Research article

### The synergistic effect of inorganic hybrid nanofibers and phytic acid-based nanosheets towards improving the fire retardancy and comprehensive performance of epoxy resin

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**Abstract.** Usually, it is difficult to achieve satisfactory fire retardancy of epoxy resin (EP) at low addition by adding inorganic nano-fillers alone. Herein, sepiolite nanofibers loaded with layered double metal hydroxide (a-SEP@LDH) and phosphorus/ni-trogen-containing flame retardant nanosheets (PAMA) were prepared via hydrothermal method, respectively. The UL-94 V-0 rating and an limiting oxygen index (LOI) value of 31.6% were achieved for EP by loading 1 wt% a-SEP@LDH and 2 wt% PAMA. Compared to adding sole a-SEP@LDH, the thermal stability of EP/a-SEP@LDH/PAMA3 was improved significantly, the total heat release (THR) and peak heat release rate (pHRR) decreased by 10.2 and 28.8%, respectively. Additionally, the total CO<sub>2</sub> production decreased by 12.5% and the char residue yield increased to 19.9 wt%. Moreover, the tensile strength and impact strength of the EP composites were remarkably improved owing to the incorporation of PAMA. To sum up, this work provides an environmentally benign, low-cost and efficient way for EP to achieve outstanding fire retardance, thermal stability and high mechanical properties at a low addition.

Keywords: polymer composites, fire retardance, thermal stability, mechanical strength, synergistic mechanism

### **1. Introduction**

Epoxy resin (EP) is widely used in coatings, electronics, construction and industrial fields owing to its excellent mechanical properties, adhesion, electrochemical insulation and corrosion resistance [1–3]. However, its inherent flammability restricts extensive applications requiring high fire requirements. Researchers are generally devoted to imparting the required fire retardancy of EP by incorporating additive flame retardants or copolymerizing with reactive flame retardants [4–6]. Adding flame retardants such as inorganic filler [7], intumescent flame retardant [8], and silicon-based flame retardant [9] into epoxy resin is a convenient and common method. However, additive flame retardants deteriorate the mechanical properties of EP due to the problem of poor dispersion in the matrix at high loading [10]. In addition, biobased flame retardant made from degradable resources can greatly lower the environmental impact [11]. Therefore, developing an efficient and ecofriendly flame retardant is essential to balance the comprehensive performances of EP composite. In our previous work, a novel one-dimensional (1D) inorganic nanofiber was prepared by the self-assembly of Ni-Fe layered double hydroxide on the surface of acidified sepiolite nanofibers (a-SEP@LDH) [12]. The thermostability and tensile strength were improved by introducing 2.3 wt% a-SEP@LDH into

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EP. However, only a UL-94 V-1 rating was obtained owing to the fact that a-SEP@LDH used alone was unable to produce a sufficient swelling char layer and then extinguish the flame promptly. It can be verified by the slight increment of char residue of EP/a-SEP@LDH in cone testing from 12.0 wt% of EP to 14.9 wt%. Chen et al. [13] investigated the synergistic effect of multifunctional layered double hydroxide-based hybrids (MgAlZn-LDH-PMoA) and modified phosphagen (HACP) in EP. Upon incorporation of 4.7 wt% MgAlZn-LDH-PMoA and 2.3 wt% HACP, a UL-94 V-0 rating and a limiting oxygen index (LOI) value of 31.0%. Moreover, the total heat release and peak heat release rate of the EP composites remarkably declined by 35.2 and 50.9%. Pappalardo et al. [14] reported on the upon the combination of 0.5 wt% of pre-modified sepiolite (OSEP) with 12 wt% of a commercial phosphorus/nitrogen (P/N) – containing intumescent flame retardants (ET), Polypropylene (PP) reached a UL-94 V-0 rating and a LOI value of 26.3%. The peak heat release rate (pHRR) was decreased from 1610 to 241 kW/m<sup>2</sup>. Therefore, employing a P/N-containing intumescent flame retardant as a synergist is a potential strategy to enhance the charring ability of EP/a-SEP@LDH system, thus improving the fire retardancy.

The traditional P/N-containing intumescent flame retardants (IFR) show good flame retardancy [15]; however, there are some disadvantages, such as poor dispersion and easy agglomeration [16]. The synthesis of a 'three-in-one' IFR with two-dimensional (2D) supramolecular nanosheets is beneficial to improve the overall properties of EP due to the barrier effect of its nanosheet structure and more contact area with the polymer matrix. Our group has reported a novel bio-based 2D hyperbranched melamine phytate nanosheets (PAMA) [17], and a 6 wt% loading in EP is required to achieve a UL-94 V-0 rating, a 37% reduction in the total smoke production (TSP) and an increase of the char residue yield from 4.4 to 26.7%. Qin et al. [18] synthesized a 2D melamine trimetaphosphate (MAP); the addition of 4% MAP increased the LOI value of EP to 30.0%, and a UL-94 V-0 rating was attained. Meanwhile, its peak heat release rate (pHRR) and total smoke production (TSP) decreased by 65.6 and 45.4%, respectively. The above results show that P/N-containing 2D hyperbranched nanosheet flame retardants have excellent smoke suppression and carbonization effect, which can be employed to synergistically boost the fire retardant capability of inorganic nano-fillers.

Hence, to further improve the flame retardancy, dispersibility, thermal stability and mechanical properties of EP/a-SEP@LDH at a lower loading, the P/Ncontaining 2D nanosheets PAMA is employed. The nanosheet structure and organic groups of PAMA are conducive to improving the dispersion of a-SEP@ LDH in the EP matrix, allowing them to fully exploit their synergistic flame retardant efficiency and mechanical reinforcement effect. In addition, the fire retardant and strengthening mechanism of EP composites will be comprehensively discussed as well.

# 2. Experimental section 2.1. Materials

Melamine (MA, chemically pure), phytic acid (PA, biochemical reagent, 70% aqueous solution), nickel nitrate hexahydrate, iron nitrate nonahydrate, sodium hydroxide (NaOH), 4,4-diaminodiphenylmethane (DDM) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl) and sodium hexametaphosphate (SHMP) were provided by KeLong Chemical Reagent Co., Ltd. (Chengdu, China). Raw sepiolite (r-SEP) was purchased from Neixiang Dongfeng Sepiolite Limited Liability Company (Neixiang, China). Epoxy resin of bisphenol A diglycidyl ether (DGEBA, E44, epoxy value of 0.43–0.47 mol/100 g) was purchased from Nantong XingChen Synthetic Materials Co., Ltd. (Nantong, China).

### 2.2. Preparation of a-SEP@LDH

The a-SEP@LDH was prepared by hydrothermal assisted coprecipitation as described in previous literature [12]. In short, a certain amount of raw sepiolite (r-SEP) was first dispersed in the aqueous solution for 30 min; then the dispersion solution was filtered. The obtained filtered cake was added into the SHMP aqueous solution subsequently and stirred for 30 min; then the pretreated sepiolite was obtained via filtering, washing with deionized water for 5 times and drying. Next, the pretreated sepiolite was dispersed in 5 mol/1 HCl solution and continuously stirred at 80 °C for 24 h. The acidified sepiolite (a-SEP) solids were filtered and washed with deionized water until pH was close to neutral, ultimately collected after drying in a vacuum oven at 80 °C for 24 h. The nitrate solution containing a certain proportion of Ni<sup>2+</sup> and Fe<sup>3+</sup> was added dropwise into the 100 ml dispersion containing 1 g a-SEP. Then the pH value of the system was adjusted to 9–10 by adding 5 mol/l NaOH aqueous solution. The obtained yellow solution was mechanically stirred at room temperature for 24 h, afterwards transferred to 500 ml Teflonlined autoclave and aged for 36 h at 120 °C. The resulting product (a-SEP@LDH) was cooled to room temperature, filtered and washed several times, and then dried to constant weight at 70 °C.

### 2.3. Synthesis of PAMA

PAMA was synthesized by a hydrothermal process according to our previous report [17]. 30.24 g melamine (MA) was dispersed in 400 ml deionized water and mechanically stirred until uniformly dispersed at room temperature. Then the phytic acid aqueous solution (0.2 mol/l) was added dropwise into the MA solution and stirred for 0.5 h. After that, the obtained white emulsion was transferred into 1000 ml Teflon-lined autoclave and aged for 48 h at 80 °C. After the autoclave was cooled to room temperature, the final product was filtered and repeatedly washed with deionized water. In the end, the resulting white powder (PAMA) was obtained by vacuum drying at 70 °C and grinding.

#### 2.4. Preparation of EP composites

The EP composites were prepared by casting method. The composition of EP samples is listed in Table 1. First, E44 monomers were placed in a 250 ml threeneck flask and mechanically stirred at 110 °C, then 50 ml of ethanol dispersion solution involving a certain amount of PAMA and a-SEP@LDH powder was added into EP matrix and stirred continually for

3 h and vacuum stirred for 3 h. Subsequently, premelted DDM (the molar ratio of epoxy monomer to DDM is 4:1) was poured into the above mixture, which was transferred to a polytetrafluoroethylene mold after stirring 10 min at 90 °C. Finally, the mixture was cured at 120 °C for 3 h and re-cured at 150 °C for 2 h; the prepared samples were labelled as EP/a-SEP@LDH/PAMA. The detailed preparation route is depicted in Figure 1. Furthermore, the prepafor ration process EP, EP/PAMA, and EP/a-SEP@LDH is the same as the above process.

### 2.5. Characterization

Laser Raman spectroscopy (LRS) measurements were implemented using inVia laser Raman spectroscopy (Renishaw, UK) with the excitation wavelength of 514 nm, the scan range was 1000–2000 cm<sup>-1</sup>.

Transmission electron microscopy (TEM) images were carried on Zeiss Libra 200FETEM (Carl Zeiss, Germany) with acceleratingvoltage 200 kV.

Fourier transform infrared (FTIR) spectroscopy tests were recorded on a Spectrum One Autoima spectrometer (Perkin-Elmer, USA) using KBr pellets scanned from 4000 to 400 cm<sup>-1</sup>.

The X-ray diffraction pattern (XRD) was measured by D/MAX-1400 rotating anode X-ray diffractometer (Rigaku, Japan) with a Cu-K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.1541 nm), the scanning speed and scanning range were 3°/min and 3–30°/70°, respectively.

The thermogravimetric analysis (TG) was performed on a Jupiter STA449C synchronous thermal analyzer (Netzsch, Germany). The powder samples were heated from 30 to 800 °C at a heating rate of 10 °C/min in N<sub>2</sub> atmosphere.

The vertical burning tests (UL-94) were carried out using the M607 horizontal vertical burning tester

Samples	E44 monomers [wt%]	a-SEP@LDH [wt%]	PAMA [wt%]
EP	100	0	0
EP/PAMA	97	0	3
EP/a-SEP@LDH	97	3	0
EP/a-SEP@LDH/PAMA1	97	2	1
EP/a-SEP@LDH/PAMA2	97	1.50	1.50
EP/a-SEP@LDH/PAMA3	97	1	2
EP/a-SEP@LDH/PAMA4	97	0.75	2.25
EP/a-SEP@LDH/PAMA5	97	0.60	2.40
EP/a-SEP@LDH/PAMA6	97	0.50	2.50
EP/a-SEP@LDH/PAMA7	98	0.67	1.33
EP/a-SEP@LDH/PAMA8	96	1.33	2.67

Table 1. The Formulas of EP composites.



Figure 1. Preparation route of EP composites.

(Qingdao Shanfang Instrument Co., Ltd., China) according to ASTM D3801, and the sample dimension was  $130 \times 13 \times 3.2$  mm.

The limiting oxygen index (LOI) was obtained by a JF-3 oxygen index tester (Nanjing Jionglei Instrument Equipment Co., Ltd., China) according to ASTM D2863-97, and the sample size was  $100 \times 6.5 \times 3.2$  mm. The cone calorimetry test (CCT) was performed according to ISO 5660 (Fire Testing Technology, UK). The size of samples was  $100 \times 100 \times 4$  mm under an external heat flux of 35 kW/m<sup>2</sup>. The distance between sample and cone heater was 25 mm.

The emission scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS) was implemented on the Ultra55 device (Germany Carl Zeiss NTS GmbH) with an accelerating voltage of 10 kV. Before the tests, the specimens were sprayed with a thin gold coating to avoid electrostatic charges.

The glass transition temperature  $(T_g)$  was determined on differential scanning calorimetry (DSC) using a DSCQ2000 (TA Instruments, UK). The powder samples using 3–4 mg went through two heating processes at a heating rate of  $10 \,^{\circ}$ C/min ranging from 25 to 275 °C under the nitrogen gas flow of 50 ml/min. The tensile properties of all samples were tested at a rate of 2 mm/min, according to GB/T1040.3–2006 standard.

The non-notched impact tests of all samples were measured according to GB/T1040.3–2008 standard with dimensions of  $80 \times 10 \times 4$  mm.

### 3. Results and discussion

### 3.1. Characterization of PAMA and a-SEP@LDH

The FTIR spectra of PAMA and a-SEP@LDH are presented in Figure 2a and 2b. In Figure 2a, the multiabsorption peaks at 3469, 3419, 3333, 3132 cm<sup>-1</sup> in MA are attributed to the stretching vibration of  $-NH_2$  [19], the bending vibration of  $-NH_2$  appears at 1652 cm<sup>-1</sup>, the peaks at 1552, 1438 and 851 cm<sup>-1</sup> are corresponding to the skeleton vibration of triazine ring [20]. For PAMA, the broad absorption band at 3360 cm<sup>-1</sup> is assigned to the stretching vibration of N-H and -OH. The broad band at 3141 cm<sup>-1</sup> is assigned to the overlay of  $-NH_3^+$  stretching vibration and partially unreacted -NH<sub>2</sub> [17]. In addition, the vibration absorption of  $-NH_3^+$  also appeared at 1509 cm<sup>-1</sup> [19]. The bending vibration of  $-NH_2$  of MA shifts to 1675 cm<sup>-1</sup> in PAMA, which is due to the intermolecular interactions between the -NH<sub>2</sub> and -OH [21]. All the vibrations of the triazine ring shift to 1396 and 778 cm<sup>-1</sup>, owing to the hydrogen bond effect between MA and PA, and the deformation of the triazine ring in the self-assembly process of nanosheets [22]. Furthermore, a series of peaks appear at 1675, 1176, 1064, 982, 519 cm<sup>-1</sup> belong to bending vibration of OH in P-OH, stretching vibration of P=O bond,

asymmetric vibration of  $PO_3^{2-}$  and the stretching and bending vibrations of P-O bond [23, 24], respectively. These characteristic peaks prove the successful protonation of the amino group in MA and the occurrence of the neutralization reaction with PA. In Figure 2b, the two absorption peaks at 3675 and 745 cm<sup>-1</sup> of a-SEP are associated to the stretching and bending vibrations of Mg-OH [25]. The band located at 3448 and 1637 cm<sup>-1</sup> originated from stretching and deformation vibrations of -OH in crystal water [26]. Moreover, the broad absorption peak at about  $1000 \text{ cm}^{-1}$  and the peak at  $456 \text{ cm}^{-1}$ belong to the Si-O-Si groups [27]. For LDH, the typical peak at 1384 cm<sup>-1</sup> is attributed to NO<sub>3</sub>, and a broad peak around 643 cm<sup>-1</sup> corresponds to the lattice vibration of Ni-O-Fe [28]. On the FTIR of



Figure 2. FTIR spectra for a) MA, PAMA, b) a-SEP, LDH and a-SEP@LDH; XRD patterns for c) MA, PAMA, d) a-SEP, LDH and a-SEP@LDH.



Figure 3. SEM image of PAMA (a) and TEM image of a-SEP (b) and a-SEP@LDH (c).

a-SEP@LDH, all the typical peaks of LDH still exist. Meanwhile, the Si–O–Si bonds of a-SEP at 1000 and 456 cm<sup>-1</sup> are also observed. The absorption peaks at 3675 and 745 cm<sup>-1</sup> associated with Mg–OH almost disappear, which is due to the fact that the partial Mg<sup>2+</sup> has been replaced by Ni<sup>2+</sup> and Fe<sup>3+</sup> [29], indicating a-SEP and LDH are assembled not only through electrostatic interaction but also through chemical binding.

The morphology of PAMA, a-SEP and a-SEP@LDH was observed by SEM. PAMA shows a nanosheet structure with an average transverse diameter of less than 5  $\mu$ m and a thickness of about 50 nm (Figure 3a). The a-SEP exhibits a smooth fiber-like structure and a diameter of around 50 nm (Figure 3b). Compared with a-SEP, the surface of the hybrids becomes rough after the formation of Ni-Fe LDH (Figure 3c), which is mainly caused by the electrostatic absorption due to the negative charge of a-SEP and the positive charge of LDH.

The XRD patterns of the PAMA and a-SEP@LDH are displayed in Figure 2. In Figure 2c, the diffraction peaks of MA are in good agreement with structures indexed by JCPDS No. 24-1654, illustrating that MA is a monoclinic crystal. There are a series of new diffraction peaks for PAMA at 8.56, 14.48, 15.28, 16.7, 18.16, 18.75, 27.57, 28.05° in contrast to MA, and these reflection peaks belong to ammonium phosphate hydrate (PDF#81-1753), indicating that the crystal structures of PAMA and MA are completely different. The characteristic diffraction peak at 8.56° is due to the layered structure of PAMA formed by the neutralization of melamine and phytic acid [30]. Furthermore, the reflection peak at 27.57° is formed by the  $\pi$ - $\pi$  stacking of triazine rings [23], corresponding to an inter-planar spacing of 0.3233 nm according to the Bragg equation. As for Figure 2d, the diffraction characteristic peaks at 11.18 and 22.41° correspond to the (003) and (006) crystal planes of Ni–Fe LDH structure [31]. The (003) reflection of LDH shows a basal spacing of 0.79 nm, demonstrating that the interlayer anion is  $NO_3^{-}$  [32]. The weak characteristic absorption peaks of a-SEP exist in a-SEP@LDH infers that Ni-Fe LDH has been successfully assembled on the surface of a-SEP fibers.

The thermal stability of PAMA, a-SEP@LDH and mixed powder (the mass ratio of PAMA and a-SEP@LDH is 2:1) had been investigated by thermal gravimetry (TG) and derivative thermal gravimetry (DTG) curves in N<sub>2</sub> atmosphere and the results are presented in Figure 4 and Table 2. The thermal weight loss of PAMA can be divided into four stages, and the peak value of each stage was reached at 83.2, 258.5, 390.0 and 551.6 °C, respectively. The first thermal decomposition from room temperature to 100 °C was due to the loss of physically adsorbed water on the surface of PAMA. The second stage occurred between 185 and 350 °C; the unstable structural groups degraded, and the release of NH<sub>3</sub> and H<sub>2</sub>O. The maximum weight loss rate ( $T_{max}$ ) occurred at about 390 °C in the third thermal-degradation stage ranging from 350 to 450 °C, corresponding to the generation of polyphosphoric acid and polyphosphate by branching and crosslinking [17, 33]. The last degradation step is beyond 500 °C, corresponding to the release of metaphosphoric acid, polyphosphoric acid and phosphoric acid [34, 35]. Regarding a-SEP@LDH, the mass loss below 200 °C was attributed to the removal of adsorbed water. When the temperature is higher than 200 °C, the zeolite water and the coordination crystal water are eliminated in a-SEP [27, 36]. Moreover, the thermal decomposition of intercalated NO<sub>3</sub> and the dehydroxylation of the LDH laminate produces metal oxide, indicating that the structure of LDH has been destroyed [37]. The first three thermal degradation stages of the mixed powder were similar to PAMA, but the overall thermal degradation rate



Figure 4. TG (a) and DTG (b) curves of PAMA, a-SEP@LDH, a-SEP@LDH-PAMA in N2.

			2		
Samples	T <sub>5%</sub>	T <sub>max</sub> [°C]	Residues at 800 °C [wt%]		
	[ C]		Experimental	Calculated	
PAMA	99.6	390.0	24.9	-	
a-SEP@LDH	162.6	303.1	80.4	-	
a-SEP@LDH-PAMA	136.5	392.5	51.8	43.4	

Table 2. The TG and DTG data of PAMA, a-SEP@LDH, a-SEP@LDH-PAMA in  $N_2$ .

was lower than that of PAMA. It should be noted that the fourth thermal degradation stage was delayed to more than 650 °C and became weak, which may be attributed to two reasons: a) the physical barrier effect of a-SEP@LDH; b) metal oxide generated by LDH will take part in the crosslinking of polyphosphoric acid by means of bridge bond [38], then promoting the formation of more stable char residue at the third stage and significantly inhibiting the release of P-containing compounds. It showed that there existed a pronounced synergistic charring effect between a-SEP@LDH and PAMA, and it can be further proved by the experimental value of residual char of the mixture was higher than the theoretical value.

# 3.2. Dispersion of a-SEP@LDH/PAMA in EP matrix

To systematically analyze the dispersion state of flame retardants in the EP matrix, the cryo-fracture cross-section of EP composites was directly observed by SEM. The roughness of the fracture crosssection reflects the interfacial interaction and dispersity between fillers and polymer matrix. As shown in Figure 5, EP exhibited a smooth surface morphology with minimal tilted ripples due to the brittle fracture (Figure 5a). In contrast, the fracture surfaces of EP composites became rougher, and the folds increased because PAMA or a-SEP@LDH may play an impenetrable obstacle to stress under external force, then leading to crack bending [39]. Due to the existence of organic groups in PAMA and abundant hydroxyl groups in a-SEP@LDH, both EP/PAMA and EP/a-SEP@LDH have relatively good compatibility [40]. However, there were still some tiny aggregates on the cross-section (shown by arrows), which are caused by the uneven dispersion of PAMA or a-SEP@LDH in EP (Figures 5b and 5c). The folds of EP/a-SEP@LDH were a little narrower than those of EP/PAMA; this difference is mainly ascribed to the smaller aggregate size of 1D nanofibers than 2D nanosheets. For EP/a-SEP@LDH/PAMA3 system (Figure 5d), the fracture surface had no obvious agglomeration; furthermore, many narrow folds were found, indicating the stronger interfacial interaction and excellent dispersion of PAMA and a-SEP@LDH, which was further demonstrated by the element-mapping of P, Si, Ni and Fe.

The XRD patterns of EP, EP/PAMA, EP/a-SEP@LDH and EP/a-SEP@LDH/PAMA3 are shown in Figure 6; all samples appear a broad diffraction peak at around  $2\theta = 18^{\circ}$ , which is the characteristic peak of amorphous structure of EP [41]. The peak at  $2\theta = 27.57^{\circ}$  caused by the  $\pi$ - $\pi$  stacking is greatly weakened in EP/PAMA, it was caused by the reaction of the excessive -NH2 group of PAMA with the epoxy group and the low content of PAMA. The typical peaks of (003) and (006) crystal planes belonging to LDH lamellas disappeared, indicating that the lamellate of LDH was no longer retained. Namely, the interlayers of LDH can be easily exfoliated because the electrostatic interaction between a-SEP and



Figure 5. Fracture surface morphologies of a) EP, b) EP/PAMA, c) EP/a-SEP@LDH, d) EP/a-SEP@LDH/PAMA3, and e) the element mapping images (P, Si, Ni, Fe) of EP/a-SEP@LDH/PAMA3.

LDH will weaken the van der Waals force among LDH laminates [12]. Surprisingly, there is no obvious characteristic peak in EP/a-SEP@LDH/PAMA system, illustrating a satisfactory dispersion state of PAMA and a-SEP@LDH in EP matrix.

# **3.3. Thermal properties analysis of EP and its composites**

In order to investigate the thermal properties of various samples, the glass transition temperature  $(T_g)$  was examined using DSC tests, as shown in Figure 7. The  $T_g$  of EP is 152.5 °C, and the  $T_g$  of EP/a-SEP@LDH is slightly higher than that of EP, which is attributed to the combined effects of the following two reasons: one is the charge transfer between a-SEP and LDH weakens the catalytic ringopening effect of the Lewis acidic sites produced by inorganic nanofiller [42], the other is a-SEP@LDH can act as a physical crosslinking point at high temperature, increasing the degree of crosslinking to a certain extent [43]. It is worth noting that the  $T_g$  of EP/PAMA increases significantly to 166.4 °C; the underlying reason is the crosslinking reaction between the surplus amino of PAMA and epoxy groups [17], improving the crosslinking density. Consequently, the increased crosslinking density and the high stiffness of 2D nanosheets PAMA will restrict the mobility of molecular chains of EP [44, 45]. For EP/a-SEP@LDH/PAMA3, its  $T_g$  is 9.7 °C higher than that of EP/a-SEP@LDH, which is the result of



Figure 6. The XRD patterns of EP/PAMA, EP/LDH, EP/a-SEP-LDH and EP/a-SEP@LDH/PAMA3.



Figure 7. DSC curves of EP and EP composites.

the coupling action of physical crosslinking of a-SEP@LDH and chemical crosslinking of PAMA, indicating that the rigidity of the molecular chain of EP can be enhanced by introducing PAMA [46], which overall elevated the  $T_{\rm g}$  of EP/a-SEP@LDH/PAMA3.

The TG and DTG curves of EP and its composites are shown in Figure 8, and the corresponding data are listed in Table 3. There was only a single degradation stage ranging from 300 to 500 °C. The  $T_{1\%}$  values of EP, EP/PAMA, EP/a-SEP@LDH and EP/a-SEP@ LDH/PAMA3 were 100.3, 117.3, 321.7 and 296.9 °C, respectively, indicating that adding flame retardants does help to improve the thermal stability of EP composites, particularly for a-SEP@LDH, owing to its outstanding thermal stability. Compared to EP, the EP/PAMA, EP/a-SEP@LDH and EP/a-SEP@LDH/PAMA3 exhibited a reduction at a temperature of 5% mass loss ( $T_{5\%}$ ), which was probably related to the earlier thermal decomposition of additives themselves, and promoting the premature thermal degradation of EP by the catalyzing effect of flame retardants [47]. It is worth noting that the  $T_{5\%}$ value of EP/a-SEP@LDH/PAMA3 was lower than that of EP/a-SEP@LDH, which was due to the fact that PAMA was earlier to decompose prior to a-SEP@LDH, while the  $T_{\text{max}}$  value was higher than that of EP/a-SEP@LDH, which was because the formed char layer had a higher thermally stability through co-catalytic carbonization effect of polyphosphoric acid formed by PAMA and metal oxides formed by a-SEP@LDH, effectively delaying the random scission of EP chain [48]. As a result, the final char residues of EP/a-SEP@LDH/PAMA3 were



**Figure 8.** Thermal analysis of EP and its composites: a) TG and the enlarged TG curves among 240–380 °C, b) DTG curves in N<sub>2</sub>.

Samples	$T_{1\%}$ $T_{5\%}$			Residues [wt	IPDT	
	[C]	[C]	[C]	Experimental	Calculated	
EP	100.3	355.3	385.1	13.4	_	597.6
EP/PAMA	117.3	322.9	382.5	19.6	13.7	691.4
EP/a-SEP@LDH	321.7	345.3	367.7	22.3	15.4	756.4
EP/a-SEP@LDH/PAMA3	296.9	338.9	387.5	23.6	14.3	787.6

Table 3. Thermal analysis data of EP and its composites in  $N_2$ .

highest among all EP composites at 800 °C. It is noteworthy that the actual yield char of EP/a-SEP@LDH/PAMA3 was 65% higher than the theoretical value, which further verified the synergistic charring effect between a-SEP@LDH and PAMA. The IPDT (Integral procedural decomposition temperature) proposed by Doyle is a thermal stability parameter of the sample, widely used to evaluate the intrinsic overall thermal stability of polymer materials during pyrolysis [49, 50]. The IPDT value is calculated with the following Equation (1), (2) and (3):

$$IPDT [^{\circ}C] = A^{*} \cdot K^{*} \cdot (T_{f} - T_{i}) + T_{i}$$

$$\tag{1}$$

$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \tag{2}$$

$$K^* = \frac{S_1 + S_2}{S_1} \tag{3}$$

where  $A^*$  is the area ratio of the total experimental curve divided by the TG thermogram ( $S_1$ ,  $S_2$  and  $S_3$ are shown in the colors of the parts of the insert),  $K^*$ is the coefficient of  $A^*$ ,  $T_f$  is the final experimental temperature (800 °C),  $T_i$  is the initial experimental temperature (30 °C). The high IPDT value means the potential application of EP in high thermal resistance coatings and thermal insulation materials, and the *IPDT* value of EP/a-SEP@LDH/PAMA3 is the maximum among all samples, indicating that it had the best thermal stability. Consequently, the co-catalytic degradation and charring functions of PAMA and a-SEP@LDH are responsible for these results.

# 3.4. Fire-retardant behavior of EP and its composites

The fire-retardancy of EP and its composites are analyzed by UL-94, LOI and CCT. The results of UL-94 test are shown in Table 4. As shown in Figure 9, the EP is easily ignited. In the case of 3 wt% total loading of flame retardants, the EP/a-SEP@LDH burns for a long time but passes UL-94 V-1 rating, due to the barrier effect and catalytic charring effect of a-SEP@LDH. However, there is no UL-94 rating achieved for EP/PAMA composites. It can be seen from Figure 9 that EP/PAMA system has an obvious blowing out phenomenon [51], but PAMA itself

Table 4. The results of EP/a-SEP@LDH/PAMA with different proportions in UL-94 tests.

	F44 monomore	9-SED@I DH	рама	UL-94 test			
Samples	[wt%]	[wt%]	[wt%]	<i>av-t</i> <sub>1</sub> *	<i>av-t</i> 2**	Dripping	Ratings
EP	100	0	0	>30	a	No	NR <sup>b</sup>
EP/PAMA	97	0	3	>30	_a	No	NR <sup>b</sup>
EP/a-SEP@LDH	97	3	0	10.3	14	No	V-1
EP/a-SEP@LDH/PAMA1	97	2	1	>30	_a	No	NR <sup>b</sup>
EP/a-SEP@LDH/PAMA2	97	1.5	1.5	13	1	No	NR <sup>b</sup>
EP/a-SEP@LDH/PAMA3	97	1	2	6	2	No	V-0
EP/a-SEP@LDH/PAMA4	97	0.75	2.25	5	4	No	V-0
EP/a-SEP@LDH/PAMA5	97	0.6	2.4	17	9	No	V-1
EP/a-SEP@LDH/PAMA6	97	0.5	2.5	>30	_a	No	NR <sup>b</sup>
EP/a-SEP@LDH/PAMA7	98	0.67	1.33	6	5	No	V-1
EP/a-SEP@LDH/PAMA8	96	1.33	2.67	15	21	No	NR <sup>b</sup>

\*average burning time after first ignition

\*\*average burning time after second ignition

<sup>a</sup>Not recorded

<sup>b</sup>No rating



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Figure 9. The video screenshots in UL-94 test (a) EP, b) EP/a-SEP@LDH, c) EP/PAMA, d) EP/a-SEP@LDH/ PAMA3 and e) the LOI histogram of EP and its composites.

cannot help to produce enough stable char layer to protect the internal EP matrix, and the blowing out effect produced by melamine is too weak to unable to kill the flame. In contrast, the best fire retardancy of EP can be obtained under the dual fire-retardant action of the condensed phase and gas phase. When the mass ratio of a-SEP@LDH to PAMA is 1:2 or 1:3 at a total loading of 3 wt%, which can pass UL-94 V-0 rating with self-extinguishing behavior, and the total combustion time is the shortest at the ratio of 1:2. However, when the proportion of a-SEP@LDH to PAMA is too high or too low, no satisfactory results can be achieved. Moreover, the EP composites cannot pass UL-94 V-0 rating when the total addition amount is slightly increased or decreased. The above results demonstrate an optimal proportion of

a-SEP@LDH to PAMA to bring about the best fire retardancy for EP. The improved fire retardancy takes into account the good synergistic effect of a-SEP@LDH and PAMA, which helps to form a continuous dense char layer within a short period so that the spread of flame is suppressed effectively. Compared with other reported work of flame retardant EP with single-component or multi-component nanomaterials (Table 5 and Figure 10) [52–61], this work really achieves UL-94 V-0 rating at the lowest addition amount by adding multi-component green flame retardant in EP. According to Figure 9, the LOI value of EP is 26.3%. Loading flame retardants can improve the LOI values of various EP composites to varying degrees. It is worth mentioning that the EP/a-SEP@LDH/PAMA3 has the highest LOI

Matrix	FR additives	Additive amount	UL-94	References
E44	CP-6B <sup>a</sup>	7 wt%	V-0	[52]
E44	P-MnMo <sub>6</sub> <sup>b</sup>	8 wt%	V-0	[53]
E44	DOPO-MMT	6 wt%	V-0	[54]
E44	FRs-rGO	5 wt%	V-0	[55]
E44	PHDT@FeCo-LDHc	4 wt%	V-0	[56]
E44	CSA/DOPO <sup>d</sup>	8 wt% (2:1)	V-0	[57]
E44	CaG/APP <sup>e</sup>	10 wt% (8:1)	V-0	[58]
E44	APP/BPOPA <sup>f</sup>	15 wt% (3:1)	V-0	[59]
E44	CBz/BG <sup>g</sup>	10 wt% (4:1)	V-0	[60]
E44	PPTA/APP <sup>h</sup>	10 wt% (1:3)	V-0	[61]
E44	a-SEP@LDH/PAMA	3 wt% (1:2)	V-0	This work

Table 5. Comparison with the previously reported work in UL-94 test (thickness of 3.2 mm).

<sup>a</sup>Organic compound hexakis (4-boronic acid-phenoxy)-cyclophosphazene (CP-6B)

<sup>b</sup>An organic phosphorus and metal oxide hybrid compound (P-MnMo<sub>6</sub>)

<sup>c</sup>Bioderived crosslinked polyphosphazene microspheres decorated with FeCo-layered double hydroxide (PHDT@FeCo-LDH) <sup>d</sup>Chitosan-based derivative (CSA)/9,10-dihydro-9-oxa-10-phosphaphenanthreene-10-oxide (DOPO)

"Chilosan-based derivative (CSA)/9,10-dinydro-9-oxa-10-phosphaphenanthreene-10-oxide (DC

<sup>e</sup>Calcium gluconate (CaG) / ammonium polyphosphate (APP)

<sup>f</sup>Ammonium polyphosphate (APP)/P/N-containing oligomer poly (piperazine phenylphosphamide) (BPOPA)

<sup>g</sup>Bio-based phosphorus-containing benzoxazine monomer (CBz)/boron-doped graphene (BG)

<sup>h</sup>Poly(piperazine phenylamino-phosphamide) (PPTA)/ammonium polyphosphate (APP)



Figure 10. Comparison of additive amount and UL-94 rating of as-designed flame retardant EP composites reported previously [52–61].

value. Based on the aforementioned findings, it is concluded that a-SEP@LDH and PAMA possess a great synergistic flame retardant effect in EP.

The cone calorimeter tests (CCT) can be used to evaluate the comprehensive combustion performance of polymeric materials. The time to ignition (*TTI*), the peak of heat release rate (pHRR), total heat release rate (THR), the peak of smoke release rate (pSPR), total CO production, total CO<sub>2</sub> production, and average effective heat combustion (av-EHC) are summarized in Table 6. The curves of heat release rate (HRR), smoke release rate (SPR), CO production (COP),  $CO_2$  production (CO<sub>2</sub>P) are shown in Figure 11.

The *TTI* values of EP composites are all shorter than that of EP, implying that the initial thermal decomposition of EP is accelerated by flame retardants, which is consistent with the results of TG. Figure 11a shows the pHRR of EP is 952.6 kW/m<sup>2</sup>, while the pHRR values of EP/PAMA and EP/a-SEP@LDH decrease to 581.5 and 797.8 kW/m<sup>2</sup>, respectively. The EP/ PAMA exhibits better heat suppression effect than EP/a-SEP@LDH, which is mainly due to the expanded char layer

Table 6. Cone calorimetric data of EP and its composites.

Samples	TTI	pHRR	THR	pSPR	Total COP	Total CO <sub>2</sub> P	av-EHC	Char residue
	[s]	[kW/m <sup>2</sup> ]	[MJ/m <sup>2</sup> ]	[m <sup>2</sup> /s]	[g]	[g]	[MJ/kg]	[wt%]
EP	96±5	952.6±18.9	112.8±1.5	0.49±0.002	3.05±0.02	71.08±0.97	22.77±0.32	11.4±1.6
EP/PAMA	95±4	581.5±79.7	109.9±8.0	0.32±0.01	3.06±0.06	63.85±1.93	22.69±0.85	19.7±1.2
EP/a-SEP@LDH	93±1	797.8±0.3	106.9±1.7	0.43±0.03	2.68±0.06	69.41±0.99	21.12±0.07	17.1±2.0
EP/a-SEP@LDH/PAMA3	89±3	568.1±15.7	96.0±0.7	0.35±0.02	2.74±0.07	60.70±0.18	17.18±2.70	19.9±1.2

formed by the thermal decomposition of PAMA [62]. Whereas a-SEP@LDH alone cannot produce a good char layer under continuous heat irradiation to protect the underlying EP matrix. Compared with EP/a-SEP@LDH, the pHRR of EP/a-SEP@LDH/PAMA3 is decreased by 28.8% and the THR is dropped to 96 MJ/m<sup>2</sup>, representing a synergistic fire retardancy existed between a-SEP@LDH and PAMA in the combustion process, thereby resulting in an effectively protective char residue to block the transmission of heat and combustible volatiles. The av-EHC reflects the combustion of flammable volatile in the gaseous phase. The av-EHC of EP/a-SEP@LDH/PAMA3 is only 17.18 MJ/kg, indicating a lower heat generation in volatile gases, which can be explained by the isolation effect of high-quality char layer and the dilution effect of non-flammable gases.

The SPR reflects the parameters of smoke release in a real fire. The pSPR of all EP composites is lower than that of EP (Figure 11b). The pSPR of

EP/a-SEP@LDH is larger than that of EP/PAMA, the related reason is the same as the pHRR date, that is the a-SEP@LDH is unable to promote the formation of a continuous char layer, resulting in the overflow of thermally degraded fragments of EP. In contrast, PAMA itself acts as a good charring agent, and the polyphosphoric acid and metaphosphoric acid generated by PAMA can catalyze the dehydration and carbonization of EP to form a swollen char layer [63]. The pSPR of EP/a-SEP@LDH/PAMA3 is the consequence of the joint action of a-SEP@LDH and PAMA. During the process of combustion, the pyrolytic products (polyphosphoric acid and metaphosphoric acid) formed by PAMA and degradative substances (metal compounds and various acid active sites) generated by a-SEP@LDH lead to the formation of continuous and dense char residues [64], so that more decomposition debris of EP composites adhere to it [65], and the char residue vield of EP/a-SEP@LDH/PAMA3 is the highest.



Figure 11. HRR (a), SPR (b), COP (c) and CO<sub>2</sub>P (d) for EP and its composites.

To study the toxicity of combustion products, the COP and CO<sub>2</sub>P curves shown in Figures 11c, 11d are similar to the HRR curves. It is noteworthy that the total COP of EP/PAMA is higher than that of EP/a-SEP@LDH, while the total CO<sub>2</sub>P is lower than that of EP/a-SEP@LDH, which maybe indicate incomplete combustion of EP/PAMA due to more protective char layer [66]. Besides, the metal oxides originating from a-SEP@LDH can be reduced by CO to generate Ni, Fe and CO<sub>2</sub> during combustion. The total COP of EP/a-SEP@LDH/PAMA3 is between EP/PAMA and EP/a-SEP@LDH, which is the result of combined actions of incomplete combustion and redox reaction of some metal oxides during combustion. With the formation of the densest continuous carbon layer, which effectively inhibits the further oxidation of CO to  $CO_2$  by oxygen, so the total  $CO_2P$ of EP/a-SEP@LDH/PAMA3 is the lowest.

### 3.5. Fire retardant mechanism

To elucidate the fire retardant mechanism, SEM, Raman, XRD and FTIR were adopted to characterize the char residues of EP and its composites obtained from CCT. The results are presented in Figure 12. As shown in Figure 12a, there are only a few discontinuous char residues for EP and obvious cracks (marked

with the blue arrow) in the interior char residue for EP. Compared with EP, the thickness of the char residues of EP composites is greatly increased. The continuous residual char of EP/PAMA can be observed (Figure  $12b_3$ ), but there are many holes on top (Figure  $12b_1$ ), resulting in a loose expanded char layer. However, its internal char layer is dense and continuous, which can relatively inhibit the transfer of oxygen and heat. Concerning EP/a-SEP@LDH, the external residual char exhibits visible defects (Figure  $12c_1$ ), while the interior char contains a few broken bubbles and serried weeny metal oxide particles formed by the thermal decomposition of a-SEP@LDH. Figure 12d shows the whole char layer is quite compact and continuous after combining PAMA and a-SEP@LDH. The co-catalytic carbonization of PAMA and a-SEP@LDH, as well as the physical reinforcement of sepiolite nanofibers, are thought to generate a high-quality char layer, which can effectively prevent the overflow of thermal degradation debris.

Raman spectroscopy is commonly used to analyze the graphitization degree of char residue. As shown in Figure 13, each figure exhibits one broad peak at  $1367 \text{ cm}^{-1}$  and one sharp peak at  $1597 \text{ cm}^{-1}$ , corresponding to D and G bands, respectively. In general,



**Figure 12.** The digital photos of the char residue and the SEM micrograph of the interior char residue: EP (a<sub>1</sub>, a<sub>2</sub>, a<sub>3</sub>), EP/PAMA (b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub>), EP/a-SEP@LDH (c<sub>1</sub>, c<sub>2</sub>, c<sub>3</sub>), EP/a-SEP@LDH/PAMA3 (d<sub>1</sub>, d<sub>2</sub>, d<sub>3</sub>)



Figure 13. Raman spectra of the residual char after CCT test for a) EP, b) EP/PAMA, c) EP/a-SEP@LDH and d) EP/a-SEP@LDH/PAMA3.

the D bands represent the disordered graphite or glassy carbon, and the G bands correspond to the absorption peak of the sp<sup>2</sup>-hybridized carbon atoms. The integral strength ratio of D to G bands  $(I_D/I_G)$ correlates to the graphitization degree of residual char. Lower values of  $I_D/I_G$  represent a higher degree of graphitization [67]. The  $I_D/I_G$  value of EP/a-SEP@LDH is 1.66, whereas the  $I_D/I_G$  of EP/a-SEP@LDH/PAMA3 is lowest among the control groups. These results illustrate that the cooperative catalyzing charring effects from PAMA and a-SEP@LDH can produce more graphitization structure, which can serve as a high-quality char layer and block the transfer of heat and gases essentially.

To further analyze the phase composition, the char residue formed in CCT tests is analyzed by XRD. As shown in Figure 14a, there is a broad diffraction peak around 25° for both EP and EP/a-SEP@LDH/PAMA3, corresponding to the (002) diffraction

of graphite. In addition. for peak EP/a-SEP@LDH/PAMA3, it shows a characteristic diffraction peak at 7.3°, which is ascribed to the sepiolite fiber structure [68]. This finding identifies that the fiber structure of sepiolite is preserved in residual char owing to its high thermal stability, and then this fiber structure physically reinforces the protective char layer during combustion. There also exists Ni, Fe alloys (PDF#12-0736), NiO (PDF#78-0423) and Fe<sub>3</sub>O<sub>4</sub> (PDF#76-1849), because Fe<sup>3+</sup>, Ni<sup>2+</sup> can undergo redox reactions with the thermal degradation products of EP such as CO (Fe<sup>3+</sup> $\rightarrow$ Fe<sup>2+</sup> $\rightarrow$ Fe,  $Ni^{2+} \rightarrow Ni, CO \rightarrow CO_2$  [12]. These metal oxides generated during thermal decomposition have a high specific heat capacity, contributing to excellent heat absorption [69]. Meanwhile, sepiolite may produce a large number of Brønsted acidic sites, Fe<sup>3+</sup> and Ni<sup>2+</sup> can act as Lewis acidic sites under high temperature, and all these acidic sites may attack EP



Figure 14. XRD patterns and FTIR spectra of the residual char after CCT test for EP and EP/a-SEP@LDH/PAMA3: a) XRD patterns; b) FTIR spectra.

molecular chains to generate cationic active sites, thereby accelerating and catalyzing the pyrolysis, isomerization and aromatization reaction of polymer [70–72], consequently promoting the formation of stable and continuous thick coke layer.

To further illustrate the role of PAMA, the FTIR of char residue from EP spectra and EP/a-SEP@LDH/PAMA3 are given in Figure 14b. The characteristic peak at 3431 cm<sup>-1</sup> is attributed to O-H or N-H stretching vibration, the peaks at 2923 and 2832 cm<sup>-1</sup> are caused by -CH<sub>2</sub>- and -CH-, respectively [73]. The absorption peak at 1589  $\text{cm}^{-1}$  is assigned to phenyl [74] and the peak at  $1105 \text{ cm}^{-1}$ belongs to C–O bond in the ether group [75]. Additionally, for EP/a-SEP@LDH/PAMA3, the characteristic peaks at 1234 and 1178 cm<sup>-1</sup> are attributed to P=O and P-O groups, respectively [76]. The peak at 1121 cm<sup>-1</sup> can be ascribed to the stretching vibration of  $PO_2/PO_3$  in phosphate carbon complexes [77]. These results demonstrate that PAMA can form polyphosphoric acid and phosphoric acid, which has an excellent dehydration and carbonization effect during combustion. The weak absorption peaks at 951 and 457 cm<sup>-1</sup> belong to Si–O–Si bond of a-SEP. The stretching vibration peak of Fe-O and the bending vibration peak of Ni–O occur at 561 and 608 cm<sup>-1</sup> [78, 79], respectively. These further prove that the a-SEP can act as physical reinforcement for the char layer and metal oxides exist in the residue. Compared to EP, a new vibrational peak appeared at 1509 cm<sup>-1</sup> in EP/a-SEP@LDH/PAMA3 is originated from the aromatic ring [80], indicating that the formed char layer has a higher degree of aromatization, thereby effectively improving the fireproofing properties.

Based on the foregoing discussion, the possible synergistic fire retardant mechanism of PAMA and a-SEP@LDH in EP may be proposed, as shown in Figure 15. In the combustion process of the EP/a-SEP@LDH/PAMA3 system, on the one hand, PAMA can thermally decompose to produce polyphosphoric acid and phosphoric acid, which promote the dehydration and carbonization of the EP molecular chain, and then forms an expanded char layer. Besides, the carbonaceous PAMA nanosheets may function as a solid physical barrier and offer strong smoke suppression properties. On the other hand, the metal oxides generated by a-SEP@LDH can effectively absorb heat. In addition, the varieties of acidic sites will accelerate the pyrolysis, isomerization and aromatization reactions of EP, facilitating an efficient protective char layer with a high graphitization structure. Meanwhile, sepiolite fiber, as a kind of inorganic nano-clay with strong thermal stability, can physically strengthen the char layer and considerably improve the thermostability of char residue. As a result, the formed high-quality and high-stability char layer can effectively inhibit the transfer of oxygen and heat between the combustible zone and the matrix.



Figure 15. Possible fire retardant mechanism of EP/a-SEP@LDH/PAMA3.

Moreover, the release of smoke and volatiles is also suppressed, and char residue increases noticeably.

## **3.6.** Mechanical properties of EP and its composites

The tensile strength and impact strength are used to analyze the mechanical properties of EP and EP composites. The corresponding results are shown in Figure 16 and Table 7. In our previous work [12], the tensile strength of EP/a-SEP@LDH with 2.3 wt% loading is 21.6% higher than that of pure EP, but when the addition of a-SEP@LDH is 3 wt%, the tensile strength is only slightly increased by 5.5% compared to EP, which may be caused by the partial agglomeration of a-SEP@LDH in EP matrix (as shown in Figure 5c). However, when PAMA is added to the system, the tensile and impact strengths of EP/a-SEP@LDH/PAMA3 are 33.9 and 43.4% higher than those of EP, respectively. Meanwhile, an increased Young modulus is also obtained. These marked improvements imply an excellent synergy between PAMA and a-SEP@LDH. The following are some possible explanations: a) as discussed in section 3.3, the physical crosslinking of a-SEP@LDH and chemical crosslinking of PAMA make for improving the crosslinking density, coupled with the 'circuitous effect' of nanofillers [81], limits the mobility of EP molecular segments to a

Samples	Impact strength [kJ/m <sup>2</sup> ]	Tensile strength [MPa]	Elongation at break [%]	Young modulus [GPa]
EP	10.6±1.3	57.9±1.9	6.2±0.5	1.22±0.02
EP/PAMA	13.8±0.7	66.0±5.0	5.8±0.4	1.63±0.02
EP/a-SEP@LDH	7.6±0.1	61.1±3.8	4.7±0.3	1.69±0.03
EP/a-SEP@LDH/PAMA3	15.2±0.2	77.5±3.5	5.8±0.4	1.73±0.02

Table 7. The mechanical properties of EP and its composites.



Figure 16. Stress-strain curves (a), tensile strength and impact strength (b) of EP and its composites.

certain extent. b) the increased dispersion of EP/a-SEP@LDH/ PAMA3 is beneficial to enhance the interfacial interaction between the nanofillers and EP matrix, thereby allowing stress to be rapidly transferred from the weak polymer interfaces to tough nanolayers or nanofibers when subjected to an external force. c) more wrinkles and surface roughness on the cross-section of EP/a-SEP@LDH/PAMA3, indicate that the combination of PAMA and a-SEP@LDH can boost fracture energy dissipation (in Figure 5d).

### 4. Conclusions

The phytic acid-based P/N-containing nanosheets (PAMA) were employed to improve the flame retardant efficiency of inorganic hybrid nanofibers (a-SEP@LDH) in EP. By adding only 1 wt% a-SEP@LDH and 2 wt% PAMA to EP, the UL-94 V-0 rating and the LOI value of 31.6% are reached. The EP/a-SEP@LDH/PAMA3 has higher thermal stability than EP, and its IPDT value is enhanced by 31.8%. Additionally, the pHRR and pSPR of EP/a-SEP@LDH/PAMA3 are significantly reduced. The fire retardant mechanism of EP/a-SEP@LDH/PAMA3 mostly depends on condensed phase behavior. During burning, polyphosphoric acid and phosphoric acid, metal oxides and various acidic sites can catalyze the crosslinking, aromatization and carbonization of EP, combining with the strengthening effect of a-SEP fiber to produce a more stable, continuous and solid char layer. Moreover, the synergistic actions of a-SEP@LDH and PAMA lead to improved dispersion and fracture energy dissipation, which are beneficial to reinforce the mechanical properties of EP. Thereby, the impact strength and tensile strength of EP/a-SEP@LDH/PAMA3 are 43.4 and 33.9% higher, respectively, than those of EP. In short, our study achieves excellent fire retardancy with a minimum amount of flame retardant in EP, along with improved mechanical properties without compromising heat resistance.

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