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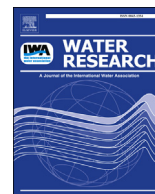
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Flame retardant property of flax fabrics coated by extracellular polymeric substances recovered from both activated sludge and aerobic granular sludge

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ABSTRACT

In this research, extracellular polymeric substances (EPS), such as EPS_{flocs} and EPS_{granules}, were successfully extracted from activated and aerobic granular sludge, respectively, and tested as bio-based flame retardant materials. Flax fabric was coated by the biopolymeric substances and its flammability was evaluated based on a vertical burning test defined in US Federal Aviation Regulation. Both EPS_{flocs} and EPS_{granules} coated flax fabrics achieved the self-extinguishment due to effective char formation. In particular, the result of the EPS_{granules} coated sample met the aviation requirements for the aircraft interior. Moreover, the presence of carbonated hydroxyapatite was identified in EPS_{granules} char residue by using FTIR and XRD analysis. It can contribute to the self-extinguishing property of the fabric by enhancing char formation. Thermogravimetric analysis also demonstrated that EPS_{granules} coated flax was able to produce greater amount of char residue and its decomposition rate was significantly reduced. This research indicates that there is a great potential to use this biopolymer as a resource for developing high performance bio-inspired flame retardant materials and contribute to a circular economy.

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1. Introduction

Wastewater treatment processes are widely implemented to protect the environment and recover clean water. The main problem is the large amount of waste sludge that is generated which needs further disposal. At present, the sludge produced from wastewater treatment processes, is considered as a waste product. The cost of handling/disposal of the waste sludge represents up to 50% of the wastewater treatment costs. However, from a circular economy point of view, wastewater treatment processes should be combined with producing resources from the waste compounds in the sewage. Thus, the waste sludge is actually a potential resource from which useful materials can be recovered.

A novel biological wastewater treatment process using aerobic sludge granulation has emerged for sewage treatment (Pronk et al., 2015). It stimulates micro-organisms to form granular biofilms

(called “granules”) rather than the traditional flocs in the process. In granular sludge, microorganisms produce extracellular polymeric substances (EPS) to form a polymeric hydrogel matrix and are thereby self-immobilized into this matrix without involvement of any carrier materials. It was found that a significant amount of EPS can be recovered from aerobic granular sludge, i.e. about 25% of granular sludge dry weight (Felz et al., 2016). If those recovered EPS can be applied to develop high performance new materials and contribute to a circular economy, the sustainability and economics of wastewater treatment can be strongly increased. Therefore, there is a great need to develop EPS-based high performance new materials.

One of the possible high performance materials could be EPS-based flame retardant materials. Currently, conventional flame retardant treatments have extensively been applied in plastic and textile industries (Innes and Innes, 2011). Different types of flame retardant agents (e.g. mineral, halogenated, phosphorus-containing, and nano-metric substrates) have been applied onto textiles as additives and solutions to enable textile products meet

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fire safety regulatory standards to fight against various fire hazards (Horrock, 2011). A 2017 market study of IHS Markit Consulting showed that 31% of the worldwide flame retardants consumption is covered by halogenated flame retardants (e.g., bromine and chlorine based agents) (IHS Markit, 2017). While the halogenated flame retardant compounds have effectively worked to diminish combustion in gas phase by releasing halogen halide and scavenging reactive free radicals during combustion (Costes et al., 2017), they have been associated with a wide range of harmful effects in human and environment, due to releasing highly toxic organic pollutants like polybrominated dioxins and furans (Dasari et al., 2013). Furthermore, three halogenated products are currently forbidden in the industrial market: penta- and octa-bromodiphenyl ether and hexabromo-mocyclododecane (Costes et al., 2017), and the usage of the halogen based flame retardant systems in textile products is gradually banned.

Based on the growing awareness of environmental issues and health & safety of users, the design of bio-based flame retardant materials is desirable as a replacement for synthetic counterparts. Bio-based materials, such as caseins, DNA and gluten, have been explored as flame retardant foaming agents for fabric and polymer (Alongi et al., 2013; Alongi et al., 2014; Das et al., 2019). In particular, caseins can be considered as polyaminoacids containing numerous phosphate groups in its micellar structure. The decomposition of caseins is assumed to be as similar as that of ammonium polyphosphate: (poly) phosphoric acid and ammonia are produced in the thermal decomposition. The (poly)phosphoric acid reacts with hydroxyl or other groups in the plastics or fabric, forming non-stable phosphate ester. In the next step, the dehydration of the phosphate ester follows. A carbon foam is formed on the surface against the heat source (charring). This carbon barrier acts as a insulation layer, preventing further decomposing of the material. In addition, releasing of ammonium dilutes the flammable gases produced from decomposition of the material and promotes intumescent char formation, preventing the spreading of the heat. (Alongi et al., 2014). Even though the content of phosphorus in caseins is less than 1%, the presence of both phosphorus and ammonia containing molecules has been shown to lead to the formation of a thermally stable char (Alongi et al., 2014). Furthermore, the combined effects of keratin protein fibre (i.e. wool) and intumescent flame retardant based on phosphorous significantly reduce heat and smoke production of polymers (Kim and Bhattacharyya, 2016). Due to the fact that, EPS recovered from aerobic granular sludge (EPS_{granules}) contains around 40% of proteins (Felz et al., 2019), and recent studies have revealed considerable accumulation of phosphorus in the EPS of sludge (Li et al., 2015), it was hypothesised that EPS_{granules} could be used to develop bio-based flame retardant materials. In addition, as activated sludge process is the conventional biological wastewater treatment process that is still widely used, the flammability of EPS_{granules} and EPS_{flocs} should be compared. Both polymers have different properties: gelling and flocculating for EPS_{granules} and EPS_{flocs}, respectively (Lin et al., 2013).

In this research, the fire ignition performance of both EPS_{granules} and EPS_{flocs} was investigated for their potential as flame retardant materials. Those biopolymers (EPS_{granules} and EPS_{flocs}) were coated onto flax fabrics, which have been widely used as fibre reinforcement, and their flame retardant performance was evaluated to determine if EPS_{granules} and EPS_{flocs} can provide flame retardant property to the flax fabrics. The flammability of the coated fabrics was evaluated by following ISO and Federal Aviation Regulation (FAR) standard tests. Thermogravimetric analysis (TGA), FT-IR and X-ray powder diffraction (XRD) analysis were employed to understand the self-extinguish behaviour of the coated flax fabrics.

2. Material and methods

2.1. EPS isolation from activated sludge flocs (EPS_{flocs}) and aerobic granular sludge (EPS_{granules})

Aerobic granular sludge was collected from the municipal wastewater treatment plant Dinxperlo in the Netherlands which is operated according to the Nereda® technology. Activated sludge flocs was collected from the municipal wastewater treatment plant Harnaschpolder in the Netherlands which is operated according to the conventional activated sludge process. The wastewater treatment process in both WWTPs achieve complete C, N and P removal. Specifically, P-removal is carried out via Enhanced Biological Phosphorus Removal (EBPR). There is no addition of FeCl₃ in both processes.

The EPS was recovered from both the collected granules and flocs according to Felz (Felz et al., 2019). Dried biomass (0.5 g) was extracted in 50 ml 0.5% Na₂CO₃ at 80 °C for 40 min with magnetic stirring. After centrifuging at 5,366×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 (4,000 rpm, 30 min), washed by di-deionized water until effluent pH reached 7 and dissolved in 5 ml 0.1 M NaOH to an EPS concentration of 3% (w/v). 50 ml of the EPS solution was recovered by ethanol precipitation and lyophilized.

2.2. Characterisation of EPS morphology by using scanning electron microscopy (SEM) and atomic force microscopy (AFM)

The morphologies of the lyophilized EPS_{granules} and EPS_{flocs} were investigated using a scanning electron microscope (SEM) (EVO MA10; Zeiss) at the following conditions: 20 kv, 100 pA, secondary electron detector (SE1). In addition, the morphologies of EPS_{granules} and EPS_{flocs} samples collected in the solution form in section 2.1 were studied by atomic force microscope. Sample preparation was carried out in air at ambient temperature and humidity using freshly-cleaved mica pretreated by 3 mM NiCl₃. Aliquots (2 µL) of the EPS_{granules} and EPS_{flocs} (5 mg/L) were deposited onto mica surfaces for 10 s, and then quickly removed by the pipette, respectively. Those surfaces were air dried (1 h) in a dust-free enclosure. Samples were scanned with a Digital Instruments Multimode atomic force microscope (Veeco Nanoscopy Iva dimension 3100).

2.3. EPS coating on flax fabrics

Twill weave flax fabric with two warp threads crossing every two-weft threads (145 g/m² areal density) was supplied from Libero (Belgium). The EPS_{granules} and EPS_{flocs} water solution (3% w/v) prepared in section 2.1 was sprayed on the surface of the flax fabrics for three times (300 ml in total) on a piece of the flax fabric with the same size (20 × 40 cm). After the coating process, the fabrics were air dried for 72 h.

2.4. 12s vertical burning test

A Bunsen vertical burning test was performed to investigate the burning characteristics of the coated flax fabric according to US Federal Aviation Regulation (FAR) 25.853 for aircraft interior (FAA, 2014). A fabric sample in the size of 304 × 55 mm was prepared and pre-conditioned at 23 °C and 50% humidity for 24 h before testing. A flame in the temperature of 850 °C was applied to the bottom edge of a vertically mounted fabric strip for 12 s. Two tests of each sample were conducted, and the flame extinguishing time duration, dripping time, and the burnt length were recorded for

each test. In comparison, the flame extinguishing and dripping times required for FAA certified materials are less than 15s and 3s, respectively, and the burnt length is less than 152.4 mm (6 in). The uncoated flax fabrics were also evaluated as reference control samples.

2.5. Fourier-transform infrared (FT-IR) analysis of the coated flax fabric before and after vertical burning test

The FT-IR spectra of the coated flax fabric before and after the vertical burning test were recorded on a FT-IR Spectrometer (Thermo Electron Scientific Instruments Corp., WI, USA) equipped with a diamond ATR accessory. Infrared spectra analysis software package OMNIC version 8.2 (Thermo Nicolet Analytical Instruments, WI, USA) was used for analysing the FTIR spectra and recording the data from the spectra. For each subsample, three replicate spectra were recorded to ensure the spectral reproducibility and assess analytical precision. All spectra were recorded in the range of 4000–550 cm^{-1} using the ATR method with a resolution of 4 cm^{-1} and 32 scans.

2.6. X-ray powder diffraction (XRD) analysis of the remained residue after vertical burning test

The XRD patterns of the fabrics 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 α 1 radiation ($\lambda = 0.154056 \text{ nm}$) in the 2θ region between 5° and 90° , step size 0.038° 2θ . 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.

2.7. Thermal stability tests

Thermal decomposition processes of uncoated flax fabrics, EPS_{granules} and EPS_{flocs} coated flax fabrics were investigated by a thermogravimetric analyser TGA-50 (Q5000, TA Instruments). Around 7 mg of specimen was heated up to 800 $^\circ\text{C}$ at a consistent heating rate of 10 $^\circ\text{C}/\text{min}$ under inert atmosphere.

3. Results

3.1. EPS yields and morphology

The EPS extracted from aerobic granular sludge, EPS_{granules}, represented $253 \pm 14 \text{ mg/g}$ volatile content of the sludge, while the EPS extracted from activated sludge, EPS_{flocs}, represented $150 \pm 20 \text{ mg/g}$ volatile content of the sludge. The yields of EPS_{flocs} is lower than that of EPS_{granules} (Lin et al., 2013).

The morphology of EPS_{granules} and EPS_{flocs} is significantly different (see Fig. 1) from each other: EPS_{granules} formed a web-like matrix with fibres entangled with each other, in Fig. 1(a). The diameter of the fibres was around 40–50 nm, this indicates that those fibres might be formed through self-assembly process. Through entanglement, the EPS_{granules} web covered the entire surface, which they attached on (Fig. 1(c)). In comparison, EPS_{flocs} did not form any fibres, instead, small patches with the size around 80–100 nm aggregated together (Fig. 1(b)). It was worth noticing that there were cracks in between the aggregated patches, especially when EPS_{flocs} attached on the surface (Fig. 1(d)). The cracks can be 300 μm in length and 45–50 nm in width. Due to the existence of cracks, it is impossible for EPS_{flocs} to form a continuous layer on the surface where it attached on. Thus, the different

morphology of EPS_{granules} and EPS_{flocs} can result to a significant dissimilar EPS coating layer on the surface: a continuous layer of EPS_{granules}, while a discontinuous coating layer of EPS_{flocs}. Thus, the different morphology of EPS_{granules} and EPS_{flocs} can result to a significant dissimilar EPS coating layer on the surface: a continuous layer of EPS_{granules}, while a discontinuous coating layer of EPS_{flocs}.

3.2. The influence of EPS coating on the flammability of flax fabric

The effects of both EPS_{granules} and EPS_{flocs} coating on the flammability of flax fabrics were clearly identified in the Bunsen vertical burning test. Fig. 2 shows the uncoated flax fabric, EPS_{flocs} coated and EPS_{granules} coated flax fabrics before, during and after burning test. The uncoated flax fabric is used as a reference control sample. During burning process, the significant difference can be seen at the moment of 5s: the uncoated flax fabric was ignited by the flame of the burner and the flame has spread over the entire fabric strip; the EPS_{flocs} coated flax fabric strip has been ignited and the flame has also spread into part of the fabric strip but has not spread over the entire fabric strip surface; the EPS_{granules} coated flax fabric has been ignited as well, but the spreading of the flame is strongly inhibited at the moment of 5s, and the flame size in this fabric during the testing was smaller than for the other two fabric samples. After igniting of 12s, the burner was removed. The uncoated flax fabric was found to be in continuous combustion until it completely burnt out. In comparison, both EPS_{flocs} and EPS_{granules} coated flax fabrics were found to stop burning, i.e., the flame was self-extinguished. As the exothermal heat still exist in burnt fabrics, there were red glows (afterglow) on both EPS_{flocs} and EPS_{granules} coated flax fabrics. The average afterglow time was recorded in Table 1. For EPS_{granules} coated flax fabrics, this afterglow time was extremely short, which is around $\frac{1}{4}$ of that for EPS_{flocs} coated flax fabric, indicating that the coating of EPS_{granules} shielded the transfer of heat. It was observed that, the afterglow on the EPS_{flocs} coated flax fabrics displayed a certain path along the surface. If the possibility of cracks formation is considered when EPS_{flocs} attached (coated) on the flax fabric surface, based on the result of SEM and AFM analysis in section 3.1, the exothermal heat may conduct along the cracks on the flax fabric surface in which there was less or hardly EPS_{flocs} coverage in the cracks. As the afterglow also consumed material, consequently, the average burnt length of EPS_{flocs} coated flax fabric was two times of that of the EPS_{granules} coated flax fabrics (Table 1 and Fig. 2).

The coating of both EPS_{flocs} and EPS_{granules} provided the flax fabric self-extinguishing property. In fact, the immediate flameout of the coated flax fabric was a remarkable result that indicate that both EPS_{flocs} and EPS_{granules} behave as a flame retardant material. The Bunsen vertical burning test performed in the current research is against US-FAR 25.853 for aircraft interior. For any material that can be certified as aircraft interior material, the required flame extinguishing and dripping times should be less than 15s and 3s, respectively, and the burnt length is less than 152.4 mm (6 in). In comparison, the flame extinguishing and dripping times for both EPS_{flocs} and EPS_{granules} coated flax fabrics were 0s, which have apparently met the standard. However, the burnt length of EPS_{flocs} and EPS_{granules} coated flax fabric was 260 mm and 130 mm, respectively, this means that only EPS_{granules} coated flax fabrics in existing coating conditions reach the requirement for the aircraft interior material.

3.3. Functional groups in EPS by FTIR analysis

In order to understand the functional groups that played a role in the self-extinguishing property of both EPS, FTIR analysis was performed on EPS coated flax fabric before and after Bunsen vertical burning test. The spectrum of uncoated flax fabric was used as

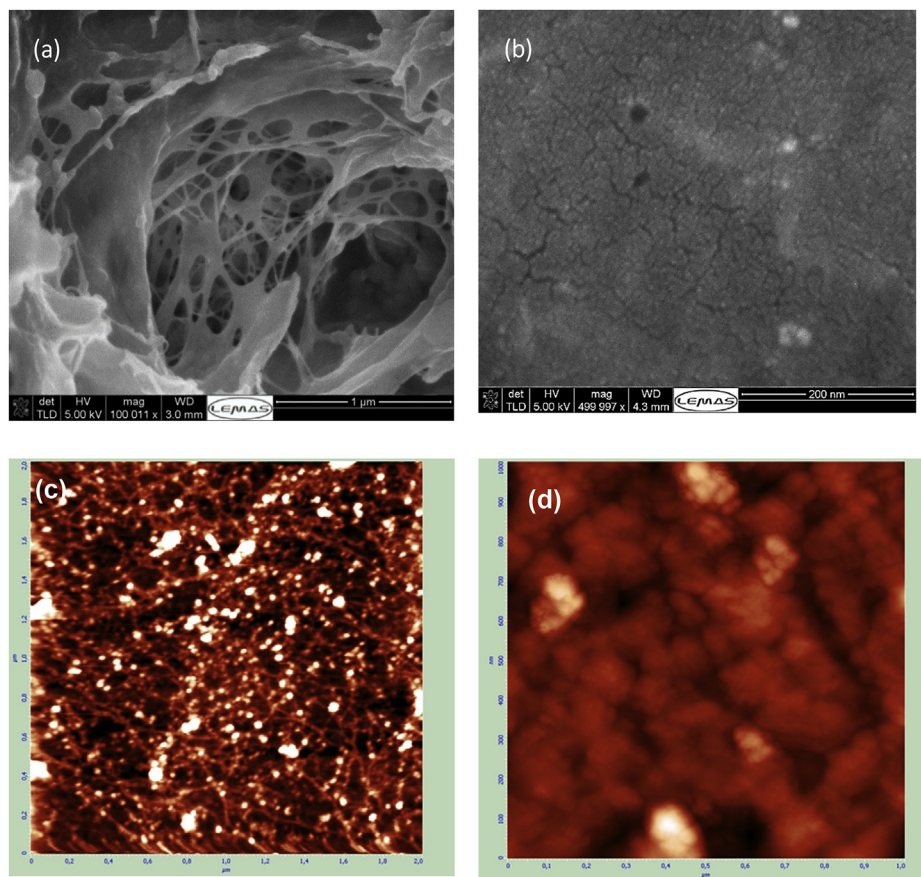


Fig. 1. Morphology of EPS_{granules} and EPS_{flocs} observed by using SEM and AFM. (a) EPS_{granules} by SEM; (b) EPS_{flocs} by SEM; (c) EPS_{granules} by AFM; (d) EPS_{flocs} by AFM. (c) is adapted from Lin et al.

a reference. As displayed in Fig. 3(a), the spectra of EPS_{flocs} and EPS_{granules} coated flax fabrics before burning are similar: a broad band at 3700–3100 cm^{-1} indicates the presence of –OH group. A relatively sharp peak at 3280 cm^{-1} is assigned to N–H group in the proteins. A peak at 1630 cm^{-1} , implies the dominant protein secondary structure is cross-beta sheet (Lin et al., 2018); a band at 1200–940 cm^{-1} with the peak value at 1050–1080 cm^{-1} implies the presence of both carbohydrates and phosphate group. In comparison to the reference spectrum of uncoated flax fabric, the coating of EPS_{flocs} and EPS_{granules} covered the FTIR signal of uncoated flax fabric, meaning the EPS coating distributed evenly on the flax fabric surface. It was noticed that there are two main differences between the spectra of EPS_{flocs} and EPS_{granules} coated flax fabrics: 1) For EPS_{granules} coated flax, the peak of the band at 1200–940 cm^{-1} is at 1050 cm^{-1} , while the peak of the same band for EPS_{flocs} coated flax fabric is at 1080 cm^{-1} , if the spectrum of uncoated flax at this region is compared, the peak value and the shape of the band at 1200–940 cm^{-1} of EPS_{flocs} coated flax fabric is more similar to that of the uncoated flax fabric. This is probably caused by the morphology of EPS_{flocs}: there are cracks in between the patches, which could make the flax fabric at the crack not completely covered by the EPS_{flocs}. 2) There is a weak peak present in the spectrum of EPS_{granules} coated flax at 870 cm^{-1} , but not in the spectrum of EPS_{flocs} coated flax fabric. This peak is normally assigned to carbonates (CO_3^{2-}) (Ribeiro et al., 2006).

EPS_{granules} coated flax fabrics turned black due to char formation. The similarities in the two spectra areas, Fig. 3(b): the broad band at 3700–3100 cm^{-1} which indicates the presence of –OH group is still present, while the sharp peak at 3280 cm^{-1}

disappeared. Likely, the protein fraction was consumed in the burning process. The peaks at 1630 cm^{-1} and 1550 cm^{-1} that are amide I and II peaks for proteins turned to one peak at 1598 cm^{-1} . This is probably due to the burning product and char formation of proteins. A new band appearing at 1408 cm^{-1} is assigned to carbonates (Socrates, 2001). The peak of the band at 1200–940 cm^{-1} shifted to 1009 cm^{-1} , which is one of the typical peaks of phosphates (Ribeiro et al., 2006). The intensity of this band increased, likely due to the burning out of the organic fraction, the inorganic fraction such as phosphate becomes dominant in the residue. In addition to the similarities, the differences in the two spectra are: Although the new band with the peak at 1408 cm^{-1} appears in both spectra, the intensity of this band is much stronger for EPS_{granules} coated flax fabrics. In addition, there is a shoulder peak at 1483 cm^{-1} , which is only present in the spectrum of EPS_{granules} coated flax, both two peaks are characteristics for carbonates (Rehman and Bonfield, 1997). The band at 876 cm^{-1} , which is also assigned to carbonates, becomes extremely sharp in the spectrum of EPS_{granules} coated flax fabric. A new band at 726 cm^{-1} only appeared in this spectrum, indicating the presence of phosphate (Elliot, 1994). The possibility that the carbonate bands were due to the formation of a calcium carbonate residue can be ruled out. Calcium carbonate decomposes at 825 $^{\circ}\text{C}$ into CaO and CO_2 (the Merck Index), while the temperature at Bunsen vertical burning test is 850 $^{\circ}\text{C}$, any calcium carbonate would disappear at this temperature. Regarding thermal stability and the typical carbonates and phosphates bands in the current spectra (Ribeiro et al., 2006), carbonated hydroxyapatite is the most possible candidate for the inert residue of EPS_{granules} coated flax fabric.

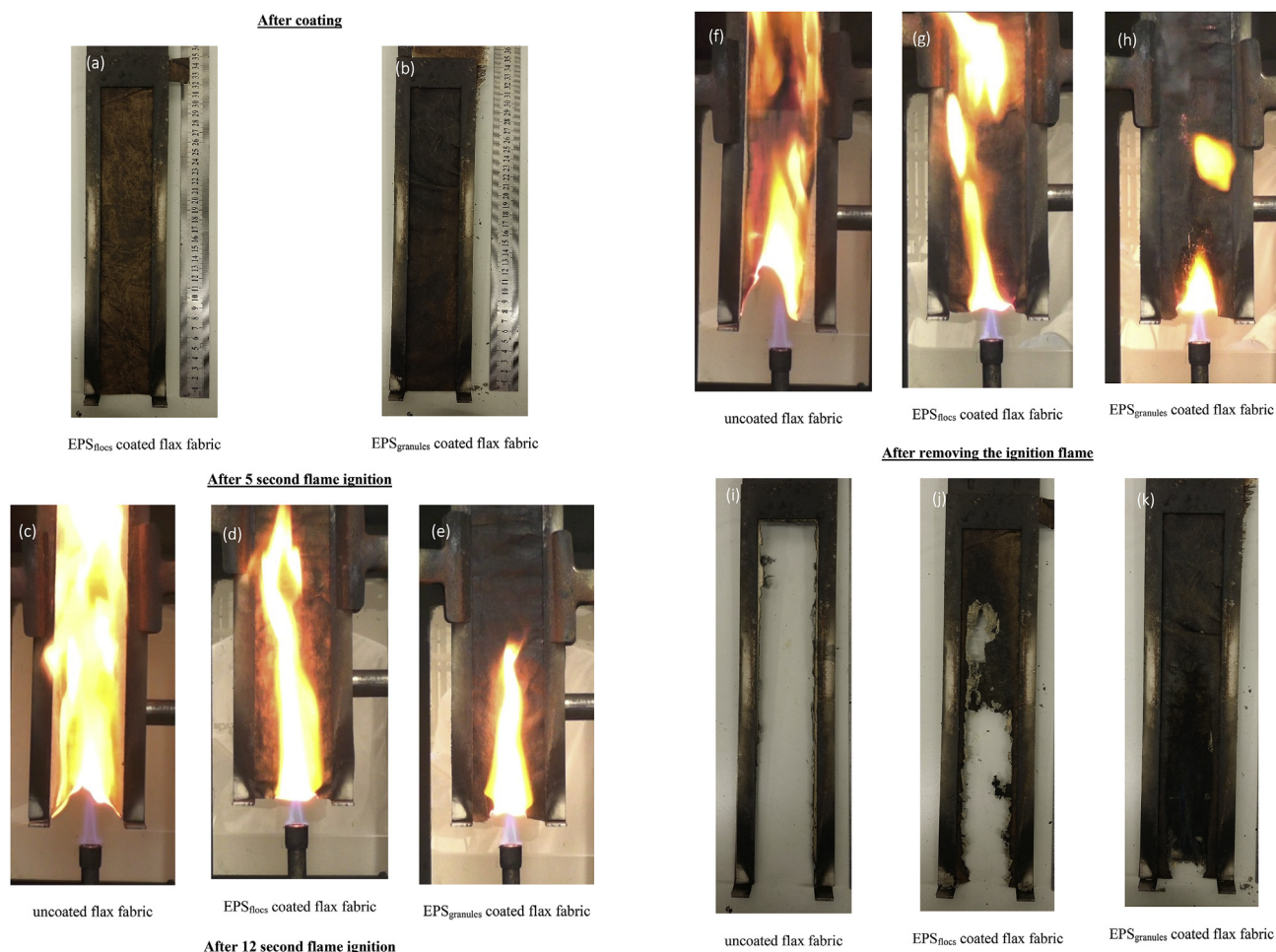


Fig. 2. The uncoated flax fabric, EPS_{flocs} coated and EPS_{granules} coated flax fabrics before, during and after burning. (a) and (b) are EPS_{flocs} and EPS_{granules} coated flax fabrics before burning, respectively. (c), (d) and (e) are uncoated flax fabric, EPS_{flocs} and EPS_{granules} coated flax fabrics after burning for 5 s, respectively. (f), (g) and (h) are uncoated flax fabric, EPS_{flocs} and EPS_{granules} coated flax fabrics after burning for 12 s, respectively. (i), (j) and (k) are uncoated flax fabric, EPS_{flocs} and EPS_{granules} coated flax fabrics after the burning was completely finished.

Table 1

US-FAR 12 s vertical burning test results.

Sample	Avg. Flame time (s)	Avg. Afterglow time (s)	Avg. Burnt length (mm)	Drip
EPS _{flocs} coated flax fabric	0	~180	260	No
EPS _{granules} coated flax fabric	0	42	130	No

Summarising, the FTIR analysis suggested that, besides the char formed, one of the dominate composites in the remaining residue of EPS_{granules} coated flax fabric after burning is carbonated hydroxyapatite, while in the residue of EPS_{flocs} coated flax fabric is phosphate.

In order to clarify if a carbonated hydroxyapatite was obtained, XRD analysis was done to the remaining residue. In the residue of EPS_{granules} coated flax fabric, the presence of carbonated hydroxyapatite [Ca₁₀(PO₄)₆(CO₃)] was successfully detected. Unfortunately, the phosphate in the residue of EPS_{flocs} coated flax fabric could not be detected, leading to the assumption that the phosphate is in an amorphous mineral.

3.4. Thermal stability analysis

To understand the impact of EPS coating on the thermal stability of flax fabric, thermogravimetric (TG) analysis was done on EPS_{flocs}

and EPS_{granules} coated flax fabrics. The same analysis on uncoated flax fabric was taken as a reference. A TG curve of uncoated flax demonstrates an initial weight loss (approx. 7%) at around 100 ~ 150 °C due to moisture evaporation. Further weight reduction at 250 °C can be related to the thermal degradation of hemicellulose of flax, which occurs at around 284 °C (Kim et al., 2018). In addition, the TG curve indicates the second thermal decomposition at around 385 °C that can be caused by the cleavage of glycosidic linkage of cellulose (Kim et al., 2017), and then fully decomposition occurs at approx. 670 °C without any residue formation, Fig. 4. The positive effects of EPS_{flocs} and EPS_{granules} coating on thermal stability of flax are clearly observed in the TG and derivative thermogravimetric (DTG) curves. There was a significant increase in residue amount of both EPS_{flocs} and EPS_{granules} coated flax fabrics. Both coated flax fabrics left approx. 28 wt% carbonaceous residues at 800 °C, Fig. 4(a), which indicates a higher amount of char formation. The EPS coating reduced the maximum decomposition rate

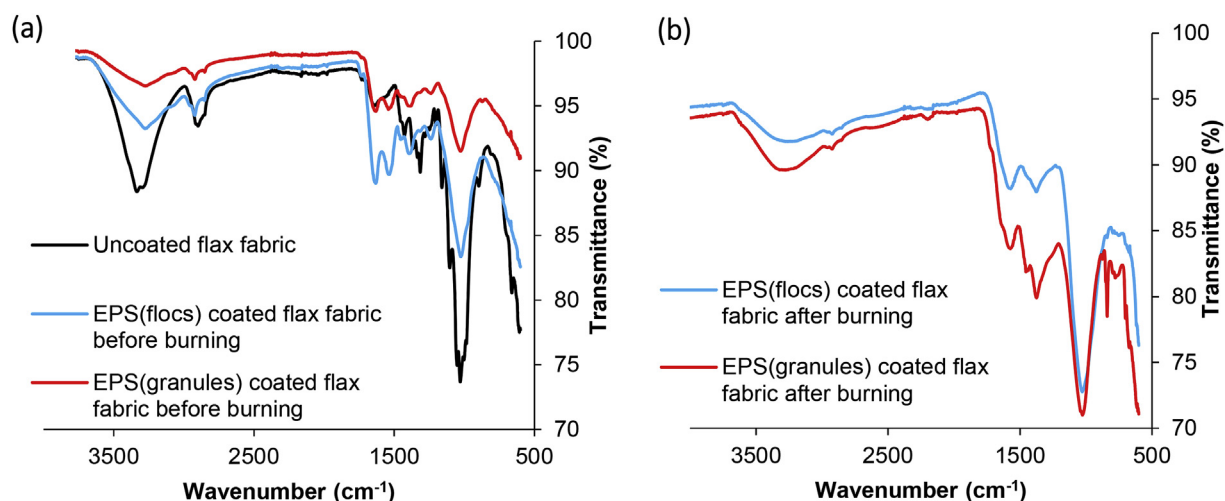


Fig. 3. FTIR spectra of the uncoated flax fabric, EPS_{flocs} coated and EPS_{granules} coated flax fabrics (a) before and (b) after burning.

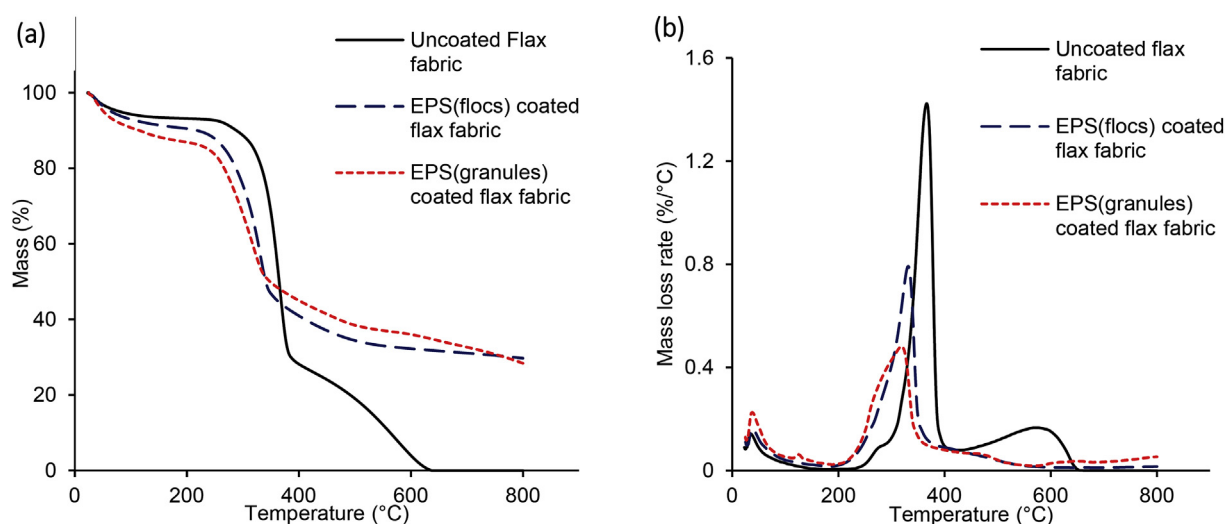


Fig. 4. TG and DTG curves of uncoated flax fabric, EPS_{flocs} and EPS_{granules} coated flax fabrics; (a) TG and (b) DTG.

from 1.4%/°C for uncoated flax fabric, to 0.8%/°C for EPS_{flocs} coated flax fabric, and 0.5%/°C for EPS_{granules} coated flax fabric, Fig. 4(b). The char and inert residue formed during decomposition were thermally stable, making further loss of material extremely slow even with the increasing of temperature. Especially, the EPS_{granules} coated flax fabric shows the lowest thermal decomposition rate, suggesting the coating of EPS_{granules} works successfully as a kind of barrier for heat and/or mass transfer; the durable char formation of EPS_{granules} coating prevented the additional thermal decomposition and pyrolysis of flax fabric.

4. Discussions

4.1. The extracellular polymeric substances extracted from both activated sludge and aerobic granular sludge have self-extinguishing property

In order to investigate the possibility of developing bio-based flame retardant material, the extracellular polymeric substances recovered from activated sludge and aerobic granular sludge were used as a coating material for flax fabric. It was found that both

EPS_{flocs} and EPS_{granules} have a self-extinguishing property. FTIR spectroscopy indicated that both EPS have proteins, and phosphate is one of the main components in the remaining residue after burning.

Biomacromolecules such as proteins (whey proteins, caseins, hydrophobins) and DNA have very recently shown unexpected flame retardant/suppressant features when deposited on cellulosic or synthetic substrates, like cotton, polyesters or cotton-polyester blends (Alongi et al., 2014b). More specifically, caseins are phosphoproteins. During burning, they are capable of influencing the cellulose pyrolysis toward the formation of char (Alongi et al., 2013). The phosphate groups in DNA will also result in phosphoric acid under thermal degradation which reacts with cellulose to enhance the char formation. In addition, the nitrogen containing base referred to the monomers of DNA releases ammonia, which can dilute the concentration of oxygen in the gas phase so that flame inhibition can be achieved (Price and Horrocks, 2009).

Considering that phosphates have been found as one of the main components in the remaining residue of both EPS_{flocs} and EPS_{granules}, they must originate from the recovered EPS. Whether they are in the format of phosphoproteins, phosphorylated

carbohydrates or phosphates minerals still needs further investigation. Based on the self-extinguishing property that they displayed in the current research, it is reasonable to category them into the phosphorus-based flame retardant category. Very recently, phosphorus-based flame retardants are proposed as halogen-free flame retardants for various polymeric materials (Schartel, 2010). Phosphoric acid is formed upon degradation of organic phosphate. They can act in the condensed phase by enhancing char formation, yielding intumescence, or through inorganic glass formation; and in the gas phase through flame inhibition (Schartel, 2010).

It seems that EPS_{flocs} and EPS_{granules} can enhance char formation, likely due to phosphate and/or the synergetic effect of both phosphate and nitrogen from amine group in proteins, thereafter decelerate the decomposition reaction and shield the heat transfer. Especially, the EPS_{flocs} and EPS_{granules} coating greatly reduced the decomposition rate to almost a half, or even one third of the uncoated flax fabric. One interesting phenomenon was: the EPS_{flocs} and EPS_{granules} coating lowered the decomposition temperature, making the coated flax fabrics start decomposition at lower temperature in a slower rate. In fact, a lot of successfully flame retarded systems start to decompose at lower temperatures than the corresponding material without any flame retardant. This also results in flame retarded systems often igniting earlier than corresponding non-flame retarded polymers. The resulted two-step or multi-step decomposition of materials seems to be the more important general feature of charring systems (Lyon, 2004; Schartel, 2010). Study of the mechanism behind the self-extinguishing property of EPS_{flocs} and EPS_{granules} can be done in future research by using cone-calorimeter, TG-MS and TG-FTIR analysis.

4.2. The extracellular polymeric substances recovered from aerobic granular sludge is a better candidate of bio phosphorus-based flame retardant

Although both EPS_{flocs} and EPS_{granules} have self-extinguishing property, only EPS_{granules} coated flax fabric reached the complete requirement for the vertical burning test for aircraft interior materials with the respect of flame retardancy. Different from EPS_{flocs}, carbonated hydroxyapatite is one of the main components in the remaining residue of EPS_{granules} coated flax fabric.

Hydroxyapatite is the most stable calcium phosphate phase at neutral pH (Koutsoukos et al., 1980). It is also thermally stable till 1300 °C (Omelson and Grynpas, 2008). Marine bacteria, oral bacteria, *E.Coli* and some other bacteria have been identified as microorganisms that are capable of metabolizing phosphorus and mineralizing apatite intra and extracellularly (Schulz et al., 2005). It was reported that carbonated hydroxyapatite was formed when hydroxyapatite-alginate was burned. Burning of alginate caused an increase of local concentration of CO₂, favoring the reaction between CO₂ and –OH[−] group of hydroxyapatite, consequently form carbonated hydroxyapatite by substitute OH[−] by CO₃^{2−} (Elliot, 1994). Thus, it is reasonable to assume that there is hydroxyapatite in EPS_{granules} which is produced by microorganisms. During burning of the EPS_{granules} coated flax fabric, the production of CO₂ from the burning of proteins and other organic material favored the formation of carbonated hydroxyapatite. Carbonated hydroxyapatite itself is already reported as a flame retardant (Lu et al., 2014). In comparison, carbonated hydroxyapatite could not be detected in the residue of EPS_{flocs} coated flax fabric by XRD analysis. This might be the reason that EPS_{granules} is a better flame retardant than EPS_{flocs}. Why there are different forms of phosphate in different EPS? How does carbonated hydroxyapatite affect char formation and reduce the decomposition rate of EPS_{granules} coated flax fabric requires better understanding in the future.

4.3. Practical and economic feasibility

The worldwide consumption of flame retardant is more than 2.25 million tonnes per year (<https://www.flameretardants-online.com/flame-retardants/market>). In volume terms, the market size is expected to grow at a global rate of 3.1% until 2021. Major flame retardant is aluminium hydroxide (38%) and second large share (31%) is the halogenated flame retardant systems consisting of brominated and chlorinated products. The halogenated flame retardants have been associated with a wide range of harmful effects in human and environment, due to releasing highly toxic organic pollutants like polybrominated dioxins and furans. Therefore, the substitution of the halogenated flame retardant with more sustainable non-halogenated products is a current trend in the flame retardant additive industry. Furthermore, the end-of-life disposal of synthetic polymer and additive is mostly done through incineration and landfilling, which result in air pollution, increase of greenhouse gases and soil contamination. Based on environmental and human concerns, bio-based flame retardants have become vital and researches have actively been conducted to develop new types of the flame retardant additives made from renewable resources.

Despite significant potential of proteins (whey proteins, caseins, hydrophobins) and DNA in the flame retardancy field, one challenging issue on the use of biomacromolecules as flame retardants is the possibility of adjusting this technology to a large scale, which is a key point for assessing its further industrial development (Alongi et al., 2014b, 2014a).

At this point, EPS_{granules} has an advantage. Aerobic sludge granulation technology currently commercialized by RoyalHaskoningDHV (RHDHV) under the name Nereda® is rapidly spreading with already 70 full-scale granular sludge wastewater treatment plants (WWTPs) worldwide built or under construction on 5 continents since 2013. About hundred plants are expected to operate by next year. Sufficient waste granular sludge can be provided. The commercial name of EPS_{granules} is Kaamera. The first Kaamera pilot production plant will be opened in October 2019 in the Netherlands. This plant can produce 400 tons of Kaamera per year. Therefore, large scale production of EPS_{granules}/Kaamera is possible. Considering the technology of coating Kaamera on the surface of the fabrics can be easily combined within the fabric production process, there is a great potential for the practical and economic feasibility of using EPS_{granules} as bio-flame retardant for fabrics.

5. Conclusions

- The extracellular polymeric substances (EPS) recovered from both activated sludge and aerobic granular sludge have self-extinguishing property. This fire resistant behaviour make them a suitable flame retardant materials for coatings.
- Flax fabric coated with EPS recovered from aerobic granular sludge meets the flame retardancy requirements in US Federal Aviation Regulation standards with the respect of flame retardancy.
- The EPS recovered from aerobic granular sludge is a better candidate of bio phosphorus-based flame retardant. Granular sludge is potential bioresource for the development of biobased materials with high performance.

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.

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References

- Alongi, J., Carletto, R.A., Di Blasio, A., Carosio, F., Bosco, F., Malucelli, G., 2013. DNA: a novel, green, natural flame retardant and suppressant for cotton. *J. Mater. Chem.* 1 (15), 4779–4785.
- Alongi, J., Bosco, F., Carosio, F., Di Blasio, A., Malucelli, G., 2014b. A New Era for Flame Retardant Materials?, vol. 17, pp. 152–153. <https://doi.org/10.1016/j.mattod.2014.04.005>.
- Alongi, J., Cuttica, F., Blasio, A.D., Carosio, F., Malucelli, G., 2014a. Intumescent features of nucleic acids and proteins. *Thermochim. Acta* 591, 31–39.
- Costes, L., Laoutid, F., Brohez, S., Dubois, P., 2017. Bio-based flame retardants: when nature meets fire protection. *Mater. Sci. Eng. R Rep.* 117, 1–25.
- Das, O., Rasheed, F., Kim, N.K., Johansson, E., Capezza, A.J., Kalamkarov, A.L., Hedenqvist, M.S., 2019. The development of fire and microbe resistant sustainable gluten plastics. *J. Clean. Prod.* 222, 163–173.
- Dasari, A., Yu, Z.-Z., Cai, G.-P., Mai, Y.-W., 2013. Recent developments in the fire retardancy of polymeric materials. *Prog. Polym. Sci.* 38 (9), 1357–1387.
- Elliot, J.C., 1994. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*. Elsevier, Amsterdam, p. 213.
- Federal aviation administration, Department of transportation, FAR25.853, Appendix F to Part 25, Vertical Test.
- Felz, S., Al-Zuhairy, S., Aarstad, O.A., van Loosdrecht, M.C.M., Lin, Y.M., 2016. Extraction of structural extracellular polymeric substances from aerobic granular sludge. *JoVE (Journal of Visualized Experiments)* (115), e54534.
- Felz, S., Vermeulen, P., van Loosdrecht, M.C.M., Lin, Y.M., 2019. Chemical characterization methods for the analysis of structural extracellular polymeric substances (EPS). *Water Res.* 157, 201–208.
- Horrock, A.R., 2011. Flame retardant challenges for textiles and fibres: New chemistry versus innovative solutions. *Polym. Degrad. Stab.* 96, 377–392.
- Innes, A., Innes, J., 2011. Flame retardants. In: *Applied Plastics Engineering Handbook*.
- Kim, N.K., Bhattacharyya, D., 2016. Development of fire resistant wool polymer composites: mechanical performance and fire simulation with design perspectives. *Mater. Des.* 106, 391–403.
- Kim, N.K., Lin, R.J.T., Bhattacharyya, D., 2017. Flammability and mechanical behaviour of polypropylene composites filled with cellulose and protein based fibres: a comparative study. *Compos. Appl. Sci. Manuf.* 100, 215–226.
- Kim, N.K., Dutta, S., Bhattacharyya, D., 2018. A review of flammability of natural fibre reinforced polymeric composites. *Compos. Sci. Technol.* 162, 64–78.
- Koutsoukos, P., Amjad, Z., Tomson, M.B., Nancollas, G.H., 1980. Crystallization of calcium phosphates. A constant composition study. *J. Am. Chem. Soc.* 102 (5), 1553–1557.
- Li, W.W., Zhang, H.L., Sheng, G.P., Yu, H.Q., 2015. Roles of extracellular polymeric substances in enhanced biological phosphorus removal process. *Water Res.* 86, 85–95.
- Lin, Y.M., Sharma, P.K., van Loosdrecht, M.C.M., 2013. The chemical and mechanical differences between alginate-like exopolysaccharides isolated from aerobic flocculent sludge and aerobic granular sludge. *Water Res.* 47 (1), 57–65.
- Lin, Y., Reino, C., Carrera, J., Pérez, J., van Loosdrecht, M.C.M., 2018. Glycosylated amyloid-like proteins in the structural extracellular polymers of aerobic granular sludge enriched with ammonium-oxidizing bacteria. *Microbiolopen* 7 (6), e00616.
- Lu, B.Q., Zhu, Y.J., Chen, F., 2014. Highly flexible and nonflammable inorganic hydroxyapatite paper. *Chemistry—A European Journal* 20 (5), 1242–1246. <https://doi.org/10.1002/chem.201304439>.
- Lyon, R.E., 2004. Plastics and rubber. In: Harper, C.A. (Ed.), *Handbook of Building Materials for Fire Protection*. McGraw-Hill, New York, NY, USA (chapter 3) 3.1–3.51.
- Omelson, S.J., Grynaps, M.D., 2008. Relationships between polyphosphate chemistry, biochemistry and apatite biomineralization. *Chem. Rev.* 108, 4694–4715.
- Price, D., Horrocks, A.R., 2009. Polymer degradation and the matching of FR chemistry to degradation. In: *Fire Retardancy of Polymeric Materials*, second ed. CRC Press, Boca Raton, pp. 15–42.
- Pronk, M., De Kreuk, M.K., De Bruin, B., Kamminga, P., Kleerebezem, R.V., van Loosdrecht, M.C.M., 2015. Full scale performance of the aerobic granular sludge process for sewage treatment. *Water Res.* 84, 207–217.
- Rehman, I., Bonfield, W., 1997. Characterization of hydroxyapatite and carbonated apatite by photo acoustic FTIR spectroscopy. *J. Mater. Sci. Mater. Med.* 8 (1), 1–4.
- Ribeiro, C.C., Barrias, C.C., Barbosa, M.A., 2006. Preparation and characterisation of calcium-phosphate porous microspheres with a uniform size for biomedical applications. *J. Mater. Sci. Mater. Med.* 17 (5), 455–463.
- Schartel, B., 2010. Phosphorus-based flame retardancy mechanisms—old hat or a starting point for future development. *Materials* 3, 4710–4745.
- Schulz, Heide, N., Schulz, H.D., 2005. Large sulfur bacteria and the formation of phosphorite. *Science* 307 (5708), 416–418.
- Socrates, L., 2001. *Infrared and Raman Characteristic Group Frequencies—Tables and Chars*. John Wiley & Sons, Chichester, p. 227.
- The flame retardants market, 2017. *Flameretrdant-online*. <https://www.flameretardants-online.com/flame-retardants/market>.