

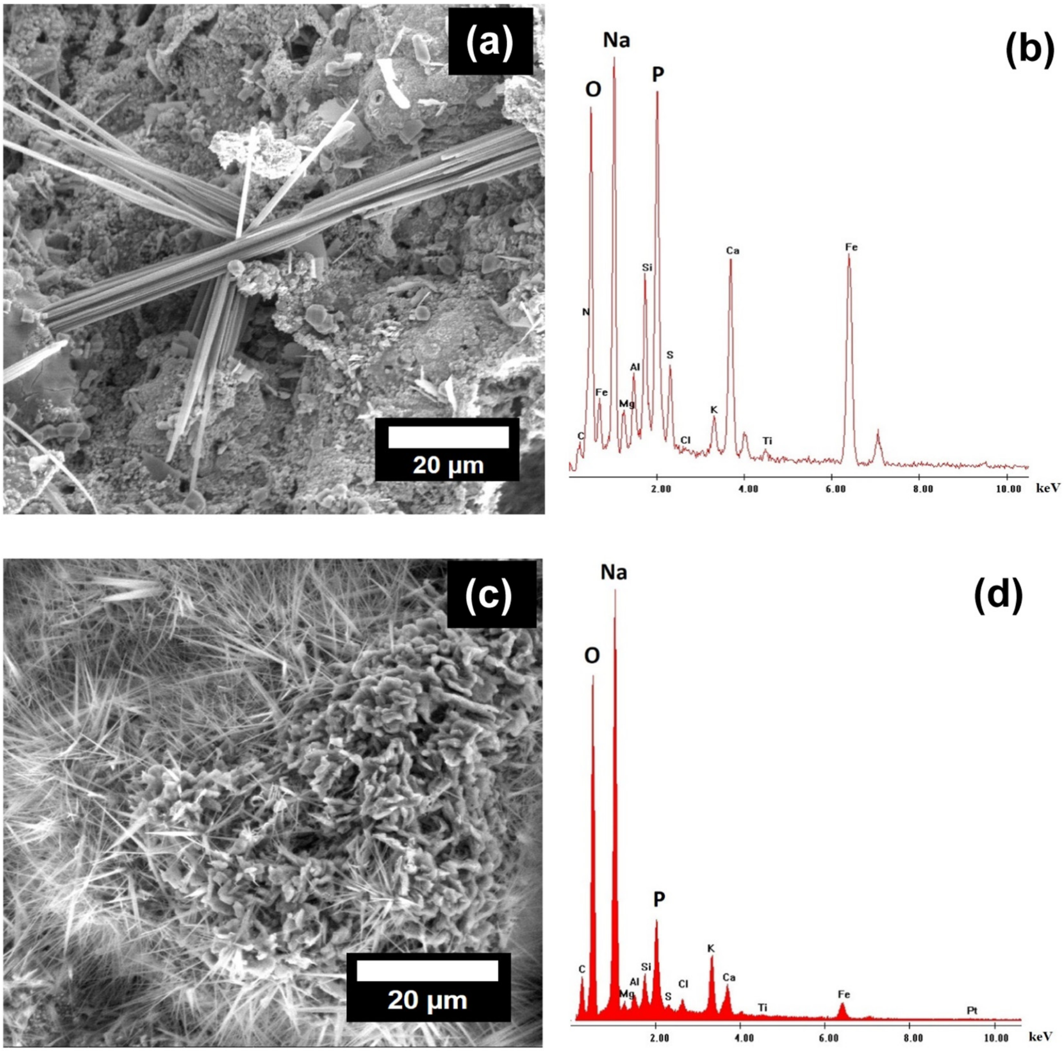

Fig. 2. ESEM images of char surfaces of (a) EPS, (c) EPS/PVA composite and EDX spectra of (b) EPS and (d) EPS/PVA composite.

phosphorus recovery as EPS may be economically favourable over the phosphorus recovery as a fertiliser.

4.2. Low carbon monoxide generation from EPS/PVA composite

Based on statistics, most people die in fires due to inhalation of smoke and toxic gases. Carbon monoxide (CO) is widely regarded as the major toxicant within these gases (Kaczorek et al., 2011). It is reported that phosphorus-based flame retardants can reduce the combustion efficiency, which is intrinsically accompanied by an increase in CO and smoke production (Schartel, 2010). Incomplete combustion due to the char formation interferes with reaction between volatile gases and oxygen, resulting in emission of less CO_2 and more CO (Kim et al., 2015; Purser, 2001). However, in the current research, the addition of EPS into PVA significantly decreased CO production rate (by 60%) while reducing the flammability of PVA at the same time. Moreover, the EPS/PVA composite achieved 28% reduction of mean CO yield compared to one of the PVA sample. Apparently, although phosphate is the important component in EPS to form char, the fire suppressing mechanism can be different from what was reported in literature. The decrease in CO emission can be attributed to the generation of gaseous products during the EPS combustion process. The released components are still unknown, but reactions of EPS under both gas phase and condensed phase (i.e., char formation) can be possible mechanisms to reduce heat release rate and CO yield. Further research is needed to investigate chemical component of EPS and understand the low CO emission of EPS.

4.3. EPS recovered from aerobic granular sludge as a candidate of bio flame retardant for synthetic polymers

Despite the growing demand for polymer matrix composites in several industries, such as building and construction, automotive, aerospace and electronics, their high flammability with the release of toxic gases during the combustion has greatly hindered their versatility in different applications. Phosphorus-based flame retardants have been intensively investigated in the plastic field, but their end-of-life disposal is still a critical environmental issue due to their limited biodegradability. Therefore, developments of phosphorus-based bio flame retardants are in high demand to solve the environmental issues. At these aspects, EPS recovered from aerobic granules can be considered as a potential candidate. With the current study and the previous research output (Kim et al., 2020) as a starting point, EPS being used as the bio flame-retardant filler for a polymer matrix has a great opportunity in the future.

5. Conclusions

- Extracellular polymeric substances (EPS), which were recovered from excess granular sludge, were successfully incorporated in PVA

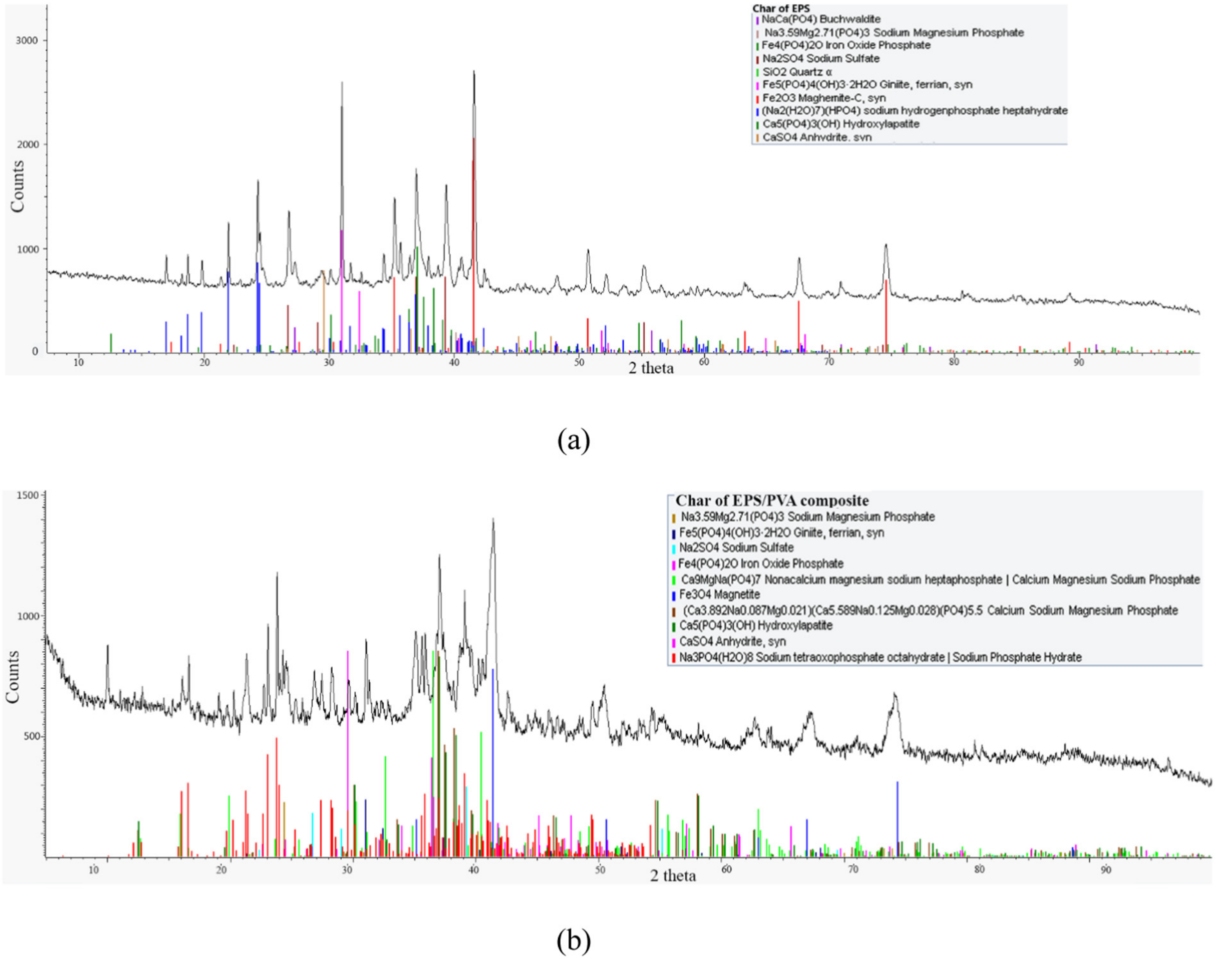

Fig. 3. XRD analysis of char of (a) EPS and (b) EPS/PVA composite.

by the solution casting method.

- Thermogravimetry analysis detected the significant increase in residue amount of the EPS/PVA composite (~ 30 wt%) compared to that of the neat PVA (~2.8 wt%) due to char forming ability of EPS.
- Microstructure and composition analyses of char from the combustion of EPS/PVA composite detected various types of phosphate whose intumescent flame retardant mechanism contributed to reduction of heat and CO release rates.
- The research output will leverage knowledge on up-cycle product development using extracted biomaterials for valuable industrial applications, where flame retardant materials are highly warranted.

CRediT authorship contribution statement

Nam Kyeun Kim: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing, Validation. **Richard Lin:** Investigation, Validation, Writing – review & editing. **Debes Bhattacharyya:** Investigation, Validation, Writing – review & editing. **Mark C.M. van Loosdrecht:** Investigation, Validation, Writing – review & editing. **Yuemei Lin:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing, Validation.

Declaration of competing interest

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

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