Simple And Green Synthesis of Calcium Alginate/Hydroxyapatite Hybrid Material Without High Temperature Treatment And Its Flame Retardancy

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Research Article

Keywords: Hybrid material, Calcium alginate, Hydroxyapatite, Flame retardancy, Mechanism

Posted Date: September 22nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-875067/v1>

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Version of Record: A version of this preprint was published at Cellulose on January 30th, 2022. See the published version at <https://doi.org/10.1007/s10570-021-04373-w>.

Abstract

Aiming to improve the thermal stability and flame retardant properties of calcium alginate, calcium alginate (CaAlg)/hydroxyapatite (HAP) hybrid material was synthesized in situ by the sol-gel method at room temperature. It was found that the HAP particles were generated from nanospheres to urchin-like microspheres, finally to wrinkled sponge microspheres with the two-dimensional nanostructured surface. The results show that the thermal stability and flame retardancy of the hybrid material were significantly improved, and its mechanism was proposed as HAP promoted the decarboxylation of alginate resulting in carbonization of CaAlg/HAP, and it was the function of solid phase before 350 °C, while the synergistic effects of gas phase and solid phase after 350 °C that led to the high flame retardancy of CaAlg/HAP.

Introduction

Alginate is a marine biomass polysaccharide, which is composed of β -D-mannuronic acid (M blocks) and α -L-guluronic acid (G blocks) in an unspecified sequence (He et al. 2021; Kabir et al. 2020). On account of its biodegradability, recyclability, low price and accessibility (Mokhena et al. 2020), alginate has been used in textile (Yu et al. 2020), decorative materials and other fields (Ahmad et al. 2021), however, some applications of alginate are restrained for its limited flammability (Xu et al. 2021). It has been found that sodium alginate (NaAlg, the most common alginate) can form polyanionic electrolytes under neutral and alkaline conditions, therefore, it can cross-link with divalent cations (Liu et al. 2016b; Liu et al. 2015b; Liu et al. 2015c; Liu et al. 2016c) and trivalent cations (Liu et al. 2015a; Liu et al. 2016a) to form a stable "egg-box" structure microstructurally, and a sol-gel reaction visually (Hu et al. 2021), resulting in better flame retardant property than NaAlg. G block is the main factor for the formation of "egg-box" (Hecht and Srebnik 2016), and M block is related to mechanical properties of alginate (Liu et al. 2020).

In order to expand the application of alginate, researchers have applied CaAlg more frequently which can be prepared by NaAlg and calcium salt as it exhibits better flame retardancy (Yu et al. 2021b), while CaAlg cannot fulfill the ideal thermal stability and flame retardancy, thus people try to prepare other hybrids to solve these defects (Xu et al. 2021). The synergistic effect between natural biomacromolecules and inorganic compounds has been a hot research direction for scientists recently. Compared with the complex and even harmful doping process of organics (Sun et al. 2021b), inorganics doping is simpler and more environmentally friendly (Chen et al. 2017). In our previous works, the flame retardant properties of CaAlg doped with inorganic substances such as calcium borate (Liu et al. 2018), Cu_2O (Shao et al. 2019), Ag_3PO_4 (Zhang et al. 2020), and AgCl (Zhang et al. 2021) have been studied.

Hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, HAP), as an inorganic phosphate, may be effectively improve the flame retardancy of alginate for it possesses a very high decomposition temperature (above 1000 °C) (Yang et al. 2018). Since HAP is a major component of human teeth and bones, its excellent biocompatibility and bioactivity make it a reliable material of synthetic teeth, artificial bones and drug carriers (Pluta et al. 2018; Sokolova et al. 2020). Now different sizes and morphologies of HAP with multiple properties and applications can be prepared by various methods (Sadat-Shojai et al. 2013; Sarker et al. 2015; Sun et al. 2017). Researchers have obtained applicable materials by combining CaAlg and HAP, such as porous HAP/CaAlg composite beads for improving the cycling performance of pectinase (Qi et al. 2020), and ultralong HAP nanowires/CaAlg hybrids with excellent mechanical properties (Jiang et al. 2017), while flame retardancy and mechanism of these hybrids have not been reported yet.

Among the existing synthesis methods of HAP, hydrothermal and sol-gel method are the common ones, while both of them require a high temperature treatment (Costa et al. 2012). For example, the linear HAP prepared by hydrothermal method needed to be treated at 180 °C for at least 12 h (Ma et al. 2017), and it must be calcined at above 1000 °C in the sol-gel method, or else resulted in amorphous HAP crystals (Ruban Kumar and Kalainathan 2010). Other methods are more complex or time consuming (Mohd Pu'ad et al. 2020; Yelten and Yilmaz 2016). However, due to the pyrolysis of CaAlg when heated, it is impossible to prepare the required hybrid materials directly and simply with phosphate by high temperature calcination or hydrothermal method. Furthermore, it would be more consistent with the concept of green chemistry if the high temperature

treatment was eliminated. Hence, the synthesis of HAP with practical value at room temperature is meaningful, although challenging.

In this direction, the green and simple sol-gel method without a high temperature treatment was implemented to prepare the CaAlg/HAP hybrid material in this study, and the dynamic characteristics of the consumed Ca^{2+} and the morphology of HAP particles were studied during the in-situ reaction. Furthermore, the thermal stability, flame retardant properties and its pyrolysis mechanism of CaAlg/HAP were explored, aiming to provide a new approach and theoretical basis to prepare alginate hybrids with high flame retardant properties.

Experiment

Materials

Sodium alginate (NaAlg, viscosity range 1.05–1.15 Pa·s, G/M = 1.83, $M_w=447,823$, $M_n=375,577$) and Eriochrome black T were purchased from Tianjin Guangfu Fine Chemical Research Institute. Disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), calcium acetate monohydrate [$\text{Ca}(\text{CH}_3\text{COO})_2$, shorthand for CA] and Sodium hydroxide (NaOH) were obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd. Ethylenediamine tetraacetic acid disodium salt ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$, 99.0 %) was supplied by Tianjin Ruijinte Chemical Reagent Co., Ltd. NaAlg was chemically pure and other chemicals were of analytical grade, and all chemicals were applied without further purification.

Preparations of CaAlg and CaAlg/HAP hybrid material

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ of 14.1425 g was dissolved in 470 mL deionized water, and the pH was adjusted to 10 with 1 mol/L NaOH, and then 15 g NaAlg was added to obtain 500 mL 3 % treated sol. Then it was placed in 45°C water bath for 4 h, stirred per 20 min until NaAlg was dissolved completely, and was cooled for 12 h to acquire a colorless transparent bubble-free sol. The pH of 3 % calcium acetate solution was adjusted to 10–11 by 1 mol/L NaOH. The treated sol was poured into a certain rectangular container and soaked in the calcium acetate solution until the shape was fixed for 24 h, and finally, it was washed and dried to a constant weight. The treated sample was labeled as CaAlg/HAP, and all processes were carried out at room temperature (Tr) except for the dissolution of NaAlg.

In order to explore the changes of HAP during its generative process, a series of investigations were carried out on the reaction of 20 g treated sol in 200 mL calcium acetate solution with different concentration as time went on.

For comparison, the sample denoted as CaAlg was prepared as the same process with CaAlg/HAP, only excluding the steps related to $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

Characterization

The morphology of samples was characterized with scanning electron microscopy (SEM, FEI Quanta FEG 250, USA).

The valence states of elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha 250Xi, USA).

Fourier Transform infrared spectroscopy (FT-IR, Thermo Fisher-Nicolet 6700, USA) was recorded in the range of 4000 – 500 cm^{-1} .

The samples were continuously scanned at 2θ with the range of 0 ~ 90° at 2°/min by an X-Ray Diffractometer (XRD, Bruker D8 Advance, Germany).

Inductively coupled plasma optical emission spectrometer (ICP, Agilent ICP-OES 730) was employed to quantitatively determine the content of Ca^{2+} and Na^+ in samples, in which the samples were treated by aqua regia, hydrofluoric acid and hydrogen peroxide.

EDTA titration method was applied to determine the content of Ca^{2+} in calcium acetate solutions treated with different calcifications.

Flame retardant performance test

Thermogravimetric analysis (TGA, NETZS 209F3, Germany) of samples was measured from 30 to 900 °C with a heating rate of 10 °C/min in nitrogen and air respectively.

The samples (size of 150×60×2 mm³) were tested in limiting oxygen index meter (LOI, LFY-606B, Shandong, China) according to ASTM D2863-1997.

The samples (size of 130×13×2 mm³) were tested by vertical burning tester (LFY-601A, Shandong, China) in vertical burning test, and the response to an open flame of a sample was determined by UL-94 in accordance with ASTM D3801-19a.

In microscale combustion calorimeter (MCC, Govmark, Farmingdale, NY, USA), samples were heated to 750 °C with 1 °C/s in a nitrogen flow of 80 cm³/min.

Cone calorimeter (CONE, FTT0242, East Grinstead, UK) operated with a heat flux of 50 kW/m² and samples in size of 100×100×2 mm³ according to ISO 5660.

Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) was conducted and samples were heated to 750 °C at a heating rate of 20 °C/min in a N₂ atmosphere, with a flow rate of 50 mL/min by a simultaneous thermal analyzer (STA8000, PerkinElmer, England) and a Fourier transform infrared spectroscopy (SQ8 rontier, PerkinElmer, England), in the range of 4000 to 450 cm⁻¹ with a resolution of 2 cm⁻¹.

Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) was performed by a thermal cracker (EGA/PY-3030D, Frontier, Korishan, Japan) and a gas chromatography/mass spectrometry (TRACE 1310-ISQLT, Thermo Fisher Scientific, USA). The pyrolysis temperatures in the furnace were set to 250 °C, 450 °C, and 750 °C respectively. The samples were heated to 280 °C at a heating rate of 10 °C/min, kept in injector for 15 s, and then the temperature was rose at 20 °C/ms.

Results And Discussion

Analysis of in situ formation of HAP

The levelling effect was considered when investigated the kinetic characteristics of Ca^{2+} , thus 3.0 wt.%, 1.0 wt.% and 0.6 wt.% of calcium acetate were used to explore the effect of the formation of HAP on Ca^{2+} consumption. The relationships of Ca^{2+} consumption rate $V_{\text{Ca}^{2+}}$ (Fig. 1a) and its reciprocal $1/V_{\text{Ca}^{2+}}$ (Fig. 1b) over time of samples were plotted intuitively, and linear relations were fitted in Fig. 1b with y for $1/V_{\text{Ca}^{2+}}$ and x for time. The fitted lines overlapped in 3.0 wt.% and 1.0 wt.% CA, therefore, Fig. 1b showed four linear formulas. The difference between formulas ① and ② indicated the treated sol consumed more Ca^{2+} with a faster rate in 0.6 wt.% CA, which was in agreement with expectation that not only the cross-linking reaction between NaAlg and Ca^{2+} , but also the ion exchange reaction among Ca^{2+} , PO_4^{3-} and OH^- to form HAP occurred. In addition, 0.81 g HAP was produced in 0.6 wt.% CA by calculation, and 0.89 g in 3.0 wt.% CA according to ICP in Table S1. Faster reaction rate and higher yield implied that 3.0 wt.% CA was the best adoption in subsequent experiments.

The in-situ generation of hexagonal HAP was monitored by XRD (Fig. 1c) and SEM (Fig. 1d-i). CaAlg and HAP began to form as soon as calcified, and the crystallinity of HAP might be confirmed after 10 min (Sinulingga et al. 2021). CaAlg exhibited a smooth layered microstructure (Fig. 1d), while the treated sol generated CaAlg and HAP after calcification for 1 min, with a dense arrangement of spherical nanoparticles of a diameter about 2 nm on the surface of CaAlg (Fig. 1e). Then the nanosheets were grown in the HAP spherical particles in all directions, forming hierarchical microspheres with one-dimensional nanowires and two-dimensional nanosheets, resulting in urchin-like microspheres with average diameters of 3 μm, 4 μm and 6

μm, when calcified for 5 min, 10 min and 30 min (Fig. 1f-h), respectively. However, when calcified for more than 30 min, the HAP microspheres narrowed their size and tended to be wrinkled sponge microspheres with an average diameter of 2 μm after 90 min (Fig. 1i), which was consistent with the constant $V_{Ca^{2+}}$ after 90 min in Fig. 1a. According to Ostwald's "rule of stages", this may be in the reason that HAP tended to form unstable and more soluble phases in the early stage of reaction, and would transform into more stable phases in the later stage (Daryan et al. 2020). CaAlg/HAP semi-interpenetrating polymer network may more tightly contact for wrinkled sponge microspheres with a larger superficial area than smooth microspheres, which was beneficial for HAP to adhere to the layered structure of CaAlg (Fong et al. 2017).

Flame retardant properties of CaAlg and CaAlg/HAP

Thermal stability

TGA was conducted under N₂ to explore the pyrolysis process without oxidation reaction, and the two samples showed a similar trend with three intense weight loss processes mainly displayed in Fig. 2a-b. The first stage of the weight loss below 200 °C was mostly the removal of free water and bound water in the samples. The first similar weight loss process suggested that the content of water and the combination with water in both samples were alike. The second stage (200–300 °C) and third stage (300–400 °C) were the primary and complex pyrolysis processes, including the breaking of glycosidic bond, dehydration, decarboxylation, decarbonylation, etc. (Zhang et al. 2021). According to Table. S2, CaAlg/HAP proceeded the second stage of pyrolysis at the lower temperature and occurred less weight loss after 200 °C, resulting in its residue of 11.58 %, which was more than that of CaAlg in 900 °C. Possibly, HAP promoted the formation of more stable char and less flammable small molecules during the thermal decomposition in N₂, granting the CaAlg better flame retardancy.

As shown in Table. S1, HAP accounted for 0.974 wt.% in CaAlg/HAP, and HAP was assumed no mass change in TGA for it can exist stably below 1000°C (György et al. 2019). If HAP had no effect on the thermal decomposition of CaAlg, the weight loss of CaAlg doped HAP calculated by the theoretical formula should be the same as the experimental CaAlg/HAP. Theoretical residue was calculated according to the following formula (Zhang et al. 2019):

$$m_{cal}(\%) = m_{CaAlg}(\%) \times \frac{1}{1+wt_{HAP}} + m_{HAP}(\%) \times \frac{wt_{HAP}}{1+wt_{HAP}}, \quad (1)$$

where m_{cal} , m_{CaAlg} and m_{HAP} represented the theoretical char of CaAlg/HAP, experimental char of CaAlg, and char of HAP (calculated as 100%), respectively, and wt_{HAP} was the mass proportion of HAP in CaAlg/HAP. The obtained theoretical TG curve (blue curve in Fig. 2a) was just a little bit above that of CaAlg. It showed that HAP promoted the carbonization of CaAlg during thermal degradation, possibly because of the thermal insulation of HAP (Liu et al. 2018).

The pyrolysis of samples in air was more complex - oxidation reactions occurred between O₂ and the products of CaAlg, leading to a further loss of weight (Xu et al. 2019). As seen in Fig. 2, CaAlg before 402 °C and CaAlg/HAP before 384 °C in both atmospheres were in consistence, however, subsequently, the oxygen reacted with the combustible gas born from previous stage, causing one more obvious pyrolysis in Fig. 2c-d. As shown in Table. S2, the lower R_{max} and more residue of CaAlg/HAP in air indicated that HAP can prevent oxygen from participating in the thermal decomposition of alginate at high temperature, resulting in a markedly better thermal stability of CaAlg/HAP, compared with that of CaAlg.

SEM and XRD of CaAlg and CaAlg/HAP after calcination in air

According to TGA, CaAlg and CaAlg/HAP were calcined in air at 250 °C, 450 °C and 750 °C for 1 h to explore the morphology and composition changes of the prepared samples. Figure 3a-c show that the morphology of CaAlg was slightly irregular deformation when heated at 250 °C and 450 °C, while at 750 °C, a densely arranged residue structure appeared. However, CaAlg/HAP was significantly different from CaAlg. When heated at 250 °C, the diameter of HAP microparticles started narrowing to about 1–2 μm, and retained the wrinkled sponge appearance, as shown in Fig. 3d, while it turned to less than 1 μm at 450 °C, there were many nanopores on the compact surface of the residue which can be observed in Fig. 3e. The XRD in

Fig. 3h meant that these nanopores were formed due to the generation and discharge of CO₂ from the decomposition of CaCO₃. As seen in Fig. 3f, when CaAlg/HAP was heated at 750 °C, the HAP particles continued shrinking to the diameter of 20 nm and the nanoparticles were closely arranged on the surface of CaAlg, indicating that the compact surface structure prevented the thermal degradation of CaAlg (György et al. 2019).

As observed in Fig. 3g, there was no CaCO₃ formed in CaAlg until about 450 °C, and a little CaCO₃ decomposed into CO₂ and Ca(OH)₂ at 750 °C. While as seen in Fig. 3h, the generation of CaCO₃ began in CaAlg/HAP when heated at 250 °C, and possibly the inner layer of alginate was covered and protected by CaCO₃. At 450 °C, CaCO₃ cracked to produce CaO and H₂O, and when the temperature rose up to 750 °C, the crystallinity of CaO increased, indicating that more CaO formed. It showed that HAP can effectively promote the carbonization of CaAlg during combustion, while HAP crystal not only was undecomposed but also a higher crystallinity at higher temperature emerged.

In terms of the above, HAP with ultra-high temperature resistance absorbed heat to form smaller particles that were tightly packed onto the surface of CaAlg. What's more, HAP promoted faster carbonization of CaAlg and produced stable CaCO₃ at around 250 °C, and CaO at around 450 °C or even higher temperature, which prevented further pyrolysis, and thus improved the flame retardant performance of the hybrid material.

Combustion properties

Table 1
Data from LOI, UL-94, CONE, and MCC.

Samples	LOI (%)	UL-94	CONE			MCC				
			TTI (s)	TSR (m ² /m ²)	EHC (MJ/kg)	Residue(%)	PHRR ₁ (W/g)	PHRR ₂ (W/g)	THR (kJ/g)	Residue(%)
CaAlg	46.5±0.5	V-0	16.0±1.0	3.6±0.2	26.4±0.1	50.7± 0.3	10.7±0.2	9.8±1.4	0.8±0.1	42.8± 0.1
CaAlg/HAP	67.0±1.0	V-0	16.0±1.0	1.12±0.3	12.3±0.1	61.7± 0.2	9.5±0.1	3.8±1.4	0.6±0.5	52.5± 0.4
TTI: time to ignition; EHC: effective heat combustion; PHRR ₁ and PHRR ₂ : the first and second peak of HRR in MCC; THR: total heat release.										

As it can be seen from Table 1, the LOI of CaAlg/HAP was 67 %, which was 20.5 % higher than that of CaAlg (Liu et al. 2021), and CaAlg/HAP cannot be ignited in the UL-94 test. The EHC of CaAlg/HAP was reduced to half of CaAlg in the CONE test, PHRR and THR in MCC were significantly reduced, and the residue in CONE and MCC of the samples showed the same tendency with TGA, as displayed in Fig. 2. All these results indicated that the doping of HAP was beneficial for the improvement of the thermal stability and flame retardant properties of CaAlg.

Figure 4a shows the variation of the total smoke release (TSR) from the samples during the CONE test over time. The TSR of CaAlg/HAP was remarkably less than that of CaAlg, possibly because the more char the hybrid material produced, the less smoke containing toxic components was released. Importantly, the less smoke release can reduce casualties in fire (Kong et al. 2021; Yu et al. 2021a).

Since most of the oxygen may be consumed in the real fire cases, the pyrolysis of samples under an anaerobic condition can be studied via MCC. MCC simulates heat release throughout the decomposition of samples in nitrogen (Mensah et al. 2018), thus it may correspond with the TGA in N₂ theoretically. As seen in Fig. 2b and Fig. 4b, the third weight loss stage in TGA at 300–400°C corresponded to the first heat release stage in MCC, while 400–600°C was the second heat release stage with little weight change, suggesting that the chemical energy was converted into heat at 300–600 °C. The less weight loss and HRR of CaAlg/HAP implied that the pyrolysis of hybrid was effectively prevented. There were two potential reasons for the decrease of HRR (Liu et al. 2016b). One was that HAP may catalyze the formation of stable char from CaAlg and contributed to a reduction

of combustible gas release, which was confirmed by the results of TGA (Fig. 2) and XRD (Fig. 3g-h). The other one was that HAP facilitated the formation of non-flammable gases from alginate such as CO₂ and water, which would dilute the concentration of flammable products.

TG-FTIR

In order to investigate whether the improvement of flame retardant properties was related to the synergistic effect of both of the aforementioned reasons, TG-FTIR was conducted to explore the generation of CO₂ and H₂O during the whole pyrolysis process.

The main functional groups containing carbonyl group C = O at 1795 cm⁻¹, carbon monoxide CO at 2182 cm⁻¹, carbon dioxide CO₂ at 2362 cm⁻¹, -CH at 2962 cm⁻¹, and = CH at 3018 cm⁻¹, and H₂O at 3732 cm⁻¹ from the 3D images of TG-FTIR were selected to explore the pyrolysis of CaAlg (Fig. 5a) and CaAlg/HAP (Fig. 5b). It was found that C = O, CO and CO₂ showed a similar generation trend, and all of them were produced apparently above 250 °C, indicating that the pyrolysis of glycosidic bonds was started and a variety of complex reactions occurred (Fig. 5c-e). What's more, CaAlg/HAP generated more C = O, CO and CO₂ than CaAlg did, especially over 350 °C, reflecting that the carboxyl groups or similar groups in CaAlg/HAP were more reactive when heated, which activated more decarboxylation and decarbonylation. The -CH and = CH were markedly generated around 450 °C, as shown in Fig. 5f-g, suggesting that the macromolecular residues from the samples went on a further crack into smaller chains. As seen in Fig. 2h, the water was formed throughout the pyrolysis process periodically. Not only -CH and = CH but also H₂O were decreased in CaAlg/HAP, implying that its degree of pyrolysis was significantly reduced. The above functional groups of CaAlg/HAP exhibited a similar trend as CaAlg did, however, it produced more CO₂ above 350 °C and the degree of pyrolysis in the later stage was alleviated. Therefore, it can be inferred that, for the carbonization mechanism of CaAlg/HAP, HAP promoted the decarboxylation of alginate, which may because the interface sites between HAP and alginate was conducive to the occurrence of decarboxylation (Fu and Mei 2021). Since HAP was not decomposed to produce phosphoric acid when heated, its flame-retardant mechanism is not similar to most of phosphates that generate phosphoric acid during heating (Sun et al. 2021a).

Collectively, it can be confirmed that the increasing release of CO₂ diluted the combustible gas in the CaAlg/HAP combustion system, and turned to an isolation among air, fuel and heat. In general, it was the combination for production of more stable char earlier and generation of more CO₂ over 350 °C together that improved the flame retardancy of the hybrid material. The high flame retardancy of CaAlg/HAP can be mainly attributed to the synergistic effects of gas phase and condensed phase.

Py-GC-MS

According to the curves in Fig. 6 and the data in Table S3-4, when the temperature rose from room temperature to 250 °C, CaAlg/HAP produced less CO₂ than the CaAlg, indicating that alginate was effectively prevented in the early stage of pyrolysis before 250 °C. However, when the temperature rose to 450 °C, CaAlg/HAP generated more CO₂ than CaAlg, and as the temperature continued rising to 750 °C, there was a further increase of CO₂, which was in line with more generation of CO₂ from 350 °C in Fig. 5d. The types and amount of pyrolysis products produced by CaAlg/HAP were less than CaAlg. Such as CaAlg/HAP produced less acetic acid than CaAlg significantly at 450 °C, and it produced less kinds of products than CaAlg at 750 °C. It was proved that the flame retardant mechanism of CaAlg/HAP was various at different stages of pyrolysis. The function of solid phase was the main flame retardant mechanism from room temperature to 350°C, while the synergistic effect of the solid phase and the gas phase worked at 350–750°C.

Flame-retardant mechanism

The speculative pyrolysis mechanism of CaAlg/HAP with no oxygen involved is presented in Scheme 2, which was extrapolated from the pyrolysis products listed in Table S3 (Xu et al. 2021). According to the morphology and XRD patterns of CaAlg/HAP calcined at 250 °C, 450 °C, and 750 °C (Fig. 2), micron-sized HAP particles with low energy were changed into nano-sized with high energy, because of gaining heat. Therefore, during the whole pyrolysis process, part of the heat was

received by CaAlg/HAP to obtain a compact structure on the surface of CaAlg, which to some extent delayed the thermal decomposition.

As shown in Fig. S3, hydrogen bonds may be formed between HAP and M blocks, which improved the thermal stability of M blocks. The interface site between HAP and alginate activated the decarboxylation of “egg-box” structure related to G blocks, which resulted in the generation of CaCO_3 , CaO and CO_2 to protect alginate when heated. Dehydration and slight decarboxylation occurred in alginate below 250°C , thus CO_2 and H_2O were the main products. Less CO_2 was produced from CaAlg/HAP below 250°C , indicating that the formation of CaCO_3 protected CaAlg and reduced pyrolysis. The glycosidic bonds inside CaAlg can be broken into M and G blocks above 250°C . M blocks were further cracked into butanedione, acetone and acetic acid in CaAlg as a general rule, while these products significantly reduced in CaAlg/HAP, indicating that less pyrolysis occurred in M blocks. However, although CO_2 accounted for 92.65 % and other components were quietly rare at 750°C , a little bit of pyrolysis products from G blocks such as acetaldehyde, 2-methylfuran and furfural can be found from CaAlg/HAP. These results suggested that HAP protected M blocks by forming hydrogen bonds with it, and promoted the partial decomposition of the “egg-box” structure to produce CaCO_3 and CaO to enhance the thickness and strength of the carbon layer as well. Moreover, CO_2 from that was to dilute the flammable gas and prevented further decomposition of alginate at high temperature. The combustion process of CaAlg/HAP in air is exhibited in Fig. 7, and more CO_2 was produced than in N_2 due to the oxidation reactions.

Conclusion

In this report, CaAlg/HAP hybrid material was in situ synthesized by a green and simple sol-gel method at room temperature. During the reaction, the HAP spherical particles were grown from nanospheres to urchin-like microspheres, and finally to wrinkled sponge microspheres which was favorable as binding with layered CaAlg for their large surface area. CaAlg/HAP presented remarkably better thermal stability and flame retardant properties, in comparison with CaAlg, such as it had more residue (above 12 %) in TGA at 900°C , and its LOI reached 67%, while HRR and TSR were significantly decreased. Furthermore, the flame retardant mechanism of CaAlg/HAP was proposed based on the experimental data and reliable theories. The wrinkled sponge microspheres absorbed energy and transformed into nanoparticles after heating, which alleviated pyrolysis of CaAlg for sharing heat from the external environment. The HAP particles with ultra-high temperature resistance covered on the surface of CaAlg, which also hindered the further decomposition of alginate. What's more, the hydrogen bonds formed by the M blocks and HAP enhanced the stability of the M blocks. The interface sites between HAP and alginate may facilitate the decarboxylation of the “egg-box” structure made up of G blocks and Ca^{2+} , resulting in the production of CaCO_3 early at 250°C , and the decarboxylation of CaCO_3 at higher temperature to produce more CaO and CO_2 . In summary, HAP promoted decarboxylation of alginate causing carbonization of CaAlg/HAP, and mainly CaCO_3 , HAP, and char were generated below 350°C in the solid phases, while synergistic effects of gas phase CO_2 and solid phases CaO , HAP, and char over 350°C that improved thermal stability and flame retardancy of CaAlg/HAP by restraining the transfer among oxygen, fuel and heat.

Declarations

Conflicts of interest

The authors declared no conflicts of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant number 51773102) and State Key Laboratory of Bio-Fibers and Eco-Textiles (Qingdao University, Grant number ZKT20).

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Figures

Figure 1

Changes of Ca^{2+} consumption rate (a) and their reciprocals (b) in 0.6 wt.%, 1.0 wt.%, and 3.0 wt.% calcium acetate solution (CA) when untreated sol and treated sol calcified into CaAlg and CaAlg/HAP over time, respectively. XRD patterns (c) of CaAlg, and treated sol dipped in 3 wt.% CA for 1 min, 5 min, 10 min, 30 min and 90 min (CaAlg/HAP). Morphology microstructures (d-i) corresponding to the different tested samples shown in Fig. 1(c).

Figure 2

(a) Thermogravimetric analysis (TG) and (b) derivative thermogravimetry (DTG) curves of CaAlg and CaAlg/HAP under nitrogen, (c) TG and (d) DTG curves of CaAlg and CaAlg/HAP under air.

Figure 3

SEM images of (a-c) CaAlg and (d-f) CaAlg/HAP after treated in air at 250 °C, 450 °C, and 750 °C for 1 h, respectively. XRD patterns of (g) CaAlg and (h) CaAlg/HAP after treated in air at 250 °C, 450 °C, and 750 °C for 1 h, respectively.

Figure 4

(a) Total smoke release (TSR) over time from CONE and (b) heat release rate (HRR) with temperature from MCC.

Figure 5

3D images (a-b) and main functional groups as a function of temperature (c-h) of CaAlg and CaAlg/HAP obtained from TG-FTIR.

The combustion process of CaAlg/HAP in air.

Supplementary Files

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