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Aluminum–organophosphorus hybrid nanorods for simultaneously enhancing the flame retardancy and mechanical properties of epoxy resin[†]

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New aluminum-organophosphorus hybrid nanorods (AOPH-NR) have been prepared by reacting aluminum hydroxide (ATH) with dibenzylphosphinic acid (DBPA) with aluminum hydroxide (ATH) and used to prepare nanocomposites with epoxy resin. In order to determine the structure-property relationship of these composites, several other phosphinic acids of the general formula (R $(CH_2)_n)_2$ POOH (R = ester, allyl, nitrile, n = 1 or 2), and corresponding AOPHs were synthesized. FTIR, Raman, TGA, and XRD examinations showed that only AOPH-NR possesses a highly hybrid structure and high thermostability. SEM and TEM confirmed the nanorod morphology of AOPH-NR. The formation mechanism can be described as a decomposing-reforming process. This characteristic causes AOPH-NR to exhibit superior properties. Limiting oxygen index (LOI) determination and cone calorimeter analysis showed that the incorporation of only 4.25 wt% AOPH-NR remarkably improved the LOI value to as much as 28.0 and led to a 23% reduction in peak heat release rate (PHRR). Dynamic mechanical analysis (DMA) indicated that the mechanical properties of epoxy resin were also improved by incorporating AOPH-NR. In this way, the aluminum-organophosphorus hybridization via reacting ATH with specific organophosphinic acids shows promise as a means of improving flame retardancy and mechanical properties simultaneously. The thermal and anti-flaming properties of composites, combined with the properties of AOPHs, allowed us to discover the important role that the release and migration of phosphorus species plays in fire-retarding materials. This provides a new insight into the design of high-performance flame retardants.

Introduction

Natural and synthetic resins are rapidly taking the place of traditional metallic and inorganic materials in various fields. This is because of their excellent properties such as low density, biocompatibility, biodegradability, clarity, and good weathering behavior. However, during use, a large number of fires are inevitable. This is because these resins are inherently flammable. Enhancing the flame retardancy of these is becoming more and more imperative, especially when they are used in fields within the electronic industry and in building materials.

To date, a large number of flame retardants, including minerals,¹⁻⁵ phosphoric compounds,⁶⁻⁹ carbon materials,¹⁰⁻¹³ and siliceous compounds,¹⁴⁻¹⁷ have been used. Of these, aluminum hydroxide (ATH) has received much attention because of its environmental friendliness, low cost, low toxicity, low smoke, and lack of corrosive gas;^{18,19} however, it has two limitations. First, more than 50 wt% of ATH is generally required for

compliance with various flame retardancy standards for polymers.^{20,21} The addition of fillers in such high amounts often leads to a processing problem and marked deterioration in mechanical properties of the composites. Second, the interfacial interaction between hydroxides and organic polymers is poor. Even though low filling levels can be achieved, the enhancement of flame retardancy is still at the loss of mechanical strength.^{22–24}

Nano-ATH and cooperative use of ATH and other flame retardants have been developed to solve these problems. Cooperative use of ATH and phosphorus-containing compounds, such as triphenyl phosphate (TPP), can reduce the deleterious effect that flame-retardant additives have on mechanical properties.²² However, this technique can cause the bleeding-out of phosphoric compounds on the surfaces of molded products.²⁵ On the other hand, nano-ATH is difficult to disperse through the polymer matrix due to its marked hydrophilicity and incompatibility between the surface characteristics of the substances. This limits the enhancement in flame retardancy.²⁶ There is still a long way to go before the expected levels of performance are reached.

Hybridization techniques, particularly inorganic-organic hybridization, have brought a new perspective to the development of high-performance flame retardants. Recent work has focused on two layered clays, montmorillonite (MMT) and

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layered double hydroxide (LDH).²⁷⁻³¹ Because of the relatively small sizes of the layered clay particles, which are obtained by intercalation, polymer-layered clay composites can markedly improve the mechanical, thermal, and physical–chemical properties of pure polymers. However, several studies on phosphorus-layered silicate systems have concluded that introducing phosphorus species is not an efficient means of enhancing the fire performance of epoxy-layered silicate nanocomposites.^{32–39} As a consequence, such hybrid systems have not been paid much attention. The main reasons for the middling performance of the phosphorus-layered silicates, in our opinion, are that general hybridization leads to fair thermostability of phosphorus species and that the layered structure may hamper the release and migration of phosphorus species to the surface, decreasing the efficiency of char formation.

The pioneering work on MMT and LDH motivated us to develop new aluminum-organophosphorous hybrid materials (AOPHs) with marked thermostability and unique one-dimensional morphology. To the best of our knowledge, these types of flame retardants have not yet been reported. AOPHs are superior to other phosphorus-layered silicate systems in several ways. First, the highly hybrid structure of AOPHs can be formed by covalent bonding from nonhydrolytic and hydrolysis condensation reactions rather than ion-exchange,40,41 This indicates greater thermostability than the phosphorus-layered silicate system. As a consequence, AOPHs release phosphorus compounds at relatively high temperatures. Second, the hybridization of phosphorus species and ATH allows for the formation of one-dimensional materials.40 Such one-dimensional structures would show different flame-retarding behavior to layered silicates. In addition, like modified layered silicates, this type of Al/P hybridization is able to inhibit the bleeding out of phosphorus during processing. In this way, it is superior to most combinations of ATH and TPP. Third, the presence of organic moieties in the hybrid plays an important role in the crystalline structure, morphology, dispersibility, and thermal properties of AOPHs. AOPHs can be made to have a large variety of compositions and a tunable number of hydroxyl groups, as determined by changes in stoichiometry. This may be of importance for tailoring the properties of AOPHs.

In this work, we prepared a new aluminum–organophosphorus hybrid nanorod (AOPH-NR) by reacting aluminum hydroxide with dibenzylphosphinic acid (DBPA). In addition, a series of other phosphinic acids were produced with the same structural formula, of R_2 POOH with DBPA and various functional groups, such as ester, allyl, and nitrile groups. Corresponding AOPHs were also prepared by reacting ATH with these phosphinic acids. The chemical and layered structures and thermal properties of the various flame retardants were investigated. The flame retardants were blended with epoxy resin to produce several composites. The morphology, thermal and mechanical properties, flame retardancy, and structure–property relationships of these composites were studied in detail.

Experimental

Materials

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cyanide, benzyl bromide, aluminum hydroxide, triethylamine, and other general solvents were purchased from Chengdu Kelong Reagent Co. Ammonium hypophosphite was purchased from Hubei Hongjing Chemical Co., hexamethyldisilazane (HMDS) from Hangzhou Guibao Chemical Co., allyl bromide from Shandong Zouping Mingxing Chemical Co., methyl hexahydrophthalic anhydride (MHHPA) from Puyang Huicheng Chemical Co., and epoxy resin (diglycidyl ether of biphenol A, DEGBA), with an epoxy value of 0.4083 mol/100 g were purchased from Lanzhou Bluestar Resin Co.

Synthesis of dibenzylphosphinic acid (DBPA)

A mixture of 9.96 g (0.12 mol) $H_2PO_2^{-}NH_4^+$ and 34.2 g (0.21 mol) HMDS was heated at 100-110 °C in N2 until the white ammonium salt disappeared. Then 120 mL CH₂Cl₂ and 14.4 mL (0.12 mol) benzyl bromide were added sequentially at 0 °C, and the mixture was stirred at room temperature for 12 h. Then, the reaction was cooled to 0 °C, and another 34.2 g (0.21 mol) HMDS was injected immediately. Stirring was continued at 0 °C for 2-3 h. Another 14.4 mL (0.12 mol) benzyl bromide was introduced and the reaction was kept at room temperature for 12 h. Then the solution was centrifuged and concentrated under reduced pressure. The residue was dissolved in MeOH/CH2Cl2 (1:1 v/v) for 30 min and the precipitated solid particles were filtered. The solution was concentrated under reduced pressure. The residue was redissolved in CH₂Cl₂ and washed three times with 4 mol L⁻¹ hydrochloric acid. The organic layer was dried over anhydrous MgSO₄. After the removal of solvent under reduced pressure, the resultant solid powder was purified by recrystallization from acetic acid and dried in a vacuum at 50 °C, giving 24.3 g (82.5%) DBPA as a white crystal; m.p.: 192 °C (reported: 190 °C⁴²). ¹H NMR (400 MHz, DMSO-d₆, ppm) δ: 7.19 (dd, J = 17.4, 10.0 Hz, 6H), 7.12 (d, J = 12.5 Hz, 4H), 3.38 (d, 12H), 2.94 (s, 2H), 2.92 (d, 4H), 2.65-2.20 (m, 3H). FTIR (neat, cm⁻¹): 2629, 2271, 1632, 1494, 1258, 1172, 954, 876, 786, 710. LC-MS (M-H⁺) m/z: 245.

Synthesis of bis(3-methoxy-3-oxopropyl)phosphinic acid (BMOPA)

The synthesis of BMOPA was almost the same as that of DBPA except that the 14.4 mL benzyl bromide was replaced by 10.32 g (0.12 mol) methyl acrylate. After the reaction, the solution was centrifuged and concentrated under reduced pressure. The residue was dissolved in MeOH/CH₂Cl₂ (1 : 1 v/v) for 30 min and the precipitated solid particles were filtered. The solution was concentrated under reduced pressure. The residue was redissolved in CH₂Cl₂ and washed three times with 4 mol L⁻¹ hydrochloric acid. The organic layer was dried over anhydrous MgSO₄. After the removal of solvent under reduced pressure, the mixture was washed with hexane and dried in vacuum at 40 °C. BMOPA was produced as a white solid powder (17.99 g, 63.0% yield); m.p.: 103 °C. ¹H NMR (400 MHz, DMSO-d₆, ppm) δ : 3.66 (m, 2H), 2.87–2.18 (m, 2H). FTIR (neat, cm⁻¹): 2623, 2091, 1743, 1440, 1252, 1180, 1046, 997, 900. LC-MS (M-H⁺) m/z: 237.

Synthesis of diallylphosphinic acid (DAPA)⁴³

Unless otherwise noted, all reagents were purified using the standard method before use. Methyl acrylate (MA), allyl

A solution of $H_2PO_2^-NH_4^+$ (4.98 g, 0.06 mol), ally bromide (29.04 g, 0.24 mol), and HMDS (19.32 g, 0.12 mol) in 120 mL

toluene was refluxed at 110 °C under a flow of nitrogen for 12 h. The solution was cooled to room temperature. After the removal of the ammonium salts by centrifugation and concentration under reduced pressure, the residue was redissolved in MeOH/ CH₂Cl₂ (1 : 1 v/v) and the precipitated solid was filtered. After concentration under reduced pressure, the resulting oil was dissolved in CH₂Cl₂ and washed three times with 4 mol L⁻¹ hydrochloric acid. The organic layer was dried over anhydrous MgSO₄. After the removal of solvent under reduced pressure, the DAPA was obtained as a pale yellow oil (7.50 g, 85.6% yield). ¹H NMR (400 MHz, DMSO-d₆, ppm) δ : 5.82–5.53 (m, 1H), 5.27–4.86 (m, 2H), 2.81–1.89 (m, 2H). FTIR (neat, cm⁻¹): 2622, 2276, 1638, 1230, 1160, 1061, 971, 918. LC-MS (M-H⁺) m/z: 145.

Synthesis of bis(2-cyanoethyl)phosphinic acid (BCEPA)

The synthesis of BCEPA was also the same as that of DBPA except that 8 mL (0.11 mol) allyl cyanide was used instead of 14.4 mL benzyl bromide. The solution was centrifuged and concentrated under reduced pressure. The residue was dissolved in MeOH/CH₂Cl₂ (1 : 1 v/v) for 30 min and the precipitated solid particles were filtered. After concentration under reduced pressure, the residue was redissolved in CH₂Cl₂ and washed three times with 4 mol L⁻¹ hydrochloric acid. The organic layer was dried over anhydrous MgSO₄. After the removal of solvent under reduced pressure, washing with hexane and drying in vacuum at 40 °C, BCEPA was produced as a white solid powder (17.6 g, 85.1% yield); m.p.: 100 °C. ¹H NMR (400 MHz, DMSO-d₆, ppm) δ 2.69–2.54 (m, 1H), 2.47 (d, *J* = 15.6 Hz, 1H), 2.06–1.76 (m, 1H). FTIR (neat, cm⁻¹): 2648, 2248, 1260, 1177, 1093, 1017, 982, 897. LC-MS (M-H⁺) *m*/*z*: 171.

Preparation of AOPHs

To prepare DBPA modified ATH, 2.8 g (19.2 mmol) DBPA was added to a suspension of 1.0 g Al(OH)₃ (a commercial product with a size of about 10 μ m, dried at 120 °C for 12 h prior to use) in 30 mL of acetic acid. The resultant suspension was stirred at 80 °C in N₂ for more than 24 h until the appearance of white floating solids. After the reaction, the white powder was collected by filtration, washed with water, ethanol, and alcohol, in that order, and then dried at 50 °C for 12 h in vacuum.

DAPA, BMOPA, and BCEPA modified ATH were prepared in the same way. One gram of ATH was reacted with a solution of phosphinic acid (19.2 mmol phosphinic acid was dissolved in 30 mL of acetic acid) at room temperature in N₂ for 36 h. After the reaction, the white powder was collected by filtration, washed with deionized water, washed sequentially with ethanol and acetone, and then dried at 50 °C for 12 h in vacuum.

Preparation of epoxy resin/AOPHs composites

To prepare epoxy resin/AOPHs composites, AOPHs were dispersed in toluene by sonication. Epoxy resin in 50 mL of toluene was mixed with the APOHs solution, followed by stirring under vacuum at room temperature for 30 min. After concentration by rotary evaporation, the curing agent methyl hexahydrophthalic anhydride (MHHPA) and the catalyst triethylamine (TEA) were added to epoxy resin/AOPHs system sequentially. The reaction mixtures were pre-cured in a mould at 110 °C for 1

h, followed by a final curing at 140 $^{\circ}\mathrm{C}$ for 16 h, giving rise to solid resins.

Instrumentation

Fourier transform infrared (FTIR) spectra were obtained on a Perkin Elmer Spectrum One spectrophotometer with a resolution of 4 cm⁻¹. Raman spectroscopic experiments were performed on a inVia-Reflex confocal laser Raman spectrometer (Renishaw Ltd) with a resolution of 2 cm⁻¹. ¹H NMR spectra were collected on a Bruker Acance spectrometer (400 MHz) using tetramethylsilane (TMS) as an internal reference and deuterated dimethyl sulfoxide (DMSO-d₆) as a solvent. Mass spectra (m/z) were recorded on a Varian 1200LC/MS. Powder X-ray diffractometer (XRD) patterns were recorded on a Panalvtical X'Pert Pro diffractometer with Cu-Ka radiation. Dynamical mechanical analysis (DMA) measurements were performed on a TA Q800 dynamical mechanical analyzer in three-point bending mode at a frequency of 1 Hz. Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 simultaneous DTA-TGA at a heating rate of 10 °C min⁻¹ for AOPHs and 20 $^{\circ}C$ min⁻¹ for composites in an N₂ and air atmosphere. Limiting oxygen index (LOI) were measured on a LFY-606 oxygen index instrument (Qingdao, China) with a test specimen bar of $120 \times 6 \times 3$ mm according to ASTM D-2863. Scanning electron microscopy of AOPHs was recorded on an S-4800 (Hitachi Ltd) field emission scanning electron microscope. Scanning electron microscopy of cross sections of composites were recorded on a TM-1000 (Hitachi Ltd) scanning electron microscope at an accelerating voltage of 10 kV. Morphological observation for AOPHs and their dispersion in the epoxy resin was performed with Tecnai G2 F20 S-TWIN (FEI Company) transmission electron microscopy. The epoxy composite samples were microtomed with a diamond knife at room temperature into sections with a nominal thickness of 100 nm. The flammability of the epoxy resins and their composites were characterized using a cone calorimeter performed in Stanton Redcroft, UK device according to ISO 5660 with an incident flux of 35 kW m⁻² using a cone-shaped heater. Results were found to be reproducible to within $\pm 10\%$.

Results and discussion

Synthesis of phosphinic acids

The use of phosphoric acids to prepare organically modified aluminum phosphates or organophosphorus modified aluminas has been the subject of intense research. Florjanczyk *et al.* have prepared aluminum phosphates from the reaction of diphenyl-phosphoric acid (DPPA) with AlMe₃, AlEt₃, Al(tBu)₃ and boehmite.⁴⁰ Vioux *et al.* have reported the preparation of organically modified alumina by grafting with phenylphosphonic acid and its organic-soluble ester derivatives.⁴⁴ Hix *et al.* have studied the hydrothermal reaction of ATH with mixtures of phosphorous and methylphosphonic acids, giving microporous aluminum methylphosphonic acids, in terms of the relatively high thermal stability of the P–C bond relative to that of the P–O–C bond. To the best of our knowledge, no such structure

has been reported previously in aluminum-organophosphorus hybrids.

In the present work, DBPA was synthesized by a one-pot intermolecular Arbusov-type reaction, as reported by Bujard and Boyd,^{43,45} between bis(trimethylsilyloxy) phosphine (BTSP) and benzyl bromide (Scheme 1). The intermediate, BTSP, was produced in situ from the reaction of ammonium phosphinate and HMDS. This method had the advantage of synthesizing a variety of compounds containing phosphorus-carbon bonds, involving symmetrical and asymmetrical phosphonic and phosphinic acids. Other phosphinic acids were prepared using a similar method. BTSP was reacted with alkyl or allyl halides, α , β-unsaturated ketones, and other unsaturated compounds (Scheme 1). The structures of all the phosphinic acids were confirmed by FTIR, ¹H NMR, and LC-MS (Fig. S1-S3, ESI⁺). The characteristic absorption bands of C=C, C=O, benzene rings, and $C \equiv N$ were observed in FTIR spectra of the four phosphinic acids. Signals indicating the hydrogens on -CH₂- and -CH₂CH₂- were found in the ¹H NMR spectra of all phosphinic acids, strongly suggesting the generation of P-C bonds. In addition, the molecular weights found in MS were identical to the calculated molecular weights.

The reaction of aluminum hydroxide (ATH) with DBPA produced AOPH-NR. AOPHs prepared from other phosphinic acids were designated as AOPH-C1, AOPH-C2, and AOPH-C3 as shown in Scheme 1. As expected, AOPH-NR possessed a unique structure and properties, which allowed us to undertake a careful investigation of the structure–property relationship, detailed in the following sections.

Characterization of AOPH-NR

Typical ATH crystalline is composed of aluminum octahedral layers with hydroxyl groups on either side.^{32,46,47} The lack of exchangeable cations such as Na⁺ makes it difficult to perform an ion exchange process using cetrimonium bromide (CTAB) or any other cation modifier like MMT and LDH. The use of aqueous solutions of phosphonic acid, nevertheless, may result in the reaction of organophosphorus compounds with aluminum

corresponding AOPHs.

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appropriate organic mediums (acetic acid or other organic acids). The chemical structure of AOPH-NR was characterized by FTIR (Fig. 1). The appearance of a characteristic absorption band corresponding to phenyl groups was observed in Fig. 1a. preliminarily supporting the reaction of ATH with DBPA. By carefully comparing the FTIR spectra of ATH, DBPA, and AOPH-NR in the range of 950-1200 cm⁻¹ (Fig. 1b), it can be seen that the absorption bands of P=O stretching at nearly 1200 cm⁻¹, P-OH stretching at 950-1000 cm⁻¹, and Al-OH stretching at 1061 cm⁻¹ greatly decreased or nearly disappeared. These results suggest the formation of P-O-Al bonds via a condensation reaction between ATH and phosphinic acids. The formation of P-O bonds is further supported by the presence of their characteristic absorption bands in the range of 1000-1100 cm⁻¹.44,50,51</sup> A great decrease in the band generated by P=O stretching and the disappearance of the band generated by Al-O stretching was observed for AOPH-NR, suggesting the existence of a large number of bidentate PO₂ or chelating monodentate structures.^{40,52} Similar results were also found in the spectra of other AOPHs (Fig. 1c-e). Nevertheless, a relatively small decrease in P=O was observed for other AOPHs, which is indicative mainly of the pendant monodentate structure. Further indications of hybrid structure were provided by Raman spectroscopy (Fig. 2). The characteristic bands of organic groups for AOPH-NR were observed. Several new bands in the range of 1000–1400 cm⁻¹, which were not present in the ATH spectrum, were seen. These bands probably correspond to the vibrations of the PO₂ unit. In addition, the near-disappearance of the vibrational modes of the P=O bond at 1280-1295 cm⁻¹ and the appearance of asymmetric and symmetric P-O vibration bands of O–P–O at 819 $\rm cm^{-1}$ and 763 $\rm cm^{-1}$ were observed. $^{\rm 53,54}$ In particular, intense P-O bands were observed at 1000-1400 cm⁻¹, possibly from the formation of Al-O-P-O-Al.55 In agreement with the analysis of FTIR, the above results are indicative of a mainly bidentate PO₂ or chelating monodentate structure for AOPH-NR. For other AOPHs, the weak P-O bands and remaining P=O bands indicate a pendant monodentate structure.

The thermal properties of ATH and AOPHs was evaluated by thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) under a nitrogen atmosphere (Fig. 3 and S4, ESI[†]). The decomposition of ATH was a single-step reaction. This can be attributed to the loss of external surface water, gallery water, and the partial dehydration reaction of ATH. In contrast, AOPH-NR decomposition required two steps. The second decomposition step mainly involved the degradation and volatilization of organophosphorus molecules, as evidenced by the complete decomposition of DBPA, shown in its TGA (Fig. S5, ESI[†]). AOPH-NR decomposed, releasing its organophosphorus species, at a higher temperature than DBPA. Other AOPHs also showed higher temperature of releasing their organophosphorus species relative to the corresponding phosphinic acids. These indicate that hybridization effectively improved the thermal stability and releasing temperature of the organophosphorus species. The decomposition temperature and





Fig. 1 Chemical structure as determined by FTIR: (a) FTIR spectra of ATH, AOPH-NR, and other AOPHs throughout the whole range. (b–e) Detailed analysis of AOPH-NR, other AOPHs, phosphinic acids, and ATH within the range of $950-1200 \text{ cm}^{-1}$. (f) Schematic illustration of the possible bonding configurations of the P–O–Al bond.



Fig. 2 Raman spectra of ATH, AOPH-NR, and other AOPHs.



Fig. 3 TGA curves of ATH, AOPH-NR, and other AOPHs in nitrogen.

residual weight of AOPH-**NR** showed a certain degree of decrease relative to ATH. This was because of the incorporation of organic moieties. Unlike other AOPHs, AOPH-**NR** showed little weight loss during the first decomposition step, indicating that the greatest number of hydroxyl groups had been consumed. As noted in FTIR, this implies a bidentate PO₂ and chelating monodentate structure. In addition, AOPH-**NR** showed a higher T_d in the second decomposition than other AOPHs. This result is associated with the higher T_d of DBPA. This can also be ascribed to the presence of a large number of chelating mondentates and

bridging bidentates in AOPH-NR, which have relatively good thermal stability relative to mondentate bridging structures.

ATH crystals have three main polymorphs, gibbsite, bayerite, and nordstrandate.⁵⁶ Because of the strong hydrogen bonds between hydroxide layers, these layers are bonded tightly together with a very narrow basal spacing of 0.485 nm. The change in crystal structure, a consequence of the chemical incorporation of phosphinic acids into ATH, was examined by powder X-ray diffraction (XRD). Fig. 4 shows the XRD patterns of ATH, AOPH-NR and other AOPHs. The near-disappearance of the XRD pattern of ATH in the AOPH-NR images indicates a significant change in crystal structure. One possible explanation is that the high degree of hybridization taking place in AOPH-NR, as shown in FTIR and Raman, has destroyed the inherent crystal structure of ATH. Other AOPHs have the same peaks as ATH at $2\theta = 18.3^{\circ}$ and 20.6° , suggesting that they share the inherent crystal lattice structure of ATH (Fig. S6, ESI[†]). This strongly indicates the organophosphorus modified aluminum structure of other AOPHs. Another notable observation made of other AOPHs is that new peaks appeared at angles below 10°. Calculations made using the Bragg equation, $d = n\lambda/(2\mathrm{Sin}\theta)$, indicates that they had wider basal spacing. This indicates an intercalated structure.³² This conclusion was further supported by TEM imaging, which showed the tactoids of a few platelets, characteristic of intercalated structures (Fig. S7, ESI[†]).



Fig. 4 XRD patterns of ATH, AOPH-NR, and other AOPHs.

The destruction of the ATH layered crystalline structure in AOPH-NR means that the intercalated structure hardly forms. Unlike other AOPHs, a strong reflection at $2\theta = 6.27^{\circ}$ ($\alpha = 14.8$ Å) appears in the XRD pattern of AOPH-NR, implying a kind of layered or fibrous morphology. In agreement with this idea, SEM and TEM images (Fig. 5) clearly show the AOPH-NR to have a nanorod morphology, with a rod diameter of <100 nm. Such a regular nanorod morphology has not been observed in previous works related to the organophosphorus-modified aluminum. In addition, this kind of morphology was not observed for ATH or for other AOPHs. These exist as solid agglomerates of relatively large size (Fig. S6 and S7, ESI[†]). The preliminary explanation for the formation of nanorods is that the destruction of the ATH crystal structure gives rise to polymeric chains with Al-O-P bridging structures, which form a close-packed columnar structure. According to this mechanism, octahedrally coordinated Al atoms bridged by three dibenzylphosphate (DBP) ligands could be formed.⁴⁰ Absorption bands corresponding to such ligands were actually observed in FTIR. The parameter α (1.480 nm) for AOPH-NR is in agreement with the diameter of the polymeric chains with Al(DBP)₃ repeating units.⁴⁰ This provides further evidence for the proposed structure. In addition, two weak reflections at $2\theta = 22.0-25.0^{\circ}$ with a *d*-spacing distance of 0.389 nm and 0.371 nm were observed (Fig. 4), which implies the presence of $\pi - \pi$ stacking interactions.⁵⁷⁻⁶⁰ When the role of $\pi - \pi$ stacking interactions in directing supramolecular architectures is taken into account, it can be supposed that the assembly of polymeric chains could be driven by π - π stacking interactions.^{61–63} Nevertheless, the exact formation mechanism of such a rod-like morphology still requires further study, in which our group is currently engaged. In conclusion, all of the above findings involving FTIR, Raman, TGA, XRD, SEM, and TEM, have allowed us to describe the structure of AOPH and the method by which that structure forms (Fig. 6).

Morphology of EP/AOPH nanorod nanocomposite

Scanning electron micrography (SEM) and transmission electron microscopy (TEM) were used to determine the microscopic morphologies of neat EP and EP/AOPHs composites. As shown in Fig. 7b–c, both SEM and TEM images of the EP/AOPH-NR composite show a good dispersion of AOPH-NR in the epoxy resin, indicating the formation of a nanocomposite. Other



Fig. 6 Structure and mechanism of formation of AOPH-NR and other AOPHs.

EP/AOPHs are only microcomposites; large particles and even agglomerates were observed in the SEM and TEM images (Fig. S8–S9, ESI†). In addition, the neat epoxy resin and EP/ATH composite displays a relatively smooth fracture surface, although some plastic-deformed veins corresponding to the shrinkage deformation of the film did appear (Fig. S8, ESI†). With the addition of AOPH-NR, irregular plastics deformation morphology, void growth, debonding of the particles from the matrix, and highly rough fracture surfaces with a platelet-like morphology were observed. These phenomena strongly suggest that the toughening mechanism was dominant in the polymer-particle composites.⁶⁴ They are also indicative of improved mechanical properties. In comparison, most of the other EP/AOPH composites showed smooth fracture surfaces, indicating limited improvement in mechanical properties.

Curing behavior

The curing behavior of the EP composites is examined by DSC (Fig. S10, ESI[†]). Large amounts of heat were released from the ring-opening reaction, more by EP/AOPH-NR than by other EP/AOPHs. This indicates a high degree of curing. In comparison, the small amount of heat released by other EP/AOPH composites is indicative of a relatively low degree of curing. In addition, the difference between the heat releasing temperature of the EP/AOPH-C2 composite and that of the EP/AOPH-C1 and EP/AOPH-C3 composites was observed. This can be



Fig. 5 Microscopic morphology of AOPH-NR: (a) SEM image and (b) TEM image.



Fig. 7 SEM images of cross section of (a) neat EP and (b) EP-4.25 wt% AOPH-NR composite. (c) TEM image of EP-4.25 wt% AOPH-NR composite.

ascribed to the reaction between allyl groups and epoxy resin. The C=C bonds in AOPH-C2 could polymerize by themselves and, at the same time, interfere with the crosslinking of epoxy by reacting with the epoxy groups. The improved dispersion of AOPH-C2 in the epoxy resin could also be a result of this reaction.⁶⁵

Dynamic mechanical analysis, DMA

Dynamic mechanical analysis (DMA) is an effective tool for the characterization of the interfaces of filled polymer systems, especially the damping spectra. Fig. 8a shows the tan (δ) of neat epoxy resin, EP/ATH, EP/AOPH-**NR**, and other EP/AOPHs composites with filler loading of 4.25 wt% as a function of temperature. The glass transition temperatures (T_g) of neat EP and EP composites were extracted in terms of the peak temperature of tan δ – T curves.^{66,67}

The incorporation of particles can cause the T_g of polymers to increase, decrease, or remain constant, depending on the dispersion of particles in the matrix and whether the polymerparticle interactions are strong, weak, or repulsive.^{68,69} The flexibility of the organic groups grafted onto the fillers has an impact on the modulus as well when several organic groups are present. The EP/AOPH-**NR** nanocomposite has a T_g close to that of neat epoxy resin but higher than that of the EP/ATH composite (Fig. 8). This indicates that the addition of AOPH-**NR** causes a greater confinement effect between chains than ATH does. This comes from the net effect of the flexibility of organic groups, dispersibility, and interfacial interactions. The incorporation of ATH and other AOPHs into EP, regardless of their dispersibility in EP and the flexibility of organic groups in AOPHs cannot efficiently increase the glass transition. This trend allowed us to suggest that the interfacial interaction between matrix and fillers, which was only a physical interaction, is not strong enough to increase T_g . The obvious decrease of T_g for EP/ATH composites was attributed to the large size of ATH or inherent aggregates (Fig. S8 and S9, ESI†), leading to a decrease in the number of particles in the polymer and to an increased confinement effect between particles. It also caused an increase in the number of defects, amount of free volume, and the mobility of the chains. The T_g of the epoxy/AOPH-C2 composite markedly decreased. As described above, this can be ascribed mainly to the lowering of the crosslink density of the epoxy composite.

Further consideration is given by the T_g dispersion depicted in Fig. 8a, which has been found to be correlated to the interfacial structure. The addition of AOPH-NR broadens the glass transition and decreases its intensity with respect to the neat epoxy resin. In addition, a shoulder of the principal peak appears in the range of 60–100 °C. This broadening of relaxation times indicated that the AOPH-NR, which are compatible with the epoxy resin and are small in size, are more readily incorporated into the network structures than other fillers. This causes increased heterogeneity within the network structure.

The results obtained from tan (δ) curves allowed us to consider the affecting factors of modulus. From Fig. 8b, the incorporation of ATH and AOPH-**NR** in the epoxy resin leads to an increase in



Fig. 8 Typical DMA results of neat epoxy resin, EP/AOPH-NR nanocomposite and other EP composites studied: loss factor curve (a) and storage modulus curves (b).



Fig. 9 TGA thermograms of neat epoxy resin and epoxy composite with a loading of 4.25 wt% AOPH-NR and other AOPHs in (a) nitrogen and (b) air at a heating rate of 20 $^{\circ}$ C min⁻¹.

storage modulus at 40 °C (the glassy state). In the glassy state, the modulus is mainly dependent on the stiffness of filler and the interactions between the matrix and the filler. The increase can be attributed to the greater stiffness of ATH and AOPHs relative to the epoxy resin because the interactions between the matrixes and fillers were here found to be less strong. The EP/AOPH-NR nanocomposite was found to have a considerably higher storage modulus in contrast to the EP/ATH composite, thus supporting that the hybridization of organophosphorus with ATH is able to enhance the reinforcement effect. This is in good agreement with the evidence derived from the SEM images of the EP/AOPH composites. In addition, the EP/AOPH-NR nanocomposites show a higher storage modulus relative to other EP/AOPHs composites. This can be partly ascribed to good dispersibility (as evidenced by SEM and T_{g} dispersion) and a large number of rigid phenyl groups in AOPH-NR. Most importantly, the nanorod morphology of AOPH-NR may play an important role owing to the large surface area and aspect ratios.70 The relatively high modulus of the EP/AOPH-C2 composite could be attributed to an improved interfacial interaction and dispersion caused by the reaction between the allyl groups and epoxy resin. Nevertheless, this reaction induces incomplete crosslinking in the epoxy resin, leading to a pronounced decrease in the modulus with increasing the temperature (Fig. 8b).

Thermal properties and flame retardancy

Many papers have been written on the thermal degradation of epoxy resin and its corresponding composites.^{16,17} However, the role of aluminum–organophosphorus hybridization on the thermal stability or flame retardancy of the corresponding

Table 1 TGA data for ATH, AOPH-NR, and other AOPHs

Sample	First stage		Second stage		
	$T_{\rm d}/^{\circ}{\rm C}$	Mass loss/%	$T_{\rm d}/^{\circ}{\rm C}$	Mass loss/%	
ATH AOPH- NR AOPH- C1 AOPH- C2 AOPH- C3	$290.0 \pm 2 \\ 268.2 \pm 2 \\ 280.7 \pm 2 \\ 278.0 \pm 2 \\ 280.0 \pm 2$	$\begin{array}{c} 27.7 \pm 0.3 \\ 4.5 \pm 0.3 \\ 16.3 \pm 0.3 \\ 19.5 \pm 0.3 \\ 22.9 \pm 0.3 \end{array}$			

composites has never been addressed. However, it has been shown that selected synthetic materials can efficiently improve the thermal stability of epoxy resin.⁷¹⁻⁷³

The thermal stability of neat EP, EP/AOPH-NR nanocomposites, and other EP/AOPH composites is given in Fig. 9 and Table 2. Neat epoxy resin, which was cured by hexahydrophthalic anhydride, begins its weight loss at 402.4 °C in N₂ and at 373.5 °C in air. It shows a single-step weight loss in N₂ and a primarily two-step weight loss in air, in which the second decomposition step involves the skeletal degradation of cured epoxy resin.²² A similar trend was observed for the EP/AOPH-NR nanocomposite. From TGA, the addition of AOPH-NR was found to significantly facilitate this decomposition in both N₂ and air. It also leads to an increase in residual weight. The facilitation of degradation of AOPH-NR was correlated to the release of organophosphorus species as described above. The migration behavior of the phosphorus species, in this case, may be as significant as the releasing behavior. Both good dispersion and nano-scale particle size are beneficial to the migration of the phosphorus species. Other AOPHs at 4.25 wt% additive loading lead to a slight decrease in decomposition temperature in N₂. Some AOPHs even caused a decrease in char residue. In addition, the incorporation of other AOPHs caused an increase in decomposition temperature in air. The residual weight in air was considerably lower than in N₂.

The flame retardancy of EP/AOPH composites was evaluated using a limiting oxygen index (LOI) and cone calorimeter. As shown in Table 2, the loading of 4.25 wt% ATH only slightly improved the LOI value, to 23.6. Although the water and Al_2O_3 simultaneously produced from the decomposition of ATH can slow down the combustion of the matrix, they failed to stop it completely in this case. In order to achieve the flame retardancy standards for epoxy resin, at least 50 wt% of ATH is required.74,75 The incorporation of only 4.25 wt% AOPH-NR improved the LOI value to as much as 28 (an increase ratio of 26.1% than neat EP), showing self-extinguishing behavior. Besides, the addition of single phosphorus compounds gives a lower increase ratio of the LOI value of about 14.0-14.4%.76,77 Comparison of ATH, single phosphorus compounds, and AOPH-NR indicated an improvement in flame retardancy due to the hybridization of phosphorus compounds. The addition of other AOPHs showed a slight increase of LOI value. The heat release curves for epoxy

	In N ₂ condition			In air condition			
Sample	$T_0/^{\circ}\mathrm{C}$	$T_{\rm max}/^{\circ}{ m C}$	Char residue at 500 °C/%	$T_0/^{\circ}\mathrm{C}$	$T_{\rm max}/^{\circ}{\rm C}$	Char residue at 500 °C/%	LOI/%
Neat EP	402.4 ± 2	423.9 ± 2	5.6 ± 0.3	373.5 ± 2	422.3 ± 2	19.8 ± 0.3	22.2
EP-4.25% ATH	395.9 ± 2	415.8 ± 2	5.2 ± 0.3	380.6 ± 2	420.5 ± 2	18.4 ± 0.3	23.6
EP-4.25% AOPH-NR	377.6 ± 2	403.7 ± 2	12.2 ± 0.3	349.8 ± 2	394.8 ± 2	22.1 ± 0.3	28.0
EP-4.25% AOPH-C1	400.1 ± 2	422.5 ± 2	4.7 ± 0.3	390.5 ± 2	424.2 ± 2	20.2 ± 0.3	23.4
EP-4.25% AOPH-C2	397.7 ± 2	420.4 ± 2	15.7 ± 0.3	373.9 ± 2	421.3 ± 2	24.3 ± 0.3	23.6
EP-4.25% AOPH-C3	398.5 ± 2	423.6 ± 2	8.9 ± 0.3	384.9 ± 2	424.1 ± 2	19.9 ± 0.3	23.8

 Table 2
 Summary of TGA data for neat epoxy resin, EP/AOPH-NR nanocomposite and other EP composites



Fig. 10 Heat release rate curve for neat epoxy resin and composites with a loading of 4.25 wt% ATH, AOPH-NR, and other AOPHs.

resin with AOPH-NR and other AOPHs at a loading of 4.25 wt% are given in Fig. 10 and a summary of the cone data is given in Table 3. As shown in Fig. 10, EP/AOPH-NR nanocomposite shows a pronounced reduction (approximately 23%) in peak heat release rate (PHRR), as indicated in Table 3, but no reduction is noted for other EP/AOPHs composites. This reduction is not very large compared to what has been seen with MMT.^{29,78,79} As shown in Table 3, the t_{ign} jumps quite a bit, from 48 to 79 and the time to PHRR is prolonged by 225 when AOPH-NR is added to EP. This delay in ignition is crucial to saving lives and property. Other parameters, such as average mass loss rate (AMLR) showed a reduction (more than 50%) relative to EP. It is worth noting that this reduction is much more pronounced than that of PHRR. For nanocomposites, the change in PHRR generally reflects a change in the mass loss rate. However, that is clearly not the case here, possibly implying a different flame retarding mechanism.

The flame retarding efficiency of AOPH-NR, we suggest, can be ascribed to its nanorod morphology and to its aluminum-

organophosphorus hybrid structure.^{80,81} First of all, these features improve the dispersibility of AOPH-NR, which is probably linked to high fire performance. Second, in otherwise identical blends, the aluminum-organophosphorus hybridization would improve the flame retardancy arising from their counteraction of the promotion of char formation, as evidenced by the increased char residue of the EP/AOPH-NR nanocomposite relative to the EP/ ATH composite. This, in addition to the observed facilitation of degradation in TGA, underlined a proposed mechanism of flame retardancy based on char formation through the cleavage of P-O-C and P-C bonds, followed by dehydration processes promoting char formation. The phosphorus species hence provided superior fire resistance by lowering decomposition temperatures of epoxy resin and increasing char yields. The nanorod morphology of the as-prepared aluminum-phosphorus hybrids may enable convenient release and migration of phosphorus species. This favors the improvement of the composite's fire-retarding properties. It was also found that the fire properties of the phosphorous-containing samples generally deteriorated in the presence of clay, typically MMT, even when the phosphorus compounds were intercalated into the clay.82 MMT showed advantages in inhibiting the release of heat because of its layered structure. Nevertheless, this structure, we suspect, hampers the migration of phosphorus species to the surface. The DBPA used to prepare AOPH-NR was not considered truly flame retardant because of its low decomposition temperature. However, when hybridized with ATH, its phosphorus-releasing temperature was increased. This may also have contributed to the good flame retarding performance observed.

Conclusions

A new aluminum-organophosphorus hybrid nanorod was prepared by reacting ATH with dibenzylphosphinic acid (DBPA). FTIR and Raman measurements suggest that the

Table 3 Cone calorimeter data for neat epoxy resin and composites with a loading of 4.25 wt% ATH and AOPHs^a

Sample	t _{ign} /s	t _{PHRR} /s	PHRR/kW m ⁻²	THR/MJ m^{-2}	ASEA/m ² kg ⁻¹	AMLR/g s ⁻¹
Neat EP	48	175	1023	109	343	0.2618
EP-4.25% AOPH-NR	79	225	789	101	761	0.1102
EP-4.25% AOPH-C1	80	185	1092	107	608	0.1635
EP-4.25% AOPH-C2	58	160	1063	99	314	0.1313
EP-4.25% AOPH-C3	78	195	1024	106	265	0.2858

^a t_{ign}: time to ignition; t_{PHRR}: time to PHRR; PHRR: peak heat release rate; THR: total heat release; ASEA: average specific extinction area; AMLR: average mass loss rate.

organophosphorus species were incorporated into ATH via the formation of Al-O-P bonds, mainly producing the chelating mondentate and bridging bidentate structure. These corresponded to the destruction of the ATH crystalline structure, as evidenced by XRD. The TGA of DBPA and AOPH-NR indicated that AOPH-NR has a favorable phosphorus releasing rate and a high phosphorus releasing temperature for multiple phosphorus species. SEM and TEM images of AOPH-NR show that it has nanorod morphology while other AOPHs displayed a solid agglomerates morphology. XRD examination preliminarily suggests a decomposing-reforming mechanism that reacting phosphinic acids with ATH resulted in the decomposition of ATH crystal structure into polymeric chains with Al (DBP)₃ repeating unit structure. Subsequently, the π - π stacking interactions between polymeric chains drove the chains to arrange into nanorods.

This feature of AOPH-NR induced special properties and performance in corresponding EP/AOPH-NR nanocomposites. SEM and TEM images indicated the good dispersibility of AOPH-NR in epoxy resin and enhanced mechanical properties, which was further evidenced by DMA measurements. TG measurements showed that the presence of AOPH-NR facilitate degradation, which is indicative of the favorable release and migration ability of phosphorus species for the EP/AOPH-NR. Such behavior mainly resulted from the large surface area, good dispersion and nanoscale of AOPH-NR. LOI measurements and cone calorimeter analysis showed that the loading of only 4.25 wt% AOPH-NR leads to a LOI increase ratio as high as 26.1% and a 23% reduction in PHRR, suggesting a remarkably high flame retarding efficiency. Relative to other flame-retardant materials, the hybrids of ATH and phosphorus compounds offer the most impressive advantages in tailoring releasing and migration behavior of phosphorus species to accommodate specific requirements. This is because of their unique one-dimensional nanorod morphology, good dispersion, and improved phosphorus degradation temperature. The application of this aluminum-organophosphorus hybridization in real-world flame retardancy applications is likely.

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