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A facile biomass-based coating for flax fabric toward plant fiber/biobased epoxy composite with enhanced fire safety

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ABSTRACT

The natural abundance, biodegradability, and low density of plant fibers, together with biobased epoxy thermoset resin, have driven the increasing popularity of plant fiber/polymer composites (PFRPs) to wider applications in various industries. However, the striving for biomass-based flame retardants (FRs) treatment for PFRPs remained a bottleneck due to polymers' inherent vulnerability against fire and the increasing environmental awareness. In this work, a facile two-step aqueous solution coating process was proposed for fabric surface treatment of flax fabric using fully biobased phytic acid and chitosan from polysaccharides. The treated flax fabric demonstrated self-extinguishing behavior when ignited and showed a decrease in peak heat release rate (PHRR) by 58% under combustion. The laminate produced by this treated flax fabric and biobased epoxy resin showed a decrease of PHRR by 36% and an increase of more than 200% for the time of torch fire burn-through, demonstrating intriguing flame retardance brought by only FRs treatment on flax fabric reinforcements. Various measurements were done to elaborate on the role of treated flax fabric in the flame retardancy of polymer composites.

1. Introduction

The natural abundance, biodegradability and low density of plant fibers have attracted increasing attention for its development in fiber-reinforced polymer composites (FRPs) [1–3]. Plant fiber/polymer composites (PFRPs) have been demonstrated to possess promising mechanical properties to partly replace some conventional reinforcement fibers such as glass, basalt and aramid fibers for FRPs [4]. Nevertheless, unlike traditional nonflammable or hardly flammable fibers mentioned above, plant fibers suffer intrinsic vulnerability against fire, which produces huge fire hazards together with the burning of flammable polymer matrix such as epoxy resin. The high flammability in most PFRPs has limited its expansion into broader applications in various sectors. Many efforts have been committed to improving its flame retardancy and fire safety, such as modification of polymer matrix, fire-protective coating on the composite surface, and surface functionalization of reinforcement fiber [5,6]. In the meantime, the quest for an environmentally benign approach in chemical engineering has promoted the use of biomass-based FRs in the development of fire-safe polymer composites [7,8]. Combined with a biobased polymer matrix, the use of biomass-based FRs in fireproofing PFRPs provides an even more eco-friendly approach, which enhances the life cycling worthiness of PFRPs for polymer composite industries [9].

The abundant functional groups and hierarchical porous structure [10] of plant fiber make the introduction of flame retardants (FRs) on plant fiber surfaces one of the promising solutions for fire-safe PFRPs. Many phosphorous [11,12] or boron-based FRs such as ammonium polyphosphate (APP) [13], boric acid [14], organic phosphonate ester [15] etc., have been reported for flame-retardant treatment of plant fiber and its polymer composites recently. For instance, Song et al [16]. proposed a layer-by-layer (LbL) strategy for surface coating of ramie fabric using an aqueous solution based on anionic APP and cationic polyethyleneimine (PEI). Peak heat release rate (PHRR) was reduced by 35% in the cone calorimeter test (CCT) under 35 $kW/m^{2,}$ with ignitability and flammability decreased too. However, the use of fossil fuel-based FRs may be improved by replacing them with biomass-based

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FRs with equivalent or better efficacy. Besides, the multi-step LbL approach is a complicated and time-consuming process that stifles the development of fire-safe PFRPs.

The polyelectrolyte complex (PEC), which constitutes oppositely charged macromolecules, can interchange between solution or solid state by tailoring the pH, concentration, and extra salt additive in the system [17,18]. Taken advantage of this phenomenon, a facile process by PEC-based two-step coating using phosphorus or boron compounds has been demonstrated widely in the flame retardant treatment of textiles for natural and synthetic fabrics [19,20]. Rodriguez et al [21]. demonstrated a two-step process for flax fabric treated by PEI and sodium hexametaphosphate (PSP). The treated flax fabric showed self-extinguishing behaviour with a decrease in peak heat release rate (PHRR) by 30%, while no biomass-based FRs were used. Phytic acid, being one of the few naturally derived phosphorus-containing FRs candidates, has shown some promising results when used as a constituent with chitosan for biomass-based PEC as additives [22,23] or coating on fabrics [24]. Nevertheless, to the best of our knowledge, few reports have demonstrated the potential of biomass-based PEC coating on plant fiber-based fiber reinforcement for the development of fireproofing PFRPs.

In this work, a biomass-based PEC coating treatment on woven flax fabric was done using phytic acid and chitosan in a facile two-step impregnation and buffer curing process. Laminate was produced by vacuum infusion process using the biobased FRs-treated flax fabric and biobased epoxy resin as the polymer matrix. The flammability of the flax fabric itself and the polymer composite were screened. The combustion behavior of the laminate was also examined. Finally, investigations of the flame-retardant coating on the gas and condense phase were conducted with a proposed mechanism for the elaboration of the behavior change from the flame-retardant behavior of coating on fabric only to the polymer composites.

2. Experimental

2.1. Materials

Phytic acid (50 wt.% water solution) was purchased from Sigma Aldrich, Spain. Chitosan (MW~1526kDa) was purchased from Fluorochem Ltd, UK. Flax fabric (area density: 200 g/m^2, type code: FlaxDry BL200) was purchased from EchoTechnilin, France. Biobased epoxy resin (Resoltech 1800 ECO) and its cycloaliphatic & aliphatic amine curing agent (Hardener 1804 ECO) were purchased from Resoltech, France, which has a ~36% biobased content after mixing. Type II water was produced by a water purification machine (Wasserlab Automatic Plus). Hydrochloric acid and acetic acid were purchased from Sigma Aldrich, Spain, and used without purification.

2.2. Preparation of polyelectrolyte aqueous solutions

Various formulations of phytic acid/chitosan polyelectrolyte solution were prepared to verify the optimal viscosity while trying to maintain a high phosphorus content in the PEC solution, as shown in Table S1. First, 2 wt.% chitosan (CH) aqueous solution with 6 wt.% acetic acid was prepared by adding the polysaccharide portion-wise into premixed acetic acid/water under intense mechanical stirring. Then, a 40 wt.% phytic acid solution was prepared by diluting 50 wt.% solution with water and additional 37wt% hydrochloric acids solution to form a solution with around 35.8 wt.% PA and 4% HCl in water. After that, equal amount of 35.8 wt.% phytic acid-based solution was slowly added into the 2 wt.% chitosan based aqueous solution under intense mechanical stirring to form a uniform and translucent solution. The final prepared chitosan/phytic acid polyelectrolyte solution named PEC was got with a concentration around 18.9 wt.% phytic acid and 0.94 wt.% of chitosan.

2.3. Dip-coating of flax fabric

The illustration for a few steps of dip-coatings of flax fabric was shown in Scheme 1. Firstly, pristine flax fabric was cleaned using deionized water under an ultrasonic bath for 0.5 hours and dried under 70 °C for 1 hour. Then, washed flax fabric named pristine flax fabric (PFL) was soaked into the PEC solution bath for 15 minutes before being squeezed and absorbed excessive solution by a roller press. After that, the PEC-soaked flax fabric was then transferred to a 0.1M acetic acid (pH around 3) buffer bath for deposition on the flax filament. A roller press was used again to remove excessive acetic acid solution, and the fabric was rinsed by and squeezed to get modified falx fabric named PEC@FL and dried at 70 °C for 6 hours. Weight-gain was calculated to be around 12 wt.%. after weighing fabrics before and after dip coating and drying.

2.4. Preparation of flax fabric-reinforced epoxy composite

The polymer composite was prepared by a widely used vacuum infusion process. 4 layers of either pristine flax fabric or PEC-coated flax fabric were used respectively to form symmetrical laminates. A commercial partly biobased epoxy resin was used with amine type curing agent. Process details, curing schedule and cutting, are the same as in our previously published paper [25].

2.5. Characterizations

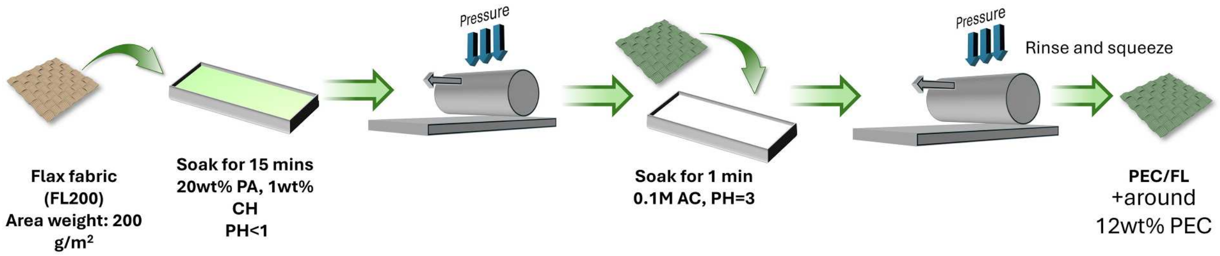
Scanning electron microscopy (SEM) and EDS were carried out on a scanning electron microscope (Apero 2, Thermo Fisher). The XPS analysis was carried out in a Thermo Scientific Multilab 2000 spectrometer fitted with a dual-anode X-Ray source (Mg K alpha and Al Kα with photon energies 1253.6 and 1486.7 eV, respectively), and a 110 mm hemispherical sector analyzer. The thermogravimetric analysis (TGA) curves under air and nitrogen atmosphere were measured with an instrument from TA Instruments (Q50) at a temperature ramp speed of 20 °C/min. TG-IR test was carried out on an infrared spectrometer (Nicolet IS 50, Thermo Fisher) with TGA coupled to screen the volatile products produced during the thermal decomposition of resin mixture in a nitrogen atmosphere at a heating rate of 20K/min. Dynamic mechanical analysis (DMA) was measured with a dynamic mechanical analyzer named Q800 from TA Instrument using a single cantilever mode with a heat ramp of 3 °C/min to 170 °C.

A vertical burning test (VFT) for flax fabric was performed following standard ASTM D6413. Microscale combustion calorimeter (MCC) test to screen flax fabric with pyrolizer under nitrogen atmosphere under a heating speed of 1 °C/s to maximum pyrolysis temperature of 900 °C. The forced flaming test was carried out on a dual cone calorimeter (Fire Testing Technology, UK) with the sample dimension of 100 mm × 100 mm × ~2 mm in the horizontal direction and positioned 25 mm away from a heat flux of 50 kW/m^2 to the ISO 5660–1:2015 standard. A torch-fire burn-through test was performed, similarly to our previous report for sample edge protection. Except for this time, a torch fire burner (φ22mm) with an outer fire temperature of around 1400 °C was used as a direct fire impingement source. The distance between the tip of the burner and the surface of the laminate was kept at 7cm. The backside temperature was recorded with a thermographic infrared camera named AT31UZ from InfiRay, China, until burn-through failure.

3. Results and discussion

3.1. PEC coating on fiber surface

As can be seen in Fig. 1, the pristine flax fabric showed a twisted yarn morphology with a diameter of around 500 μm. The single flax fiber has a diameter of around 30~60 μm. After the PEC coating on the flax fiber, the surface morphology showed a conformal PEC-based organic coating layer on both the surface and conjunctions of the multiple single fiber,



Scheme 1. Schematic illustration for the dip coating, roller press, and buffer curing process for preparing the PEC-coated flax fabric (PEC@FL).

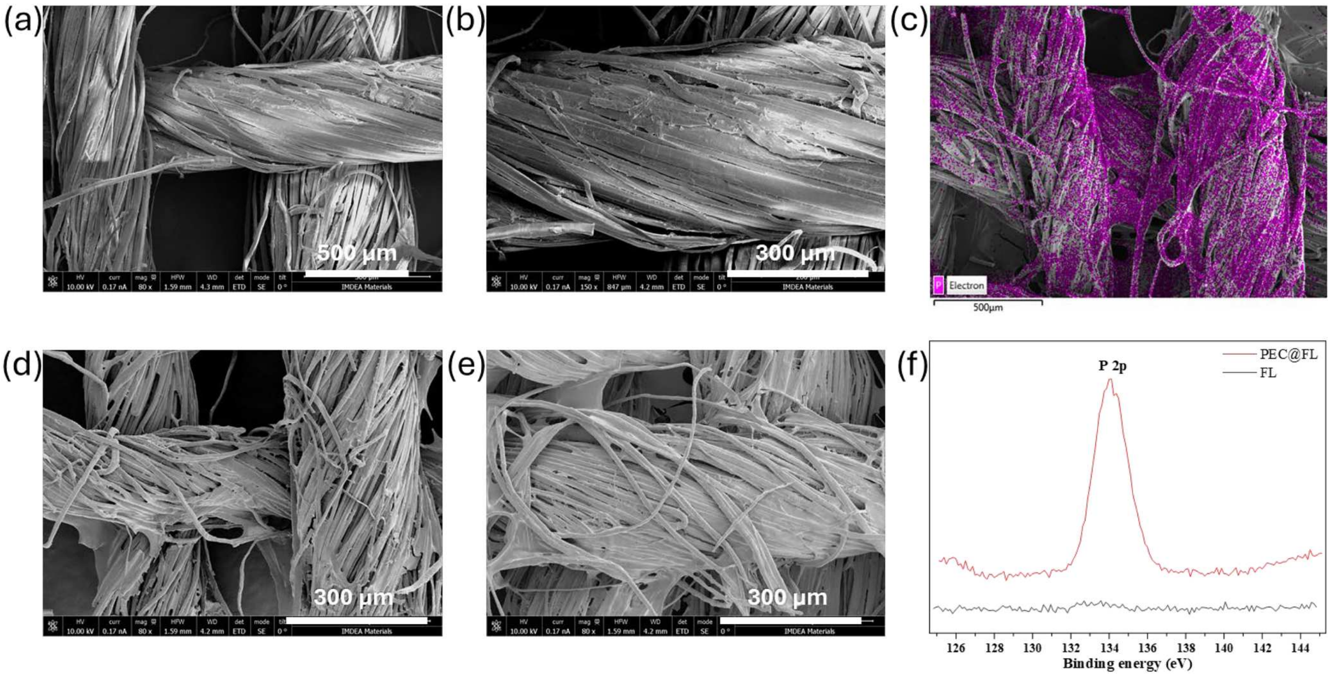


Fig. 1. Surface morphology of pristine flax fabric FL (a, b) and PEC@FL flax fabric (d, e). EDS images for P elements of PEC@FL (c). High resolution curve of P2p spectrum for both FL and PEC@FL (f).

with some debris film derived from the excessive coating deposition. The EDS map shown in Fig. 1 (c) also demonstrated the presence of phosphorus elements on the surface of flax fiber yarns, indicating the presence of phosphorus-based compounds deposited on the surface. FTIR spectra were obtained to compare the surface composition of FL and PEC@FL. As can be seen from Figure S1 (a), a few new peaks around 1530 cm^{-1} and 1155 cm^{-1} were formed, which may indicate the stretching vibration of O-P-O bond and P=O [22]. Due to the large presence of flax fabric-based cellulose composition, even after the coating, the signals of new peaks were still relatively weak. XPS results showed that a new peak of P_{2p} formed after the PEC coating on the flax fabric in the high-resolution spectrum curve. These new peaks formation around P_{2s} and P_{2p} were also visible in the full survey of the XPS spectrum, as shown in Fig. 1(f). Hence, it can be said that the deposition of the PEC coating layer on the surface of flax fiber was done successfully using a facile method with only a few steps.

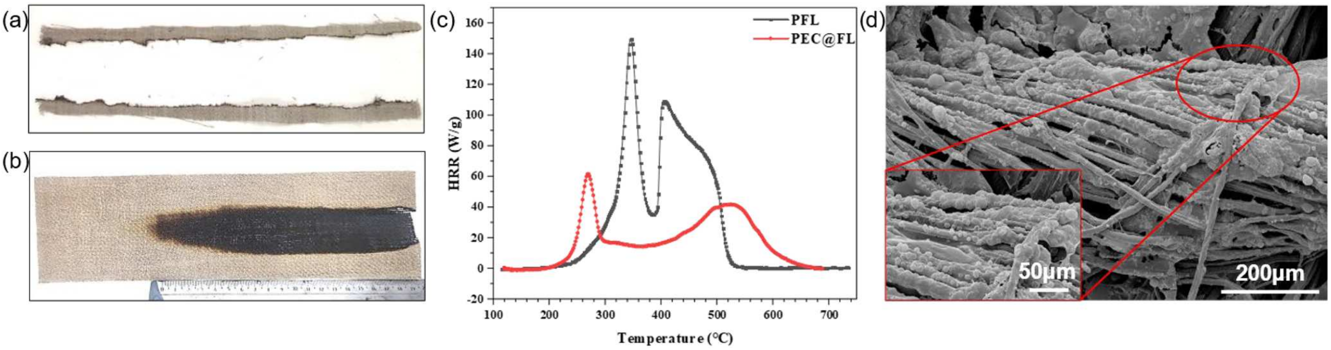


Fig. 2. Digital pictures after vertical flame burning tests for PFL (a) and PEC@FL (b). Heat release rate versus temperature curves for both fabrics under PCFC tests (c). SEM image of PEC@FL residue after the vertical burning test.

3.2. Flame retardancy

3.2.1. Flammability of fabric

The self-extinguishing properties of flax fabric before and after coating treatment were screened with vertical burning tests. As can be seen in Fig. 2(a, b), the pristine flax fabric burned out with no residue left, displaying high flammability and low self-extinguishing properties. After applying P, N coating deposition on the flax fiber yarns, the PEC@FL fabric showed self-extinguishing properties with a much less damage length after flame-out. The introduction of biobased flame-retardant deposition on fiber surface formed a charring layer, as can be seen in Fig. 2(b), which may prevent the spreading of fire and fuel supply. However, it is worth noting that the self-extinguishing behavior of reinforcement fabric cannot only represent the burning behavior of the laminate, as the fabric is only one constituent of the polymer composite systems.

3.2.2. Heat release from combustion of flax fabrics

The MCC measurement provided a facile way to measure the heat release rate and capacity of the flax fabrics with a minimal sample weight. As can be seen in Fig. 2(b) and Table 1, flax fabrics before and after PEC deposition both showed a two-peak pattern curve under anaerobic decomposition in the pyrolizer and complete oxidation combustion at the combustor chamber. After the deposition of PEC on flax yarns, the peak heat release rate (PHRR) was decreased from 160 g/W for pure flax fabric PFL to 62 g/W for that of PEC-treated flax fabric (PEC@FL), indicating a strong suppression effect on the release of combustible volatiles. In addition, the heat release capacity (HRC) and total heat release (total HR) were decreased respectively by 18% and 42% compared to those pristine fabrics. HRC was calculated by deconvolution of HRR curve due to the multiple step degradation of flax fabrics before and after coating.

The temperature of peak heat release rate ($\mathrm{PHRR_T}$) shifted to an earlier and lower value for PEC-coated fabric compared to that of no coating applied. This was also observed in the TGA and CCT test, as shown in Figure S2 and Fig. 3(c). This may be attributed to the catalyzing effect derived from phosphate compounds, which promote the dehydration and crosslinking of cellulose and char formation [26,27]. It is worthy to be noted that the phosphate compounds were derived from the decomposition of phytic acid and chitosan based PEC coating materials, indicating the influence of coating materials on the decomposition and charring of flax fabrics. This formation of char shields the fiber yarns from burning completely, thereby showing self-extinguishing behavior.

3.2.3. Combustion behavior of composites

CCT test was employed to measure the heat release behavior of flax fabric reinforced epoxy composites under horizontal configuration with 50 kW/m^2 external heat flux radiation. As shown in Fig. 3 and Table 2, the Pure FL/EP exhibited a single peak pattern curve for heat release rate versus time with a very subtle shoulder before the curve peak. This suggested that the Pure FL/EP displayed mainly a thermally thin type of sample under burning with very limited charring capability, which may contributed by the flax fabric's limited charring capabilities [28]. At the end of the test, nearly no residue was left for Pure FL/EP as both two constituents, fiber and epoxy resin, showed nearly no residue when measured in TGA tests.

Table 1
PCFC results of untreated and PEC-coated flax fabric.

Samples	HRC (J/g-K)	Peak HRR(W/g)	T_p (°C)	Total HR (KJ/g)
PFL	294	150	346	15.9
PEC@FL	123	62 (-58.6%)	267	9.3 (-42%)

Note: HRC= heat release capacity, T_p= temperature of peak heat release, Total HR= total heat release

After the deposition of the PEC-based flame-retardant coating layer of flax fibers, the polymer composites using PEC@FL fabric showed change in terms of heat release curve patterns. The one single peak of heat release rate (HRR) curve from Pure FL/EP was transformed into two peaks pattern curve for modified polymer composites. The HRR curve of PEC@FL/EP demonstrated a thick charring behavior with an additional peak at the end of the test, which may be due to the thermal oxidation of cracked chars.

In terms of PHRR value, a decrease of more than 35% reduction in PHRR was achieved for PEC-modified flax fabric reinforced laminate compared to that for composite with pristine flax fabrics. The fire growth rate index (FIGRA) value is defined as the derivative value of the PHRR value with the time-to-PHRR, as can be calculated from the CCT results [29,30]. The FIGRA value was decreased from 15.4 to 6.8, as shown in Table 2. This suggested that the fire propagation speed may be much delayed and slowed. With the decreased of FIGRA and increased total heat release (THR) suggested that the composite burned with less intensity but for a longer time. In the meantime, the mean effective heat of combustion (EHC) was almost PEC@FL/EP and Pure FL/EP, which may indicate that the coating had limited capability for gas phase behavior [31].

Smoke release and mass loss can also be recorded throughout the CCT tests, as some results of this are shown in Fig. 3(b, c). The peak smoke production rate (PSRR) value was also decreased by more than 30% for modified laminates compared to that of Pure FL/EP, indicating a suppression of smoke release potentials, while the total smoke production (TSP) was increased. The mass loss behavior under the forced flaming scenario demonstrated a decreased slope value, indicating the presence of flame-retardant coating delayed thermal decomposition rate in the through-thickness direction. The decreased mass loss rate lowered fuel generation and combustion in the gas phase, which correlates with the decreasing heat release rate in Fig. 2(a). In addition, the higher residue value after the CCT test also suggested high charring capabilities for the modified laminate. Overall, the fire safety of composites with treated plant fabric was improved while its flammability remains to be further reduced, which mainly due to only the fabric constituent used in composites were flame retarded while no FRs possessed in the polymer matrix.

3.2.4. Resistance to torch fire burn through

Resistance to fire is one of the important properties of fire-safe polymeric materials in various applications. Compared to carbon, glass, and basalt fibers as reinforcement for polymer composites, natural fibers reinforced polymer composites possessed a much vulnerable capability for resistance to fire penetration and avoiding burn-through [5]. In this study, we implemented a lab-scale torch fire burn-through test to try to preliminary measure the properties of two laminates by mimicking a strong jet-like fire impingement through the thickness direction, as shown in Fig. 4(a). Due to the auto switch function of the thermography camera, there were around 10s of measurement value deviation during the test. Torch fire was applied on one side of the laminate with edge protection by calcium silicate board to ensure through-the-thickness direction damage and thermal transfer. A thermographic camera recorded the temperature distribution of the backside.

In Fig. 4(d), the temperature for the central point of the back side (T_B) was plotted against time, which demonstrated fire insulation properties through the thickness. For the Pure FL/EP, the temperature versus time curve displayed a steep slope value with temperature radically rising from the start of fire impingement and reaching almost 300 °C in less than 20 seconds. At the 20s of torch fire impingement, the temperature distribution on the back side of both laminates was shown in Fig. 4(b, c), which displayed a drastic difference between Pure FL/EP and PEC@FL/EP. The time to burn-through failure for Pure FL/EP was 30 seconds, indicating a poor fire resistance capability for laminates without flame retardant treatment on flax fabric, as shown in Fig. 4(e).

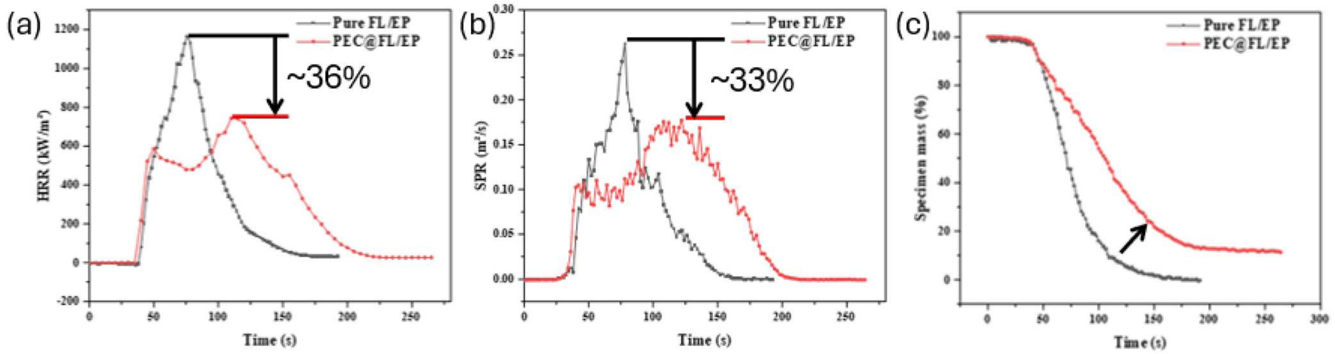


Fig. 3. Cone calorimeter results for both laminates using flax fabric with and without PEC coating for heat release rate (a), smoke production rate (b), and specimen mass loss temporal curves (c).

Table 2
CCT test results under horizontal configuration and 50 kW/m^2 irradiation.

Sample	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	PSRR (m^2/s)	TSP	Residue (%)	Mean EHC (MJ/Kg)	FIGRA (kW/sm^2)	MARHE (kW/m^2)
Pure FL/EP	36	1167	56.5	0.26	12.9	0	22.2	15.4	446
PEC@FL/EP	33	744	77.1	0.18	18.1	11.3	22.3	6.8	420

Note: TTI=time to ignition, PHRR=peak of heat release, THR= total of heat release, PSRR=peak of smoke rate release, EHC= effective heat of combustion, FIGRA= fire growth rate index, MARHE= maximum average rate of heat emission.

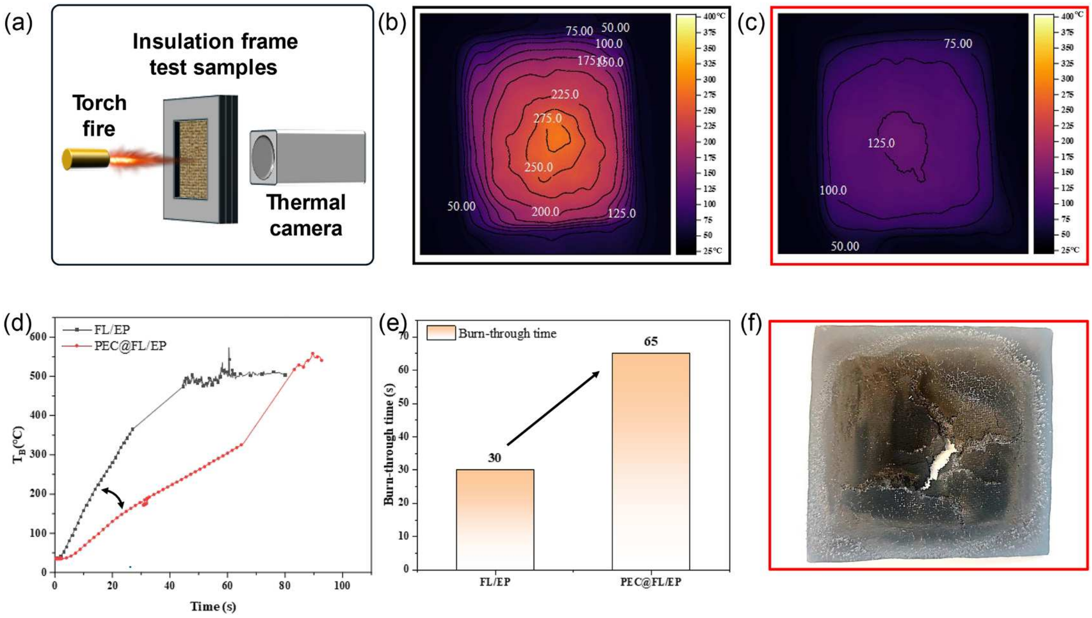


Fig. 4. (a) schematic illustration for the torch fire burn-through test results. (b, c) Temperature distribution for the back side of the tested laminate at the time of 20 seconds flame impingement. (d) Temperature versus time curve for the central point on the back side of laminates. (e) Bar chart of the burn-through time for both laminates. (f) Digital images of PEC@FL/EP laminate after burn-through tests.

Nevertheless, after the PEC flame-retardant deposition on the reinforcement fabric surface, the time to burn-through failure was increased by more than 100% to 65s. The T$_B$-time curve also demonstrated a much lower slope value, indicating the strong delaying effect for thermal transfer through the thickness directions for modified laminate. Digital images of both Pure FL/EP and PEC@FL/EP are shown in Figure S2 (b) and Fig. 4(f). For Pure EL/EP, a loose, brittle char morphology with fabric-shaped microstructure was left after fire damage at the central area around the failure crack. This was partly due to the nearly no charring capability of the resin matrix or the limited charring capability of the flax fabric. However, the PEC@FL/EP composite showed a much more compact char morphology without fiber-like microstructure around the burn-through crack area. The change in fire insulation, burn-through time as well as char morphology after the test all indicated a possibility for enhancing the against fire damage for polymer composite with flax-based natural fiber reinforcements.

3.3. *Dynamic mechanical properties*

As continuous fiber-reinforced polymer composites, the dynamic mechanical properties of natural fiber polymer composites under elevated temperatures are also crucial for their application. As shown in Fig. 5(a, b), the DMA results demonstrated that there is little interference after the PEC coating on the reinforcement fabric. The temperature for

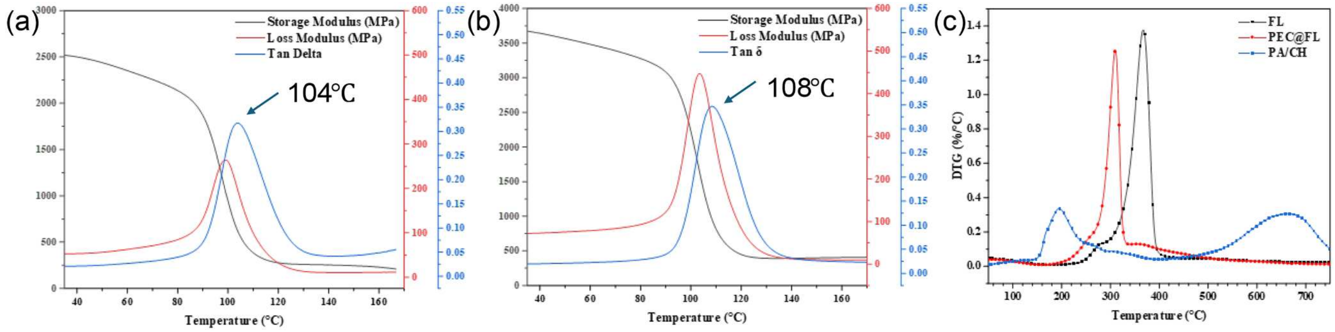


Fig. 5. Dynamic mechanical properties curves for Pure FL/EP(a) and PEC@FL/EP(b). mass loss rate curves for TGA test of flax fabrics and its PEC materials solely (c).

the glass transition temperature (peak of Tan δ) was very close. The storage modulus at 30 °C of PEC@FL/EP was relatively higher than that of Pure FL/EP. This indicated the flame-retardant coating on reinforcement fabric showed little interference in terms of thermos-mechanical properties. Nevertheless, as the novel PEC coating acted as interface constituents between polymer matrix and fibers, the influence of PEC coating on the mechanical properties of laminate is also important, which will be further discussed in further work.

3.4. *Investigation of fire safety mechanism*

3.4.1. *Thermal stability of flax fabrics*

As shown in Figure 5(c) and Figure S2 (a), the $\mathrm{DTG_{max}}$ of PEC@FL is lower than that of FL fabric without any treatment, indicating the decomposition speed was accelerated with the introduction of the PEC complex. Phytic acid is a phosphorus acid-based compound, which has been suggested by various reports on the catalytic decomposition function, thereby lowering $\mathrm{DTG_{max}}$ value to around 300 °C. On the other hand, the residue value of PEC@FL showed a huge increase of almost 100% compared to that of pristine fabric after decomposition in the N_2 atmosphere. The polymer matrix used in composite possesses a $\mathrm{DTG_{max}}$ value of around 350 °C with nearly no charring capability, as shown in our former work [25]. The thermal stability of the whole composite material is assumed to be changed due to the introduction of phytic acid and chitosan complex compounds on the surface of reinforcement fabric, which may play a role in the decomposition process of materials.

3.4.2. *Residue morphology*

Fig. 6(a, d) shows the digital images of char residue after CCT tests for two types of laminates. The Pure FL/EP had very few residues left after the forced flaming test, which is expected due to the limited charring capabilities of the composites without FRs. In terms of PEC@FL/EP, the sample after flame-out demonstrated a thick charring layer, indicating a strong charring capability. This drastic change in charring behavior also corresponds to the recorded mass loss curve in Fig. 3(c) in the cone calorimeter test.

Residue morphology after the CCT test was screened under the SEM test, as shown in Fig. 6(b, c, e, f). In terms of residue morphology for Pure FL/EP after the CCT test, the char left a multi-single fibre-like micromorphology for each layer of flax fabric. The SEM image with higher magnification shown in Fig. 6(c) suggests that the char from Pure FL/EP is brittle and loose, which may fail to form a char barrier effect. In contrast, the char morphology from PEC@FL/EP in Fig. 6(e, f) displayed a yarn-like morphology with a much more compact structure derived

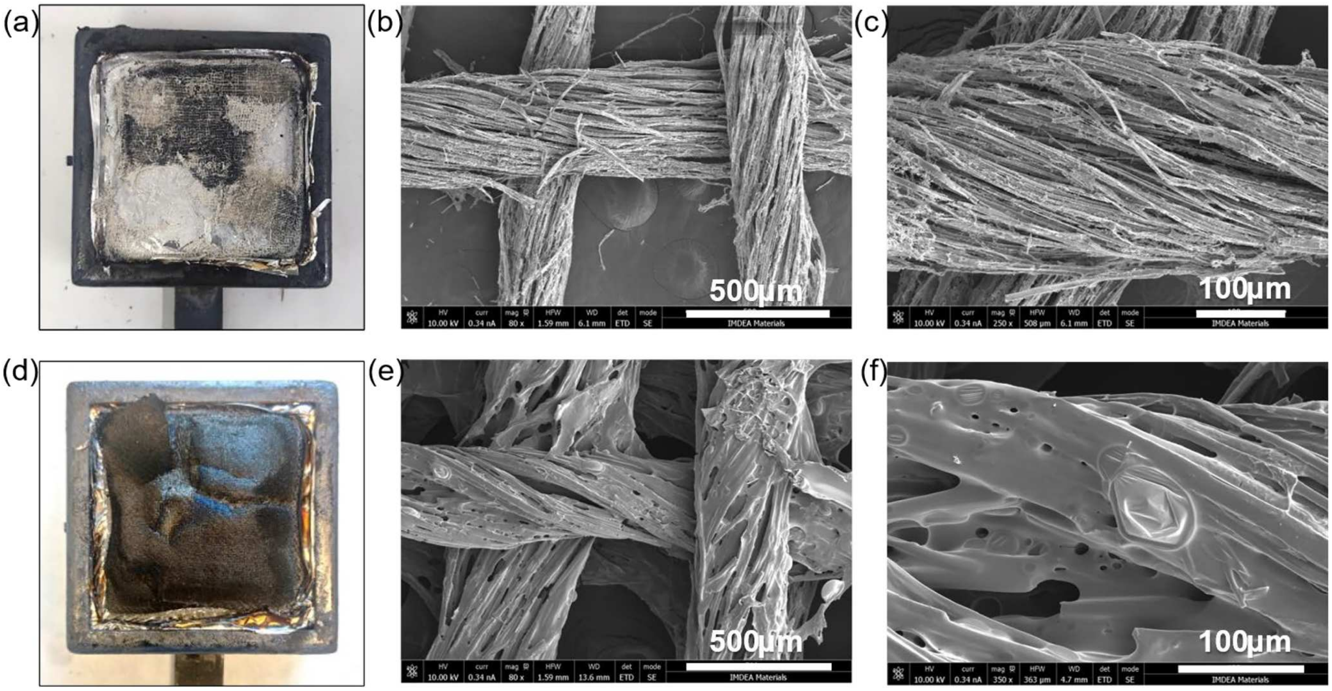


Fig. 6. Digital photos of char micromorphology after CCT test for Pure FL/EP (a) and PEC@FL/EP (b). SEM images of char residue morphology for Pure FL/EP (b, c) and PEC@FL/EP (e, f).

from each layer of flax fabrics. With multiple layers of residue from flax fabrics forming a compact char barrier, this char residue was assumed to stifle the thermal and mass transfer of combustible fuels during combustion in CCT tests.

3.4.3. *Volatiles produced under anaerobic decompositions*

The flame retardant behavior was investigated by implementing the TGA-FTIR test in a nitrogen atmosphere to mimic the anaerobic decomposition and detect released combustible fuels during the combustion process [32].

In Fig. 7(b), the Gram-Schmidt intensity of PEC@FL/EP was decreased compared to that of Pure FL/EP, which was also shown in the 3D map of Fig. 7(d, e). When mapping the FTIR curves of volatile compounds emitted during the decomposition of the two laminates before and after the DTG_{max}, the result curves are shown in Fig. 7(a, c). The intensity around 1730 cm^{-1} was decreased for PEC@FL/EP compared to that of Pure FL/EP alongside the rise of temperature in Fig. 7(f), which corresponded to volatiles containing carbonyl bond [33]. The intensity for peaks around 3000 cm^{-1} and 1510 cm^{-1} corresponded to the aromatics and aliphatic C-H bonds were like for both samples [34]. The peak around 1110 cm^{-1} may correspond to the C-O stretching vibration in ester groups. As can be seen, most peaks existed in two laminates. The results from the TGA-FTIR test and the mean EHC values for two laminates indicated limited gas phase behavior for the biomass-based flame-retardant coating.

The decreased intensity of certain flammable volatiles released into gas phase imparted the fuel supply for the combustion of composites, which also indicated the enhanced thermal/mass barrier effect in the condensed phase. Results indicated that PEC coating played little role in the gas phase based on TGA-FTIR results, which also corresponds with the EHC value remain almost unchanged in CCT test at Table 2 and the enhanced charring seen from Fig. 6.

3.4.4. *Proposed flame retardant mechanism*

After several investigations into both the condense phase and gas phase and the fire hazard results measured from the cone calorimeter, the flame-retardant behavior of this biomass-based coating on reinforcement fabric for the combustion behavior of laminate was proposed. As can be seen in Fig. 2(d), for the flax fiber-based natural fabric reinforcement alone, the phytic acid and chitosan-based PEC coating layer catalyzed the dehydration and crosslinking reactions of cellulose, hemicellulose, or lignin compositions and promoted the char formations upon thermal degradation and fire damage. The formation of a micro-scale intumescent effect on the fiber yarns stifles the thermal transfer into the fibers inside the coatings layer, thereby showing self-extinguishing behavior during the VFT test.

However, the self-extinguishing behavior of the fabric reinforcement itself does not transfer its efficient flame retardancy into the final natural fiber-reinforced thermoset polymer composite. In terms of the monolithic laminate, the fiber reinforcement weight ratio is around 40∼45% with no flame retardant additives in the resin matrix in our processing method. The PEC-based coating on the natural fiber yarns formed part of the interface between the fiber reinforcement and resin matrix. During the combustion of laminate, the phytic acid/chitosan-based PEC coating promotes mainly each layer of natural fiber to form a compact char structure, as shown in Fig. 6(e, f). With multiple layers of this char structure stacking up to stifle fire damage and thermal transfer through the thickness direction, the laminates demonstrated lower PHRR results and FIGRA value as well as longer time for torch fire burn-through, as shown in Table 2 and Fig. 4.

4. Conclusions

In this work, a facile, few-step coating process based on biomass-based flame retardant coating was designed and deposited the flax fiber reinforced bio-epoxy resin, forming highly environmentally benign polymer composite materials with all components used being mostly

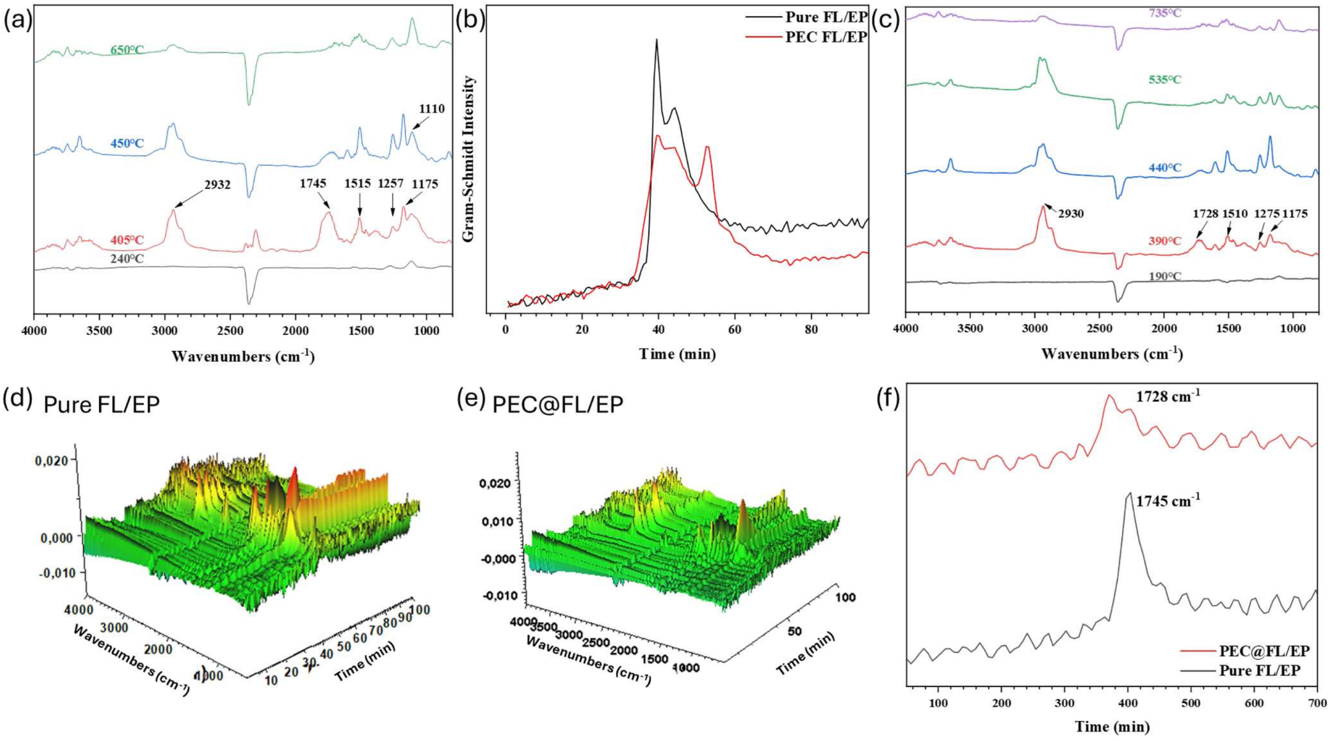


Fig. 7. FTIR curves of gaseous products released from Pure FL/EP (a) and PEC@FL/EP at different temperatures (a, c). Gram-Schmidt IR intensity of gaseous release products from two laminates(b). 3D construction map of the relationship between temperature, wavenumbers, and intensity of Pure FL/EP (d) and PEC@FL/EP(e). Intensity profiles versus temperature for peak at around 1740 cm^{-1} for two laminates.

biobased materials. The aqueous bio-mass coating solution based on phytic acid/chitosan was developed and tailored to adapt to the widely used pad-dry process. The PEC-coated flax fabric demonstrated self-extinguishing behavior with micro intumescent char forming on the fiber yarns. The laminate using this PEC-coated flax fabric and bio-based epoxy resin demonstrated the capability of lowering the fire hazards compared to that of Pure FL/EP as the peak heat/smoke release rate, mass loss rate, and fire propagation were lowered. The resistance to torch fire burn through was also improved after coating deposition. The flame-retardant behavior changed from natural fabric to polymer composites. In conclusion, this biomass-based coating strategy demonstrated the potential of biobased flame retardant coating for natural fiber-reinforced biobased thermoset composites.

CRediT authorship contribution statement

Xiang Ao: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Robert Crouse:** Investigation, Data curation. **Gloria Guerrero-Muñoz:** Investigation, Data curation. **De-Yi Wang:** Writing – review & editing, Resources, Methodology, Conceptualization.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2024.111057.

Data availability

Data will be made available on request.

References

[1] O. Faruk, A.K. Bledzki, H.P. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000-2010, Prog. Polym. Sci. 37 (11) (2012) 1552–1596.

[2] M. George, M. Chae, D.C. Bressler, Composite materials with bast fibres: Structural, technical, and environmental properties, Prog. Mater. Sci. 83 (2016) 1–23.

[3] S.V. Joshi, L. Drzal, A. Mohanty, S. Arora, Are natural fiber composites environmentally superior to glass fiber reinforced composites? Composites Part A 35 (3) (2004) 371–376.

[4] S.O. Ismail, E. Akpan, H.N. Dhakal, Review on natural plant fibres and their hybrid composites for structural applications: Recent trends and future perspectives, Composites Part C: Open Access 9 (2022).

[5] X. Ao, A. Vázquez-López, D. Mocerino, C. González, D.-Y. Wang, Flame retardancy and fire mechanical properties for natural fiber/polymer composite: A review, Composites Part B 268 (2024) 111069.

[6] N.K. Kim, S. Dutta, D. Bhattacharyya, A review of flammability of natural fibre reinforced polymeric composites, Compos. Sci. Technol. 162 (2018) 64–78.

[7] M. Wang, G.-Z. Yin, Y. Yang, W. Fu, J.L. Díaz Palencia, J. Zhao, N. Wang, Y. Jiang, D.-Y. Wang, Bio-based flame retardants to polymers: a review, Adv. Ind. Eng. Polymer Res. 6 (2) (2023) 132–155.

[8] L. Costes, F. Laoutid, S. Brohez, P. Dubois, Bio-based flame retardants: when nature meets fire protection, Mater. Sci. Eng.: R: Reports 117 (2017) 1–25.

[9] A.D. La Rosa, G. Recca, J. Summerscales, A. Latteri, G. Cozzo, G. Cicala, Bio-based versus traditional polymer composites. A life cycle assessment perspective, J. Clean. Prod. 74 (2014) 135–144.

[10] W. Woigk, C.A. Fuentes, J. Rion, D. Hegemann, A.W. van Vuure, C. Dransfeld, K. Masania, Interface properties and their effect on the mechanical performance of flax fibre thermoplastic composites, Composites Part A 122 (2019) 8–17.

[11] M.S. Özer, S. Gaan, Recent developments in phosphorus based flame retardant coatings for textiles: Synthesis, applications and performance, Prog. Org. Coat. 171 (2022) 107027.

[12] X.-L. Li, X.-H. Shi, M.-J. Chen, Q.-Y. Liu, Y.-M. Li, Z. Li, Y.-H. Huang, D.-Y. Wang, Biomass-based coating from chitosan for cotton fabric with excellent flame retardancy and improved durability, Cellulose 29 (9) (2022) 5289–5303.

[13] X.-C. Jiang, P. Li, Y. Liu, Y.-W. Yan, P. Zhu, Preparation and properties of APP flame-retardant ramie fabric reinforced epoxy resin composites, Industrial Crops Products 197 (2023) 116611.

[14] W. Guo, E.N. Kalali, X. Wang, W. Xing, P. Zhang, L. Song, Y. Hu, Processing bulk natural bamboo into a strong and flame-retardant composite material, Industrial Crops Products 138 (2019) 111478.

[15] P. Khalili, B. Blinzler, R. Kadar, R. Bisschop, M. Forsth, P. Blomqvist, Smoke Flammability, Mechanical Behaviours and Morphology of Flame Retarded Natural Fibre/Elium((R)) Composite, Materials. (Basel) 12 (17) (2019) 2648.

[16] X. Song, F. Song, X.-M. Ding, J.-M. Wu, X.-H. Wang, F. Wang, R. Feng, X.-L. Wang, Y.-Z. Wang, Construction of bio-based ramie fabric/epoxy resin composites with high flame retardant and mechanical performances, Industrial Crops & Products 194 (2023) 116281.

[17] M. Tirrell, Polyelectrolyte Complexes: Fluid or Solid? ACS. Cent. Sci. 4 (5) (2018) 532–533.

[18] Q. Wang, J.B. Schlenoff, The Polyelectrolyte Complex/Coacervate Continuum, Macromolecules. 47 (9) (2014) 3108–3116.

[19] D.L. Smith, N.A. Vest, M.O. Convento, M.D. Montemayor, J.C. Grunlan, Buffer induced ionically crosslinked polyelectrolyte treatment for self-extinguishing polyester, Npj. Mater. Degrad. 8 (1) (2024) 14.

[20] K.M. Holder, R.J. Smith, J.C. Grunlan, A review of flame retardant nanocoatings prepared using layer-by-layer assembly of polyelectrolytes, J. Mater. Sci. 52 (22) (2017) 12923–12959.

[21] D. Rodriguez-Melendez, D.L. Smith, S.G. Fisher, R. Sonnier, H. Vahabi, J. C. Grunlan, Two-Step Polyelectrolyte Complex Coating for Flame Retardant Flax, Macromol. Mater. Eng. 309 (1) (2023).

[22] T. Zhang, H. Yan, L. Shen, Z. Fang, X. Zhang, J. Wang, B. Zhang, A phosphorus-, nitrogen- and carbon-containing polyelectrolyte complex: preparation, characterization and its flame retardant performance on polypropylene, RSC. Adv. 4 (89) (2014) 48285–48292.

[23] Z. Zhang, X. Li, Z. Ma, H. Ning, D. Zhang, Y. Wang, A facile and green strategy to simultaneously enhance the flame retardant and mechanical properties of poly (vinyl alcohol) by introduction of a bio-based polyelectrolyte complex formed by chitosan and phytic acid, Dalton. Trans. 49 (32) (2020) 11226–11237.

[24] X.-W. Cheng, J.-P. Guan, X.-H. Yang, R.-C. Tang, F. Yao, A bio-resourced phytic acid/chitosan polyelectrolyte complex for the flame retardant treatment of wool fabric, J. Clean. Prod. 223 (2019) 342–349.

[25] X. Ao, R. Crouse, C. González, D.-Y. Wang, Impact of nanohybrid on the performance of non-reinforced biocomposites and glass-fiber reinforced biocomposites: Synthesis, mechanical properties, and fire behavior, Constr. Build. Mater. 436 (2024) 136922.

[26] B.K. Kandola, A.R. Horrocks, Complex char formation in flame-retarded fibre-intumescent combinations—II. Thermal analytical studies, Polym. Degrad. Stab. 54 (2-3) (1996) 289–303.

[27] S. Gaan, G. Sun, Effect of phosphorus flame retardants on thermo-oxidative decomposition of cotton, Polym. Degrad. Stab. 92 (6) (2007) 968–974.

[28] Y. Quan, Z. Zhang, R.N. Tanchak, Q. Wang, A review on cone calorimeter for assessment of flame-retarded polymer composites, J. Therm. Anal. Calorim. 147 (19) (2022) 10209–10234.

[29] S. Bourbigot, X. Flambard, Heat resistance and flammability of high performance fibres: A review, Fire Mater. 26 (4-5) (2002) 155–168.

[30] A.B. Morgan, M. Bundy, Cone calorimeter analysis of UL-94 V-rated plastics, Fire Mater. 31 (4) (2006) 257–283.

[31] A.P. Mouritz, Z. Mathys, A.G. Gibson, Heat release of polymer composites in fire, Composites Part A 37 (7) (2006) 1040–1054.

[32] H. Vahabi, Analysis of Flame Retardancy in Polymer Science, Elsevier, 2022.

[33] W.Wu Klingler, V. Rougier, Z. Huang, D. Parida, S. Lehner, A. Casutt, D. Rentsch, K. B. Hedlund, G.A. Barandun, V. Michaud, S. Gaan, Recyclable flame retardant phosphonated epoxy based thermosets enabled via a reactive approach, Chem. Eng. J. 466 (2023) 143051.

[34] M. Zhang, J. Xiao, W. Tang, Y. He, P. Tan, M. Haranczyk, D.Y. Wang, A Novel Benchmarking Approach to Assess Fire Safety of Liquid Electrolytes in Lithium-Ion Batteries, Adv. Energy Mater (2024) 2401241 n/a(n/a).