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Phosphotungstic acid intercalated Zn,Al-layered double hydroxides/nanocellulose based 3D lightweight foam thermal insulation materials

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Abstract

In this study, [PW_{12}O_{40}]^{3-} anions have been intercalated into Zn,Al-Layered Double Hydroxides(ZnAl-NO_{3}-LDHs) to synthesize ZnAl-PW_{12}O_{40}-LDHs by ion-exchange reaction. The chemical composition and structure were analyzed by XRD, FT-IR, ICP, and SEM. Then, the nanocellulose based 3D lightweight foam thermal insulation materials was prepared by ZnAl-PW_{12}O_{40}-LDHs and CNF compound with H_{3}BO_{3}. The TG showed that ZnAl-PW_{12}O_{40}^-LDHs significantly reduced the maximum decomposition rate and increased the carbon residual rate at 800 °C, which indicated that ZnAl-PW_{12}O_{40}^-LDHs can improve the oxidation resistance of CNF composite materials at high temperature. The fire resistance of different samples were evaluated by back temperature test and alcohol lamp flame test, CNF/50%ZnAl-PW_{12}O_{40}-LDHs/2%H_{3}BO_{3} showed best thermal stability and flame-retardant properties, which can be contributed to the decomposition products of ZnAl-PW_{12}O_{40}^-LDHs, acting both as phase flame retardant and condensed phase flame retardant.

1. Introduction

With the increasing seriousness of environmental pollution and depletion of oil resources, developing a biodegradable and environment-friendly lightweight thermal insulation materials attracted more and more attention [1, 2], as it can reduce energy consumption and improve energy efficiency. Due to its excellent characteristics, the thermal insulation materials was widely used in the aviation, aerospace, chemical, construction, machinery, storage and energy areas [3, 4]. At present, nanocellulose foams [5], especially with thermal insulation and flame retardant effect, are considered to be one of the biodegradable foams with broad development prospects [6, 7]. In order to improve the flame-retardant properties of nanocellulose foams, various types of flame retardants have been developed. However, nanocellulose foams composite with LDHs has been rarely reported.

Layered double hydroxides (LDHs) are two dimensional materials [8], their normalized formula can be written as [M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}]^{x+}(A^{n-})_{x/n} \cdot mH_{2}O [9], where M^{2+} and M^{3+} each represent the divalent and trivalent metal cations, which are the main components of layer boards, x represents the molar ratio of M^{3+}/(M^{2+} + M^{3+}), usually between 0.2 and 0.4 [10, 11]. A^{n-} is a counter anion, which is located in the interlayer and can be exchange by other anion [12]. Because of their layered structure and high anion exchange capacity, LDHs has been applied to many fields including flame retarding [13, 14]. During combustion, hydroxyl groups and interlamellar anion of LDHs are released in the form of water and CO_{2}, which can reduce the concentration of combustion gas and block O_{2}. The mixed metal oxide of decomposition product can also catalyze the formation of more stable carbon laye, so as to protect the inner material from being exposed to air and suppress smoke production [15–17].
Table 1. Composition ratio of ZnAl-PW12O40-LDH/ nanocellulose lightweight thermal-insulated foams.

| CNF/ZnAl-PW12O40-LDHs/H3BO3 | CNF(g L⁻¹) | ZnAl-PW12O40-LDH(%) | H3BO3(%) |
|-----------------------------|------------|---------------------|----------|
| CNF                         | 10         | —                   | —        |
| CNF/37.5%ZnAl-PW12O40-LDHs  | 37.5       | —                   | —        |
| CNF/25%ZnAl-PW12O40-LDHs/2%H3BO3 | 25       | 2                   | —        |
| CNF/37.5%ZnAl-PW12O40-LDHs/2%H3BO3 | 37.5   | —                   | —        |
| CNF/50%ZnAl-PW12O40-LDHs/2%H3BO3 | 50       | —                   | —        |
| CNF/62.5%ZnAl-PW12O40-LDHs/2%H3BO3 | 62.5    | —                   | —        |

Organic or inorganic anions can be intercalated into LDHs to modify the properties the material [18]. Heteropoly acid can be used for flame retardant and improve their thermal stability by taking advantage of heteropoly acid’s catalytic desulfurization and toxicity reduction performance. Heteropoly acid show good flame retardant and efficient smoke suppression effect in wood, as catalyzed by heteropoly acid, the flame retardant poplar can be dehydrated into ester and cured into carbon, which can effectively delay the pyrolysis of inner wood, reduce the heat and smoke release in the wood combustion process, enhance the thermal stability of materials. Herein, in this paper, [PW12O40]³⁻ anions have been intercalated into ZnAl-NO3-LDHs to synthesize ZnAl-PW12O40-LDHs by ion-exchange reaction and characterized by XRD, IR, and SEM. Afterwards, ZnAl-PW12O40-LDHs were used as flame retardant in CNF to prepare a 3D lightweight foam thermal insulation materials, demonstrating both efficient fire-retardant performance and thermal stability.

2. Experimental section

2.1. Materials
Zn(NO3)2·6H2O, Al(NO3)3·9H2O, H3PW12O40·xH2O were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nanocellulose were provided by Tianjin Woodelfbio cellulose Co., Ltd. (China). All chemicals were used without further purification. The distilled water was produced in our laboratory.

2.2. Synthesis of Zn-Al LDHs
Zn-Al LDH was synthesized by a traditional co-precipitation. For the sake of increasing the charge density of layer sheets, the Mg/Al molar ratio was fixed at 3 [19]. In brief, Zn(NO3)2·6H2O (11.16 g, 0.0375 mol), Al(NO3)3·9H2O (4.7 g, 0.0125 mol) were dispersed in 60 ml deionized water in a three-neck flask with vigorous stirring. Controlling the pH at 8.0 using a NaOH (2 M) solution, keeping the reaction temperature at 65 °C and protected with N2 gas. The precipitated LDH slurry was filtered and washed with H2O until pH = 7. Finally the samples were dried in an oven at 60 °C for overnight to obtain the LDH powders [20].

2.3. Synthesis of ZnAl-PW12O40-LDHs
The above washed LDH slurry was dispersed in 250 ml of deionized water again. Then 100 ml of Na3PW12O40 aqueous solution was added into the above solution drop-wise under vigorous stirring and N2 protection. After that, the reaction keep going at 50 °C for 14 h, followed by centrifugation, washing, and drying to obtain the ZnAl-PW12O40-LDHs powders.

2.4. Preparation of ZnAl-PW12O40-LDHs/nanocellulose based foam materials
The ZnAl-PW12O40-LDHs slurry and nanocellulose were mixed at the mass ratio as table 1 as follows, H3BO3 was drop wise added into the mixture. The uniformly mixed solution was placed into a vacuum freeze-dryer at −20 °C for 12 h, then followed by a programmed vacuum drying under pressure of 4.5 Pa. The drying process was divided into five stages, firstly keep the temperature at −5 °C for 3 h, then followed by 10 °C for 5 h, 20 °C for 10 h, 30 °C for 10 h, 40 °C for 15 h. After that we get the ZnAl-PW12O40-LDHs/Nanocellulose Based Foam Materials

2.5. Characterization
Powder X-ray diffraction (XRD) patterns was recorded on a Rigaku Corporation D/Max 2500 X-ray diffraction, using Cu Kα radiation (λ = 1.5405 Å) at 40 kV with 80 mA current. The scanning rate was 5° min⁻¹ over the angular range 5° < 2θ < 80°. FTIR spectra were recorded on a Nicolet Avatar 330(USA) over the range of 600 ~ 4000 cm⁻¹ using the KBr pellet technique (ca. 1 mg of sample/300 mg of KBr) to determine the functional groups of the samples. The morphology of the samples was observed by SEM using a JSM-6490LV scanning electron microscope (JEOL Ltd., Japan). Chemical composition (Zn, Al, W) of the samples was estimated using a AVIO 500 inductively coupled plasma (ICP) from PerkinElmer.
2.6. Thermal stability and thermal insulation property

The thermal stability of all samples were evaluated using TGA (TGA Q50, TA Instrument), which was carried out under a nitrogen atmosphere from 30 °C to 800 °C at a heating rate of 5 °C min⁻¹.

2.7. Back temperature test

XC-24-K-12 thermocouple and OM-DAQ-USB-2400 data acquisition & recorder (OMEGA, USA) were used to test fire resistance performance of thermal-insulated foam materials. In brief, laid the thermal-insulated foams above the steel plates, and fixed the thermocouple on the back of steel plates, the temperature curves were recorded.

2.8. Alcohol lamp Flame Test

Thermal-insulated samples with a size of 50 mm * 50 mm * 5 mm were vertically fixed, the Alcohol lamp Flame was used to ignite the samples. The angle between the samples and the flame was fixed at 30° to ensure full contact.

3. Results and discussion

3.1. Characterization and thermal stability of ZnAl-NO₃-LDH and ZnAl-PW₁₂O₄₀-LDH

The XRD patterns of as-synthesized ZnAl-NO₃-LDH and ZnAl-PW₁₂O₄₀-LDH are shown in figure 1 and table 2. The XRD pattern of the ZnAl-NO₃-LDH exhibits the typical characteristics of an LDH phase with a rhombohedral packing of the layers [18, 21]. The sharp Bragg reflections indexed as (003), (006), (009), and (110) which correspond to the basal and higher-order reflections, were observed at 2θ = 9.94°, 19.92°, 33.76°, and 60.30° respectively. The interlayer distance value d(003) of LDH is calculated as 0.8888 nm, which in accordance with the reported value of 0.88 nm. After the ion-exchange interaction of [PW₁₂O₄₀]⁻³ into the interlayer galleries of ZnAl-NO₃-LDH, the XRD pattern showed some different with lower diffraction angle, weaker and wider crystallizing peak, which indicates a less-organized stacking arrangement after H₃PW₁₂O₄₀
intercalated. Besides, the corresponding interlayer distance \( d_{003} \) was expanded to 1.109 nm, indicating that \( \left[ \text{PW}_{12}\text{O}_{40} \right]^{3-} \) anions have successfully replaced \( \text{NO}_3^- \) in the interlayer galleries to form ZnAl-PW12O40-LDH.

The FT-IR spectra of \( \text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O} \) ZnAl-NO3-LDHs and ZnAl-PW12O40-LDHs are shown in figure 2. The band around 3450 cm\(^{-1}\) shown in the spectrum of LDH was assigned to the stretching vibration of the hydroxyl groups of LDH layers and interlayer water molecules. ZnAl-NO3-LDHs had an obvious peak at 1386 cm\(^{-1}\), which could be ascribed to the nitrate anions in the interlayer spaces of ZnAl-NO3-LDHs, however this peak was obviously weakened as to ZnAl-PW12O40-LDHs, suggesting \( \left[ \text{PW}_{12}\text{O}_{40} \right]^{3-} \) anions has replaced the interlayer nitrate anions. However, the characteristic absorbance of \( \left[ \text{PW}_{12}\text{O}_{40} \right]^{3-} \) anions can still be found in the spectrum of ZnAl-PW12O40-LDHs, with absorption peak at 1031, 910, 824 and 600 cm\(^{-1}\) which indicating the existence W–O and W–O–W, further confirming intercalation of the PW12O40 anion.

The chemical composition of LDHs was shown in table 3. The formula of ZnAl-NO3-LDHs was Zn\(_{0.76}\)Al\(_{0.24}\)(OH)\(_2\)(NO\(_3\))\(_{0.24}\)·0.59H\(_2\)O. After intercalation of the PW12O40 anion, the chemical composition becomes Zn\(_{0.73}\)Al\(_{0.27}\)(OH)\(_2\)(PW\(_{12}\)O\(_{40}\))\(_{0.037}\)(NO\(_3\))\(_{0.16}\)·0.58H\(_2\)O. The new chemical elements indicates that PW12O40 has partly replace NO3 interlayers.

The morphologies of ZnAl-NO3-LDHs and ZnAl-PW12O40-LDHs were characterized by SEM (figure 3). The morphology of ZnAl-NO3-LDHs shows an obvious single-layer lamellar structure, which is successively stacked layer by layer to form a large aggregate, with thickness of the single sheet about 100 nm. The morphology of ZnAl-NO3-LDHs in each layer is uniform and arranged in close order, which indicates that the prepared samples have ideal uniformity and regularity. After intercalation modification, ZnAl-PW12O40-LDHs showed granular form, with average diameter of 100 ~ 200 nm, the dispersion of the whole sample was improved, but there were still large aggregates existed, which was consistent with the XRD analysis results.

### 3.2. Characterization of ZnAl-PW12O40-LDHs/Nanocellulose based foam materials

The morphology of the CNF/50%ZnAl-PW\(_{12}\)O\(_{40}\)-LDHs/2%H\(_3\)BO\(_3\) was characterized by scanning electron microscopy (SEM), as shown in figure 4, which shows a unique 3D porous structure with irregular circular cell of 200–300 \( \mu \)m in diameter. The existing porous structure making it good performance of thermal Insulation.

ZnAl-PW\(_{12}\)O\(_{40}\)-LDHs were uniformly dispersed in the pore wall of CNF matrix without no agglomeration, indicating that ZnAl-PW\(_{12}\)O\(_{40}\)-LDH could be well loaded in CNF with well compatibility.

The thermal stability of CNF/ZnAl-PW\(_{12}\)O\(_{40}\)-LDHs/H\(_3\)BO\(_3\) lightweight thermal-insulated foams was investigated by TG as shown in figure 5. The corresponding detailed data are also summarized in table 4. All the samples displays a three-step thermogravimetric profile, firstly, a loss of mass between 20 ~ 160 °C in the sample was observed, associated with physisorbed water and decomposition of a small part of \( \left[ \text{PW}_{12}\text{O}_{40} \right]^{3-} \). Subsequently, a greater loss ranging between 160 ~ 400 °C was observed, which associated with the de-hydroxyl of CNF and a part of ZnAl-PW\(_{12}\)O\(_{40}\)-LDHs dehydrolyzed to form metal oxides, accompanied by decomposition. 

![Figure 2. FT-IR spectra of H\(_3\)PW\(_{12}\)O\(_{40}\)·xH\(_2\)O ZnAl-NO3-LDHs and ZnAl-PW\(_{12}\)O\(_{40}\)-LDHs.](image)

### Table 3. Elemental analysis of ZnAl-NO3-LDHs and ZnAl-PW12O40-LDHs.

| Samples          | Zn/%  | Al/%  | W/%  | Chemical formula                      |
|------------------|-------|-------|------|---------------------------------------|
| ZnAl-NO3-LDHs    | 5.57  | 42.80 | —    | Zn\(_{0.76}\)Al\(_{0.24}\)(OH)\(_2\)(NO\(_3\))\(_{0.24}\)·0.59H\(_2\)O |
| ZnAl-PW12O40-LDHs| 3.47  | 22.50 | 37.13| Zn\(_{0.73}\)Al\(_{0.27}\)(OH)\(_2\)(PW\(_{12}\)O\(_{40}\))\(_{0.037}\)(NO\(_3\))\(_{0.16}\)·0.58H\(_2\)O |
of $[\text{PW}_{12}\text{O}_{40}]^{3-}$. After 400 °C, metal oxides such as ZnO, MgO and WO$_3$ were sintered by dehydroxylation of ZnAl-PW$_{12}$O$_{40}$-LDHs. Besides H$_3$BO$_3$ in the research was added as adhesion agent between ZnAl-PW$_{12}$O$_{40}$-LDHs and CNF as it could effectively cross-linked the hydroxyl group between them.

There is basically no significant difference in the first thermal decomposition stage between all the six thermal insulation materials, however great difference occurred in the second thermal decomposition stage. Compared with pure CNF foam materials, the composite of ZnAl-PW$_{12}$O$_{40}$-LDHs significantly reduced the maximum decomposition rate of the second stage and increased the residual mass at 800 °C. This can be explained as follows: $[\text{PW}_{12}\text{O}_{40}]^{3-}$ under high temperature could decompose H$_3$PO$_3$ or HPO$_3$$_2$ covered on the surface of the material, which inhibited the dehydroxylation reaction of CNF and ZnAl-PW$_{12}$O$_{40}$-LDHs, displaying the condensed phase flame retardation. Moreover, $[\text{PW}_{12}\text{O}_{40}]^{3-}$ could decompose W(PO$_4$)$_2$ and WO$_3$, further improved the thermal stability of materials. When adding 50% ZnAl-PW$_{12}$O$_{40}$-LDHs, $CR_{800}$ °C reached 39.17% compared to only 20.82% of pure CNF, which shows the best thermal stability. These results obviously suggest that the ZnAl-PW$_{12}$O$_{40}$-LDHs nanofillers can significantly increase the thermal stability of CNF foam materials.

The fire resistance was tested under 35 kW m$^{-2}$ thermal radiation, back temperature curves was shown in figure 6. All the materials showed the similar tendency, the back temperature rise rapidly with the extension of irradiation time until the temperature reached 250 °C, after that, the heating rate slowed down. As can be seen from the temperature details ranged 200 °C–250 °C, temperature rate basically slowed down with increasing the
content of ZnAl-PW12O40-LDHs, that is, it takes longer time to reach the same temperature, as the back temperature results shown in Table 5. Take reaching 250 °C as an example, the pure CNF takes 1155 s, but 50% ZnAl-PW12O40-LDHs / 2% H3BO3 needs 2602 s, which shows excellent thermal insulation performance. However, overadding will cause serious agglomeration, which showed negative effects. We also noted that CNF / 37.5% PW-LDHs showed better thermal insulation performance than CNF / 37.5% PW-LDHs, indicating H3BO3 can not only act as adhesion agent but also enhance the fire resistance of the material.

The fire resistance test result is consistent with the thermogravimetric analysis. We qualitatively evaluated the combustion behavior of the pure CNF foams and CNF foams compound with ZnAl-PW12O40-LDHs after being exposed directly to an open alcohol lamp flame. As shown in Figure 7(a), the pure CNF foams ignited just 1 s, resulting in a significant flame spread and then extinguished in 5 s, only a little charcoal remains after 18 s burning. CNF foams burn very rapidly and shrinkage visibly during the whole combustion process. By contrast, CNF foams compound with ZnAl-PW12O40-LDHs can withstand continuous exposure to the alcohol lamp flame without ignition, leaving integrated carbon layer, clearly demonstrating the [PW12O40]−3 intercalation modification LDHs induced great improvement to the fire resistance. The decomposition product of ZnAl-PW12O40-LDHs, such as ZnO and MgO, promote the instant dehydration, esterification and solidification of CNF, and then forming a integrated carbon layer protecting the inner internal material.

4. Conclusion

In conclusion, [PW12O40]−3 anions have been intercalated into ZnAl-NO3-LDHs to synthesize ZnAl-PW12O40-LDHs successfully by ion-exchange reaction. Then CNF composite with different loadings of ZnAl-PW12O40-LDHs and 2% H3BO3 were prepared to form a unique 3D lightweight foam thermal insulation materials. The TG, CONE, back temperature test and alcohol lamp flame test results showed that the thermal stability and flame-retardant properties of composites can be improved when adding ZnAl-PW12O40-LDHs. This can be explained as follows, firstly, the gas such as NO2 and H2O produced by ZnAl-PW12O40-LDH can dilute oxygen and reduce the concentration of combustible gas, acting as gas phase flame retardant. Secondly, H3PO3 or
HPO₃ produced by $[\text{PW}_{12}\text{O}_{40}]^{3−}$ covered on the surface of the material, promote the instant dehydration, esterification and solidification of CNF, and then forming the integrated carbon layer, which acts as both a gas barrier and thermal shield, causing the delayed thermal degradation of the internal base material and emission of volatile combustible gases, displaying the condensed phase flame retardation. Thirdly, decomposition product under high temperature, such as ZnO, MgO, WO₃ and $\text{W(PO₄)}_2$, catalyzed the formation of more stable and graphitized carbon layer, which further improved the thermal and flame retardant properties.

Table 5. Back temperature test results of CNF/ZnAl-PW₁₂O₄₀-LDHs/H₃BO₃ lightweight thermal-insulated foams.

| Samples                                  | $t_{200} \, ^\circ\text{C}$ | $t_{250} \, ^\circ\text{C}$ | $v_{200} \, ^\circ\text{C}/(\text{s})$ | $v_{250} \, ^\circ\text{C}/(\text{s})$ |
|------------------------------------------|-------------------------------|-------------------------------|--------------------------------------|--------------------------------------|
| CNF                                      | 685.36                        | 1155.04                       | 0.2918                               | 0.2165                               |
| CNF/37.5%ZnAl-PW₁₂O₄₀-LDHs               | 791.96                        | 1787.96                       | 0.2525                               | 0.1399                               |
| CNF/25%ZnAl-PW₁₂O₄₀-LDHs/2%H₃BO₃         | 812.36                        | 1535.04                       | 0.2462                               | 0.1629                               |
| CNF/37.5%ZnAl-PW₁₂O₄₀-LDHs/2%H₃BO₃       | 891.24                        | 1890.00                       | 0.2244                               | 0.1323                               |
| CNF/50%ZnAl-PW₁₂O₄₀-LDHs/2%H₃BO₃         | 960.12                        | 2602.72                       | 0.2083                               | 0.0961                               |
| CNF/62.5%ZnAl-PW₁₂O₄₀-LDHs/2%H₃BO₃       | 855.04                        | 1807.16                       | 0.2340                               | 0.1384                               |

Notes: $V_{200} \, ^\circ\text{C}$—Back temperature rising rate at 200 °C; $V_{300} \, ^\circ\text{C}$—Back temperature rising rate at 300 °C.

Figure 7. Combustion photos of lightweight thermal-insulated foams (a) CNF; (b) CNF/50%ZnAl-PW₁₂O₄₀-LDHs/2%H₃BO₃.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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